UNIVERSITE DE LIMOGES

Ecole Doctorale Sciences, Technologie, Santé
Laboratoire des Sciences de l'Eau et de l'Environnement

N° [68-2008]

THESE

Pour l'obtention du garde de

DOCTEUR DE L'UNIVERSITE DE LIMOGES

Discipline : Chimie et Microbiologie de l'Eau

Présentée et soutenue publiquement par

Mohammad Reza SALSABIL

Le 28 Novembre 2008

Etude comparative des digestions aérobie et anaérobie de boues biologiques urbaines traitées par procédés physique, chimique et thermique : application pour la réduction de la production de boues

(Comparative Study of the Digestion of Urban Biological Sludge Pretreated by Physical, Chemical, and Thermal Processes: Applied to Reduce Sludge Production)[1]

Directeurs de Thèse : Magali CASELLAS et Christophe DAGOT

JURY

Rapporteurs :

M[me] Hélène CARRERE	Chargée de Recherches, INRA Narbonne
M. Gérard MERLIN	Professeur, Université de Savoie

Examinateurs :

M. Jean Christophe BAUDEZ	Ingénieur, CEMAGREF
M. Michel BAUDU	Professeur, Université de Limoges
M[me] Patricia CAMACHO	Ingénieur, Suez Environnement
M[me] Magali CASELLAS	Maître de Conférences, Université de Limoges
M. Christophe DAGOT	Professeur, Université de Limoges

[1]This thesis is supported by part by the Iranian Institute for Energy and Hydro Technology (IEHT).

To Parvaneh and Matin

Table of Contents

List of Figures

List of Tables

Abstract

A comparative study of aerobic and anaerobic digestion of sludge after three pretreatment techniques in the aim of enhancing sludge reduction has been proposed. The disintegration and solubilization techniques are based on mechanical (US), thermal (Bain-Marie and autoclave), and oxidative (ozonation) treatments. An evaluation of the efficiency of the global treatment and the economic aspects was performed to demonstrate their efficiency. The best solubilization results were obtained with ultrasound treatment with specific energy of 200000 kJ.kg-TSS^{-1} and 50W, ozonation treatment with an ozone dose of 0.101gO_3.g-TSS^{-1} and thermal treatment at 90°C duration 60 minutes. In the solubilization step, thermal treatment is more successful in solubilization of COD and BOD when compared to ultrasonic and ozonation treatments. In contrast, ultrasonic pre-treatment is more successful in solubilization of TSS, VSS and DD_{COD} compared to ozonation and thermal pre-treatments. A comparative study of the aerobic and anaerobic biological digestion of sludge samples pretreated by US, thermal, and ozonation pretreatments revealed that sonication led to the highest sludge production reduction and the lowest elimination expenses (33% cost reduction compared to non pretreated sample digested in aerobic digester). Moreover, in terms of biodegradation, the highest rate of soluble COD, q_{COD} values, TSS and VSS removal efficiency, and biodegradability (BOD_5/COD_S) for both conditions (aerobic and anaerobic) correspond to the digestion of sludge pretreated by ultrasonic. Anaerobic digestion, because of a potential biogas recovery, is economically and environmentally more effective than its aerobic counterpart.

Résumé

Une étude comparative de la digestion aérobie et anaérobie de boue d'épuration ayant subi trois techniques de prétraitements est présentée dans le cadre de la réduction de la production de boue. Les trois techniques sont les ultrasons, des traitements thermiques et l'ozonation. L'efficacité globale des différents traitements et les coûts engendrés sont évalués pour démontrer leur efficacité. Les meilleurs résultats en terme de Solubilization ont été obtenus avec traitement aux ultrasons pour une énergie spécifique de 200000 kJ.kg-TSS^{-1} et 50W, avec oxydation à l'ozone avec une dose of 0.101gO_3.g-TSS^{-1} , avec un traitement thermique à 90°C pendant 60 minutes. Ce dernier permet une meilleure Solubilization de la DCO et de la DBO comparé aux traitements aux ultrasons et à l'ozone. Une étude comparative de la digestion aérobie et anaérobie des boues prétraitées par les trois techniques montre que le traitement aux ultrasons amène à la réduction de boue la plus importante, avec le coût le plus faible (33% de réduction, comparé à l'échantillon non traité en aérobie). De plus, le traitement aux ultrasons suivi de la digestion, qu'elle soit aérobie ou anaérobie, correspond en terme de biodégradation, au plus fort taux DCO soluble, de valeurs de q_{COD}, d'efficacité de réduction des MES et MV et de taux de biodégradabilité,. Cependant, la digestion anaérobie, en raison de la récupération possible du biogaz, est économiquement et environnementalement plus intéressante que la digestion aérobie.

Keywords: *pre-treatment; solubilization; biodegradability; aerobic and anaerobic digestion; sludge reduction; biogas; ultrasonic; ozonation; thermal treatment.*

Acknowledgement

This Ph.D. thesis would not have been possible without the help, cooperation, and support of many people.

First of all I would like to offer my deepest thanks and gratitude to Professor Christophe DAGOT for his patient help, encouragement, and support during my thesis. His support and inspiration, as well as his guidance and direction, made this work possible and successful.

I would like also to thank Dr. Magali CASELLAS for her time and effort in reviewing this work. I have always benefited from her valuable guidance and suggestions. She had the kindness to carefully examine and review the manuscripts and to provide me with her valuable remarks and suggestions.

I am also grateful to the Institute for Energy and Hydro Technology (IEHT), for funding and financing my research at University of Limoges.

My sincerest thanks go to Professor Michel BAUDU for his kindness and support during my stay in France.

Special thanks also to all my graduate friends, especially group members for their generous sharing of the literature and their invaluable assistance.

I will also thank my friend, Mr. Hamid MEGHDADI, for his assistance in English text reviews and corrections.

Finally, I wish to express my love and gratitude to my beloved families; for their moral support and endless love, through the duration of my entire life.

List of abbreviations

BOD = Biochemical Oxygen Demand (mg-O_2. L^{-1})

COD = Chemical Oxygen Demand (mg-O_2. L^{-1})

$COD_{S\text{-}NaOH}$ = Soluble COD after an alkaline hydrolysis (mg-O_2. L^{-1})

COD_S = Soluble COD (mg-O_2.L^{-1})

COD_{S0} = Initial Soluble COD (mg-O_2.L^{-1})

COD_P = COD in Particulate (mg-O_2.L^{-1})

COD_{P0} = Initial COD in Particulate (mg-O_2.L^{-1})

COD_T = Total COD (mg-O_2.L^{-1})

S_{COD} = COD Solubilization (%)

DD_{COD} = Degree of Disintegration of COD (%)

TOC = Total Organic Carbon

DS = Dry Solids (g. L^{-1})

TS = Total Solids (g. L^{-1})

SS = Suspended Solids (g. L^{-1})

VS = Volatile Solids (g. L^{-1})

TSS = Total Suspended Solids (g. L^{-1})

VSS = Volatile Suspended Solids (g. L^{-1})

S_{TS} = Solubilization of TS (%)

TSS_0 = Initial Total Suspended Solids (g.L^{-1})

TSS_f = Final Total Suspended Solids (g.L^{-1})

SVI = Sludge Volume Index (ml.L^{-1})

N_S = Soluble Nitrogen (mg-N.L^{-1})

N_T = Total Nitrogen (mg-N.L^{-1})

P_S = Soluble Phosphorus (mg-P.L^{-1})

P_T = Total Phosphorus (mg-P.L^{-1})

WWTP = Waste Water Treatment Plant

WAS = Waste Activated Sludge

RAS = Return Activated Sludge

WAO = Wet Air Oxidation

SRT = Sludge Retention Time

HRT = Hydraulic Retention Time

AGF = Anoxic Gas Flotation

PPM = Part Per Million

OSA = Oxic-Settling-Anaerobic

AOP = Advanced Oxidation Process

PVC = Poly-Vinyl Chloride

SCWO = Super Critical Water Oxidation

PRSP = Processes for Reduction Sludge Production

PSRP = Process to Significantly Reduce Pathogens

PFRP = Process to Further Reduce Pathogens

RSP = Reduction of Sludge Production

ESP = Excess Sludge Production

EPS = Etracellular Polymeric Substances

SEM = Scanning Electron Micrographs

BSA = Bovine Serum Albumin

PE = Population Equivalent

EU = European Union

SE = Specific Energy ($kJ.kg^{-1}$-TSS)

US = Ultrasonic

O_3 = Ozonation

BG = Biogas

atm = Atmosphere

NL = Newton Litter

r_{COD} = COD uptake rate ($mg\text{-}O_2.L^{-1}.d^{-1}$)

r_{BG} = Biogas production rate ($mL\text{-}BG.d^{-1}$)

q_{COD} = Instantaneous specific soluble COD uptake rate ($mg\text{-}COD_S.gVSS^{-1}.d^{-1}$)

$q_{protein}$ = Instantaneous specific soluble protein uptake rate ($mg\text{-}protein_S.gVSS^{-1}.d^{-1}$)

$q_{carbohydrate}$ = Instantaneous specific soluble carbohydrate uptake rate ($mg\text{-}carbohydrate_s.gVSS^{-1}.d^{-1}$)

q_{BG} = Instantaneous specific biogas production ($mL\text{-}BG.gVSS^{-1}.d^{-1}$)

Y = Global yield of biogas production (mL-BG.$gCOD_S^{-1}$)

C_{t0} = Concentration in influent ($mg.L^{-1}$)

C_{tf} = Concentration in effluent ($mg.L^{-1}$)

E_S = The rate of energy used for sludge pre-treatment (J or kJ)

E_T = Total energy of aerobic digestion (kJ)

E_A = Energy consumption of air compressor (kJ)

E_{Ag} = Energy of agitator (kJ)

E_H = Energy of heater (kJ)

E_{CH4} = Energy of produced methane (kJ)

DO = Dissolved Oxygen ($mg.L^{-1}$)

pH = potential Hydrogen

Re = Removal yield (%)

S = Solubilization (%)

SD = Standard Deviation

X = Mean

P = Power (W)

W = Watt

J = Joule

w = Weight (g)

H = high (cm)

g = Gram

L = Litter

mL = Milliliter

mol = molar = molarity

N = Normality

V = Sample Volume (L)

t = Sonication time (s)

T = Temperature (°C)

0 = Initial value

f = Final value

S = Parameter value in the soluble phase

T = Parameter value in the total phase

P = Parameter value in the particulate phase

S_0 = Initial soluble

P_0 = Initial particulate

t_0 = Time of inlet

t_f = Time of outlet

in = Inlet

eff = Effluent

out = Outlet

θ_c = Age of sludge

φ = Diameter

ΔHr° = Endothermic reaction

Introduction

Introduction

Urban municipal sewage treatment plants use physical and biological processes to treat wastewater. The well-known biological process called “activated sludge process” is the most widely used process for biological wastewater treatment nowadays, but it results in the generation of a considerable amount of waste that has to be disposed of. This sludge contains high fractions of volatile solids (VS) and retains large amounts of water before a possible drying (>95% by weight), resulting in the production of extremely large volumes of residual solids, and significant disposal costs. In fact, treatment and disposal of excess sludge from wastewater treatment plants account for 25–65% of the total plant operation cost. Thereby, the conventional method converts a water pollution problem into a solid waste disposal problem.

This problem is becoming more and more pressing both in developing and industrial countries. In the latter, the disposal of excess sludge is one of the most serious challenges in biological wastewater treatment for two main reasons:

1. New wastewater treatment regulations are causing a rise in the number of plants. In the European Union (EU) countries, after the implementation of the *Urban Wastewater Treatment Directive 91/ 271/EEC*, the vast majority of the EU population will be served by sewage treatment facilities by the year 2005. This increase in the number of wastewater treatment plants is translated into a higher production of sewage sludge. An increase of nearly 40% is expected between 1998 and 2005, resulting in a generation of about 9.4 million tons (dry weight) every year, while for the year 2010 it is expected to exceed 10 million tons.

2. Sludge disposal routes are subject to more stringent environmental quality requirements imposed by legislation (*the Sewage Sludge Directive 86/278/EEC*, *the Organic Farming Regulation (EEC) 2092/9*, *the Landfill Directive 1999/31/EC* and *the Commission Decision 2001/688/EC*).

In order to take into account the positive aspects of sludge on soil, as well as to reduce the impact of waste on the environment (soil, vegetation, animals and man), the revision of the *Directive 86/278/EEC* and the development of a Bio-waste Directive have been planned as necessary actions.

In the past, legislations were based on soil protection, but today we prefer to have legislations mainly based on the biodegradable waste.

The main alternative methods for sludge disposal in European Union (EU) are: landfill, land application and incineration, accounting for nearly 90% of total sludge production.

Ocean disposal of sludge is nowadays forbidden in practice, and sludge deposits in landfills are to be phased out, even though 35–45% of the sludge in Europe is disposed of in this manner. Legislation concerning land application of sludge is being tightened in order to prevent health risks to man and livestock due to the potentially toxic elements in the sewage sludge, i.e. heavy metals, pathogen and persist organic pollutants. Incineration ash will have to be treated as hazardous waste (due to the heavy metals content and general toxicity), resulting in high treatment cost for this alternative. Moreover, government and environmental groups seem reluctant to consider alternatives such as energy recovery from incineration or use of incineration ash as construction material and other beneficial uses (Pérez-Elvira *et al*., 2006).

Hence, deposition of sludge and its components will not be accepted in the future. These points to direct use of sludge on land as the most sustainable alternative. This is also reflected in the working document for a proposed new sewage sludge directive of (EU) (Anon, 2000).

Urban sludge land disposal has been restricted in France since July 2002 (French law 92-3 of 3 January 1992). Incineration is quite expensive and needs the treatment of off gas in order to remove toxic compounds: it is thus highly debated. The main disposal route is land application (or agricultural use), but it is subject to reservations from farmers and consumers.

There is therefore a growing interest in developing technologies to reduce the wastewater sludge generation. Several systems combining biological and physicochemical treatment have been studied in order to improve the aerobic and anaerobic biodegradability of solid waste. They have resulted in shorter reaction times that have enabled hydraulic retention time to be reduced and, consequently, digesters sizes too. Most mechanical and physicochemical pre-treatment tested so far has targeted cell lysis: ultrasound disintegration (Tiehm *et al*., 2001-b; Neis, 2000), shear stress forces (Rivard and Nagle, 1996), alkaline pre-treatment (Rajan *et al*., 1989; Mace *et al*., 2001), thermal pre-treatment (Li and Noike, 1992) and alkaline combined with thermal hydrolysis (Rocher *et al*., 1999; Tanaka *et al*., 1997) as well as other oxidation processes (ozone, hydrogen peroxide, …).

The goal of this work is to study some current minimization techniques for reducing sludge production in biological wastewater treatment processes. An overview of the main technologies is given considering three different strategies: The first option is to reduce the production of

sludge by introducing additional stages in the wastewater treatment with a lower cellular yield coefficient compared to the one corresponding to the activated sludge process (lysis-cryptic growth, uncoupling and maintenance metabolism, predation on bacteria, anaerobic treatment). The second choice is to act on the sludge stage. As anaerobic digestion is the main process in sewage sludge treatment for reducing and stabilizing the organic solids, two possibilities can be considered: introducing a pre-treatment process before the digestion reaction (physical, chemical or biological pre-treatments), or modifying the digestion configuration (two-stage and temperature-phased anaerobic digestion, anoxic gas flotation). And, finally, the last minimization strategy is the removal of the sludge generated in the activated sludge plant (incineration, gasification, pyrolysis, wet air oxidation, supercritical water oxidation).

Several strategies are currently being developed for the minimization of sludge production on biological wastewater treatment plants. In this manuscript we will give an overview of processes which result in sludge minimization. Three kinds of pre-treatment will be considered: mechanical (US), Oxidative (O_3) and thermal (Bain-marie and Autoclave).

The objective of this study is to quantify and understand the changes related to ultrasonic, ozonation and thermal pre-treatment, and to measure its effects on the sludge solubilization and subsequently the potential ability to improve aerobic and anaerobic digestion.

This study includes two parts. In the first section, sludge solubilization is evaluated and in the second section, the rate of sludge biodegradability, sludge reduction improvement and economic analysis in both aerobic and anaerobic conditions are investigated.

During the solubilization step, the optimum parameters for each treatment technique are determined using bench scale studies. The aim of these treatments is to solubilize and/or to reduce the size of organic compounds, especially refractory compounds, in order to make them more easily biodegradable. Final quantity of residual sludge and time of digestion can thus be reduced and biogas production can be increased.

In the biodegradability step, we will proceed to study sludge digestion and biodegradability for each technique using pilot plant methods in aerobic and anaerobic conditions. Because of pretreatment done in each technique, in the sludge digestion processes, the biogas production is increased and the total amount of organics in the final sludge residue is reduced and therefore so is the amount of sludge residue.

One of our objectives is to validate the association of a specific sludge pretreatment (ultrasonic, ozonation, and thermal treatment) and a biological treatment (aerobic or anaerobic digestion). In a second hand, another objective is to qualify this efficacy. We will compare sludge digestion and biodegradability of the treated sludge with those of untreated sludge in order to better understand the effect of pre-treatment on the sludge. At the end of the test, results will let us compare sludge obtained from these three pre-treatments along with the control sample (under aerobic and anaerobic conditions), and further choose the most cost effective pre-treatment leading to the highest sludge elimination efficiency.

In this manuscript, in the both solubilization and biodegradability parts, we will answer to the following major questions:

1. What is the purpose of pre-treatment?
2. What are the probable effects of Pre-treatment on sludge treatment?
3. What are the differences between pre-treated samples with unpre-treated sample in the sludge digestion processes?
4. What are the possible effects of Pre-treatment on sludge biodegradability?
5. During sludge digestion and disposal steps, does pre-treatment lead to a decrease in sludge mass and volume and how much the disposal costs is reduced and is this economically reasonable?
6. Is it possible to establish a correlation between solubilization/specific energy input and removal efficiency improvement?

Chapter 1

Review of literature

Chapter 1: Review of literature

1. Wastewater treatment and sludge production

1.1 Wastewater treatment

Wastewater collected from municipal and communities must ultimately be returned to receiving waters or to the land. The complex question of which contaminants in wastewater must be removed to protect the environment has to be answered specifically for each case. The answer to this question requires local condition and need, together with the application of scientific knowledge, engineering judgment based on past experience, and consideration of requirements and regulations each country and region.

1.1.1 Types of wastewater

Not all wastewaters have the same composition and the technology for their treatment is different in each case. Wastewater can be characterized in accordance with its origin.

The components that make up the wastewater flow from a community depend on the type of collection system used and may include the following: (Ceccaroni, 2001)

- Domestic or municipal (also called sanitary) wastewater. Wastewater discharged from residences and from commercial, institutional, and similar facilities.
- Industrial wastewater. Wastewater in which industrial wastes predominate.
- Agriculture wastewater.
- Related to main drainage (Storm water). Runoff resulting from rainfall and snowmelt.
- Related to livestock production operation.

An especially important feature is the presence of pathogenic organisms, which can prejudice a possible alternative reuse of treated water, such as irrigation.

1.1.2 Characteristics of wastewater

Wastewater is any water that has been adversely affected in quality by anthropogenic influence. It comprises liquid waste discharged by domestic residences, commercial properties, industry, and/or agriculture and can encompass a wide range of potential contaminants and

concentrations. In the most common usage, it refers to the municipal wastewater that contains a broad spectrum of contaminants resulting from the mixing of wastewaters from different sources.

Before any water or wastewater can be treated, it must be first characterized. Thus, characterization needs to be addressed. Wastewaters may be characterized according to their quantities and according to their constituent physical, chemical, and microbiological characteristics (Table 1-1).

Table 1-1: Classification of the physical, chemical and biological descriptors of wastewater.

Physical	Chemical	Biological
	Inorganic	
Suspended Solids	**pH**	**Protista**
Temperature	**Chlorides**	**Viruses**
Colour	**Alkalinity**	**Bacteria**
Odour	**Nitrogen**	**Fungus**
Turbidity	**Phosphorus**	**Algae**
Density	**Sulfur**	**Animals**
	Oxygen	**Pathogens**
	Organic	
	Proteins	
	Carbohydrates	
	Fats, Oils	
	Surface active agents	
	Phenols	
	Pesticides	
	Restaurant grease	

1.1.2.1 Physical characteristics

The most important physical characteristic of wastewater is its total solids content, which are composed floating matter, settleable matter, colloidal matter and matter in solution. Other important physical characteristics include odour, temperature, density, colour, and turbidity.

1.1.2.2 Chemical characteristics

The discussion of chemical characteristics of wastewater is presented in four parts: organic matter, the measurement of organic content, inorganic matter, and gases. Chemical processes

are usually used in conjunction with the physical unit operation and biological unit processes to meet treatment objectives.

1.1.2.3 Biological characteristics

The most important biological characteristics of wastewater is the principal groups of micro-organisms found in surface water and wastewater as well as those responsible for biological treatment and the pathogenic organisms found in wastewater. For example: bacteria, viruses, fungi, algae, protozoa, plants and animals.

1.1.3 Municipal waste water treatment plant

In a wastewater treatment plant (WWTP), the main goal is to reduce the level of pollution of the inflow water. That is to remove, within certain limits (depending on local legislation), too high amounts of pollutants in the water prior to its discharge to the natural environment.

The treatment of wastewater consists in reducing the organic and mineral matter load. Nevertheless, there is a transfer of pollution of the liquid phase (water) towards more concentrated phase (sludge) and a gas phase (CO2, N2, etc). The production of waste sludge is thus completely dependent on the ways of wastewater treatment.

The traditional method of wastewater treatment comprises three principal parts:

- Physical treatment (preliminary pre-treatment)
- Primary treatment
- Secondary treatment or biological treatment

Table 1-2 shows the composition of domestic wastewater before treatment. In this table, different compounds of weak, medium, and strong sludge are represented.

Table 1-2: Typical composition of untreated domestic wastewater (Metcalf and Eddy, 1991).

Contaminant	Weak	medium	Strong	Unit
Solids total (TS)	350	720	1200	
Total dissolved solids (TDS)	250	500	850	
Fixed	145	300	525	
Volatile	105	200	325	mg/l
Total suspended solids (TSS)	100	220	350	
Fixed	20	55	75	
Volatile	80	165	275	
Settleable suspended solids (SSS)	5	10	20	ml/l
Biochemical oxygen demand (BOD_5)	110	220	400	mg/l
Total organic carbon (TOC)	80	160	290	mg/l
Chemical oxygen demand (COD)	250	500	1000	mg/l
Total Nitrogen (N_T)	20	40	85	
Organic	8	15	35	
Free ammonia	12	25	50	mg/l
Nitrites	0	0	0	
Nitrates	0	0	0	
Total Phosphorus (P_T)	4	8	15	
Organic	1	3	5	mg/l
Inorganic	3	5	10	
Chlorides (Cl)	30	50	100	mg/l
Sulfate (SO_4)	20	30	50	mg/l
Alkalinity (CaCO3)	50	100	200	mg/l
Grease	50	100	150	mg/l
Total coliform	10^6-10^7	10^7-10^8	10^7-10^9	No/100 ml
Volatile organic compounds (VOC_S)	<100	100- 400	>400	µg/l

Figure 1-1 illustrates different parts of a conventional activated sludge system in municipal wastewater treatment plant.

1.1.3.1 Physical pre-treatment

The aim of this step is removing large particles of wastewater (sands, bits of glass, oil, grease,). These wastes are recovered and treated separately.

1.1.3.2 Primary treatment

Those operations used for the treatment of wastewater in which change is brought about by means of or through the application of physical forces are known as unit operations. Because they were derived originally from observation of the physical word, they were the first treatment methods to be used. Today, physical unit operations form the basis of most process flow diagrams.

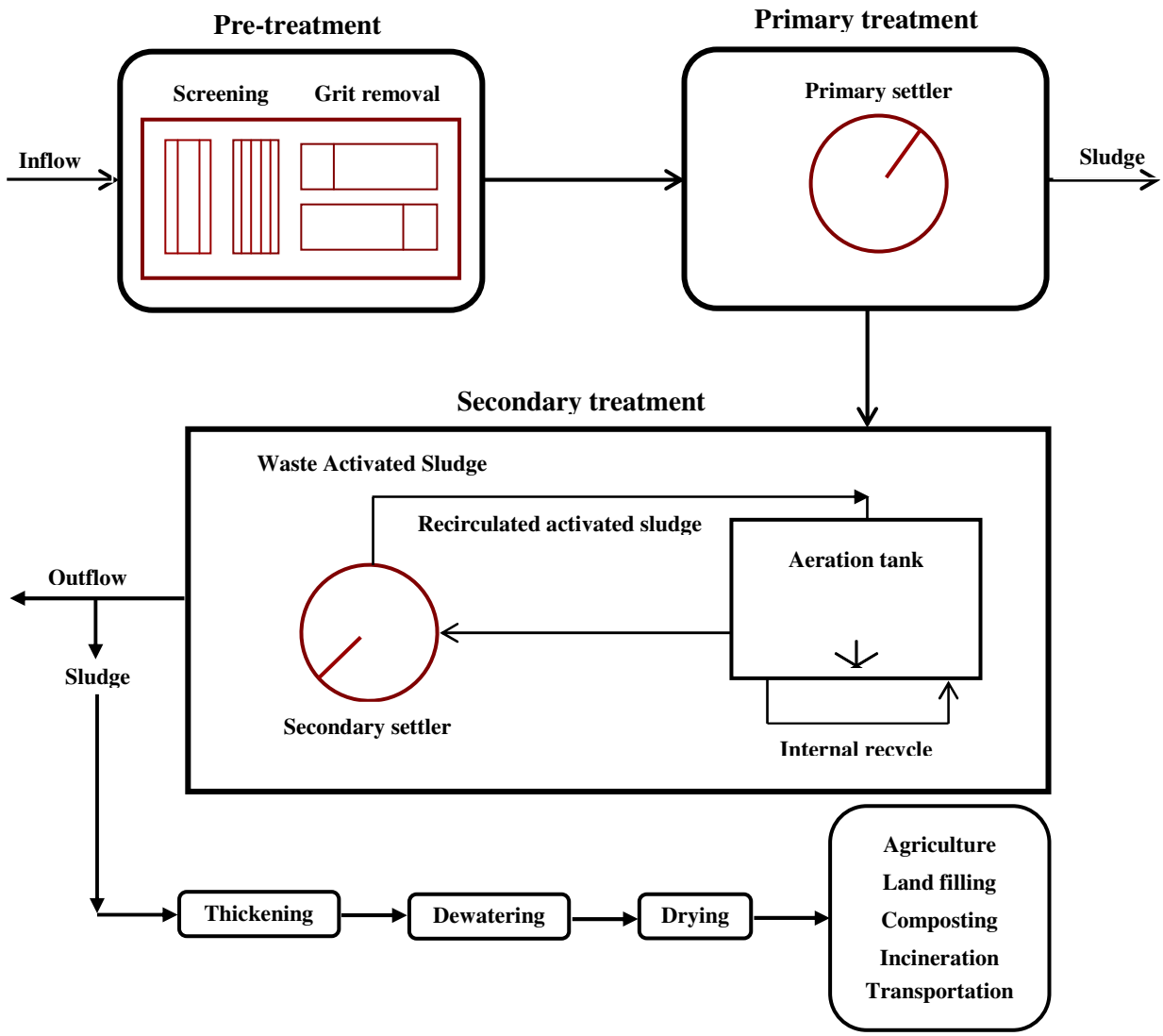

Figure 1-1: Scheme of a traditional wastewater treatment plant with activated sludge.

1.1.3.3 Secondary treatment (biological)

The objectives of the biological treatment of wastewater are to oxide the organic matter and remove the non-settleable colloidal solids. For domestic wastewater, the major objective is to reduce the organic content and, in many cases, the nutrients such as nitrogen and phosphorus. In many locations, the removal of trace organic compounds that may be toxic is also an important treatment objective.

1.1.3.4 Tertiary treatment (advance)

Advanced wastewater treatment is defined as the additional treatment needed to remove suspended and dissolved substance remaining after conventional secondary treatment.

1.2 The sludge Production and treatment

Sewage treatment plants generate sludge as the single largest residual product of the sewage treatment process. Many treatments such as dewatering, digestion, burning, land filling and use in agriculture have been carried out for the disposal of excess sludge. Because these treatments cost a great deal, an increasing interest exists in the reduction in the amount of sludge produced in the wastewater treatment process (He *et al*., 2006).

The excessive production of sludge, resulting from the biological process of wastewater treatment, is important, and will be prohibited in an immediate future, thus the attention is paid to potential technologies for the reduction of these sludge. Recently, some techniques of sludge reduction were developed by the physical (mechanical), chemical (oxidation) and biological (enzymatic) methods, coupled or separated (Liu, 2003).

The sludge treatment and disposal present many important technical challenges and the associated capital and operating costs may be as high as 50% of the total cost of the wastewater treatment process (Zhang *et al*., 2007-a).

1.2.1 Origin of sludge production

The sludge production is a function of the wastewater treatment system used for the liquid phase. In principle, all the biological treatment processes generate sludge. The processes that receive raw wastewater in primary settling tanks generate the primary sludge, which is composed of the settleable solids of the raw wastewater. In the biological treatment stage, there is the so-called biological sludge or secondary sludge. This sludge is the biomass that grows at the expense of the food supplied by the incoming sewage mixed with inorganic sludge. If the biomass is not removed, it tends to accumulate in the system and eventually leaves with the final effluent, deteriorating its quality in terms of suspended solids and organic matter. Depending on the treatment system, the primary sludge can be sent for treatment together with the secondary sludge. In this case, the resultant sludge of the mixture is called mixed sludge. In treatment systems that incorporate a physicochemical stage for improving the performance of primary or secondary settling tanks, a chemical sludge is produced.

Thus the sewage sludge is classified into four major groups: (Degrémont, 1989)

- Primary sludge: primary sludge is produced by primary settling at first of WWTP. The sludge is fresh, that is to say non-stabilized (high content of organic matter) and highly fermentable. Because of the nature of new facilities, they tend to disappear.

- Secondary sludge resulting from secondary treatment. They are mainly composed by the biomass present in excess in the system and by the material resistant to the biological treatment. They were recovered after the secondary clarifier, in the wastewater treatment plant. These are fresh organic sludge, mainly in the form of flocculated bacteria. Their fermentability depends on the time of stay in the aeration basin.

- Mixed sludge: the mixture of primary and secondary sludge is called mixed sludge. Their composition is dependent on the quantity of primary and secondary sludge produced.

- Physicochemical sludge: these are derived from sludge treatment using flocculants minerals (iron salts or aluminium). The physicochemical treatment is used mainly on sludge of industrial wastewater treatment plants.

The primary sludge, in their composition, are highly fermentable and do not require prior treatment to improve their biodegradability. In contrast, secondary sludge is much more difficult to degrade in an organic way (Lafitte-Trouqué and Forster, 2002).

Different effluent treatment processes produce different qualities and quantities of sludge. In a wastewater treatment plant, the characteristics change during the year or even for a day because of variations in the composition of the raw water. Whatever their origin may be, urban sludge consists of organic and mineral matter accumulated in the different steps of water treatment and their composition varies depending on the effluent and treatments carried out. However, they are generally made up of 95% water and 5% dry matter which give power fermentable very high.

The parts that are most important to classify and determine the quality of sludge treatment and their final destination are: organic matter (volatile matter), nutrients, pathogens, metals, and trace organic compounds.

Table 1-3: characteristics of sludge classes (OTV, 1997).

Parametres	Class A sludge	Class B_1 sludge	Class B_2 sludge	Class C sludge	Class D sludge
pH	6	7	7	7.5	7
TS (g/l)	12	9	7	10	30
VS (%)TS	65	67	77	72	50
H (%) VS	7	6	6.7	7.4	7.7
O (%)VS	35.5	33	33	33	35
S (%)VS	1.5	1	1	1.5	2.1
C (%)VS	51.5	52.5	53	51	49
N (%)VS	4.5	7.5	6.3	7.1	6.2
C/N	11.4	7	8.7	7.2	7.9
P (%)TS	2	2	2	2	2
Cl (%)TS	0.8	0.8	0.8	0.8	0.8
K (%)TS	0.3	0.3	0.3	0.3	0.3
Al (%)TS	0.2	0.2	0.2	0.2	0.2
Ca (%)TS	10	10	10	10	10
Mg (%)TS	2	2	2	2	2
Fe (%)TS	0.6	0.6	0.6	0.6	0.6
Fats (%)TS	18	8	10	14	10
Proteins (%)TS	24	36	34	30	18
Fibres (%)TS	16	7	10	13	10
PCI (KWh/t) TS	4200	4100	4800	4600	3000

It is important to note that sludge can be categorized in five classes (see Table 1-3).

- Class A sludge: Primary sludge with physicochemical characteristics. This is a strong sludge with high load.
- Class B_1 sludge: Biological sludge with weak load – extended aeration.
- Class B_2 sludge: biological sludge with medium load.
- Class C sludge: A mixture of sludge of types A and B_2.
- Class D sludge: Biologically stabilized sludge – mesophylic aerobically digested sludge – thermophylic aerobically stabilized sludge.

1.2.2 Characteristics of secondary sludge

Sludge production is the sum of three things: the accumulation of inorganic compounds, the accumulation of refractory organic compounds and microbial growth (Paul *et al.*, 1999). The sludge is composed of mineral and organic substances closely related; the proportion of each fraction having a strong influence on the properties of the sludge. The mineral fraction is mainly composed of particles and varied cations such as silicates, oxides of iron or calcium

phosphate (Salhi, 2003), whereas the organic fraction is composed of rather large polymers (cellulose, lignin), macromolecules, bio-molecules (proteins, sugars), humic acids and a lipid fraction (Trably, 2002).

In the case of activated sludge, organic matter is dominating. According to Paul *et al*. (2005), 60% of sludge is composed of inert organic matter and according to Lehne *et al.* (2001), the activated sludge is composed of 70% of micro-organisms (bacteria mainly). Due to the constraints prevailing at the wastewater treatment plant, bacteria-free purification adopts a floc structure. They agglomerate and form aggregates denser than water. These flocs settle, are recovered at the clarifier and are treated, thus forming a large fraction of the sludge.

Removal of organic materials by biological oxidation is a core technology in wastewater treatment process. New cells (sludge), carbon dioxide, soluble microbial products and water are the end products for this process. Activated sludge process has been applied worldwide in municipal and industrial wastewater treatment practice. Daily production of excess sludge from conventional activated sludge process is around 0.5 – 1.2 kg-VSS/kg-BOD_5 or 15 -100 L/kg-BOD_5 removed, in which over 95% is water. It is evident that the general purpose of activated sludge process is in the removal of organic pollutants rather in cultivation of excess sludge. In 2006, the excessive sludge to be treated in the European Union countries reached 7.7 millions dry materials including 0.8 millions dry materials for France.

With the expansion of population and industry, the increased excess sludge production is generating a real challenge in the field of environmental engineering technology. So far the regulations of food safety, agriculture and sludge disposal in most countries are being more and more stringent in relation to application of bio-solids in agriculture and dumping into the sea (Liu *et al.*, 2001).

It should be realized that biomass production is an important economic factor because the sludge generated is a secondary waste that must be disposed of in an environmentally sound and cost-effective manner. Currently, production of excess sludge from activated sludge process is one of the most serious problems encountered in wastewater aerobic treatment.

The treatment of the excess sludge may account for 25 - 65% of the total plant operation cost (Horan, 1990; Zhao and Kugel, 1997). An ideal way to solve sludge-associated problems is to reduce sludge production in the wastewater purification process rather than the post-treatment of the sludge generated.

1.2.3 Sludge treatment processes

Activated sludge treatments have three main objectives: reduction of fermentablility, reduction of the mass of sludge and reducing health risks. The sludge is transformed into biosolids using a number of complex treatments such as digestion, thickening, dewatering, drying, and lime stabilization. Figure 2 illustrates a sludge treatment processes:

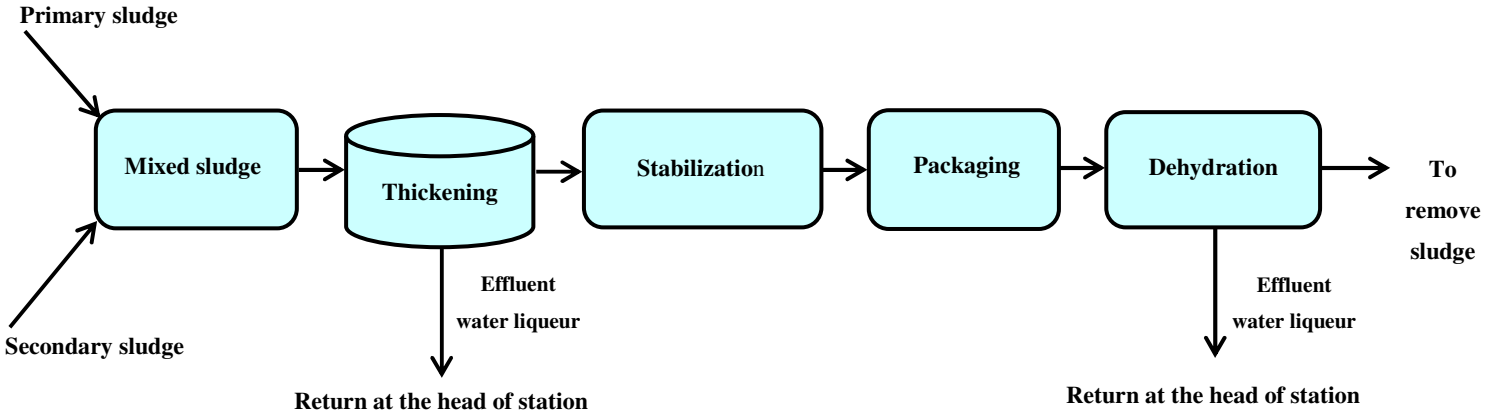

Figure 1-2: Principle diagram of a chain of sludge treatment.

An example of line of treatment sludge consists of four main steps:

1.2.3.1 Sludge thickening

This phase will focus sludge, and thus reduce their volume. Depending on the nature of the sludge, this operation is usually done by decantation gravity (static) or flotation. It can also be done by draining or centrifugation. The sludge is thickened, and the water withdrawn is returned at the head of station, in order to eliminate pollution dissolved in the soluble fraction. At this stage, the dryness obtained (dry matter) is of the order of 1 to 10%, depending on the facilities (OTV, 1997).

1.2.3.2 Sludge stabilization

The principal purpose of sludge stabilization is to reduce pathogens, eliminate offensive odours, and control the potential for putrefaction of organic matter. Sludge stabilization can be accomplished by biological, chemical, or physical means. Selection of any method depends largely on the ultimate sludge disposal method. As an example, if the sludge is dewatered and incinerated, frequently no stabilization procedure is employed. On the other hand, if the sludge is applied on land, stabilization is necessary to control odours and pathogens (Degrémont, 1989; OTV, 1997; Qasim, 1998).

Various methods of sludge stabilization are (1) anaerobic digestion, (2) aerobic digestion (3) chemical stabilization, and (4) thermal (physical) conditioning. Biological techniques can degrade the organic matter, and lead to a reduction in the matter. However, the chemical and physical techniques block the action of micro-organisms by inhibition of their metabolism (OTV, 1997). In recent years, because of its inherent energy efficiency and normally low chemical requirements, anaerobic digestion process is the most widely selected stabilization process at medium and large sized municipal plants (Qasim, 1998).

1.2.3.3 Sludge conditioning and dewatering

Sludge dewatering is necessary to remove moisture so that the sludge cake can be transported by truck and can be applied as bio-solids over farm lands, or disposed of by land filling or incineration. The solid particles in municipal sludge are extremely fine, are hydrated, and carry electrostatic charges. These properties of sludge solids make dewatering quite difficult. Sludge conditioning is necessary to destabilize the suspension so that proper sludge-dewatering devices can be effectively used.

Sludge-dewatering systems range from very simple devices to extremely complex mechanical processes. Simple devices involve natural evaporation and percolation from sludge lagoons or drying beds (planted bed). Complex mechanical systems utilize sludge conditioning; followed by centrifugation, vacuum filtration, filter presses, and belt filters. The selection of any device depends on the quantity and type of sludge and the method of ultimate disposal (Qasim, 1998).

At conditioning step, in order to release the water content in sludge, it is necessary to reduce the stability of colloids and facilitate their aggregation. The process can be physical (heat treatment) or chemical (adding minerals or polyelectrolyte). Heat treatment at 150°C–200° C for 30 to 60 minutes is the most effective in reducing particulate hydrophilic (Degrémont, 1989), but it induces a strong odour problem (Haug *et al.*, 1978).

Therefore, and because of lower cost, chemical flocculation is more often used. It involves a number of agents coagulants (charging opposite of particles contained in the sludge), and/or agents flocculants (formation of hydrated complexes).

In the dewatering step, the dryness of obtained sludge is 15 to 40%, depending on the sludge and the facilities used (OTV, 1997).

1.2.3.4 Sludge disposal

There are, at present, two major methods for disposal of sludge produced: (1) Agricultural recovery and (2) Incineration. Until recently, the sludge could also be put landfill. The nature of the sludge, geographical location and the local economic conditions guide the choice of the best way of disposal.

a) Agricultural Production

In 1997, in France, less than 60% of the productions of sludge were recovered in agriculture. Indeed, sewage sludge provides nutrients to the soil (minerals, organic matter) (OTV, 1997).

The use of sewage sludge in agriculture is highly regulated (decree on December 8, 1997 and arrested on 8 January 1998). The regulation imposes salaries, sets limits on the maximum concentration of certain pollutants (e.g. heavy metals) and prohibits or limits the application on some crops (Gomez Palacios *et al.*, 2002).

b) Incineration

In 1997, in France, approximately 15% of the production of sludge was treated by thermal oxidation (co-incineration) (OTV, 1997). This method is to burn the sludge in an incinerator, alone or with trash. After thermal oxidation, it remains by-products which, according to their nature, can be incorporated into some concrete used for roads or foundations or is land-filled.

Because of the prohibitive costs of transport, the treated sludge is incinerated mainly in urban areas (Spinosa, 2001). However, this technology requires large amounts of energy and sludge with high dryness. In addition, it is essential to deal with waste gases, which are a source of pollutants and toxic compounds.

2. Reduction of excess sludge production

Increased attention has been given to minimization of sludge production from activated sludge process since environmental regulations are being more and more stringent in relation to excess sludge disposal (Liu *et al.*, 2001).

Strategies for minimization of excess sludge production from activated sludge process are becoming a very practical and urgent issue. Therefore, it appears to be necessary to review

techniques that can be applied for reducing sludge production from industrial scale activated sludge process.

This study, therefore, reviews strategies developed for minimization of excess sludge production, such as ultrasonic, thermal and ozonation sludge processes. In these modified activated sludge processes, excess sludge production could be reduced by 20 -100% without significant effect on process efficiency and stability.

The wastewater treatment in municipal and industrial plant produces sludge, or biosolids, which are currently spread on filed (for about 60%), incinerated (15%) or stabilized and stored (25%) (in France). Because of demographic growth, and above all because of the increase in wastewater collection rates and the improvement in the treatment efficiency of plants, this sludge production grows each year. Sludge removal is a real problem in many cases and new technologies, named PRSP (Processes for Reduction Sludge Production) or PRSV (Processes for Reduction of Sludge Volume) in this study, could be new solutions. The aim of these PRSP is to reduce the sludge production directly at source, i.e. in the wastewater treatment lane.

The idea underlying all these processes is to limit the quantity of excess sludge leaving the WWTP. Although the sludge treatment was a few years ago only a secondary element in the water treatment network, it become today, notably with these new sludge treatment processes, completely integrated in the water treatment lane (Chauzy *et al.,* 2003).

The concentration of suspended solids in the tank, also normally known as "**sludge**", i.e. all living bacteria, dead bacteria and suspended solids entering the tank that have not biodegraded (such as fibres, cellulose, etc.), will increase naturally. This sludge is not easily or not at all biodegradable by the biomass present in the biological tank, either due to the preliminary hydrolysis stage, which is kinetically limiting, or due to its refractory nature. However, a small part of this sludge, namely the dead cell, can be consumed by the active biomass: this is known as cryptic growth (Chauzy *et al.,* 2002).

The various methods may be applied to the liquid treatment chain and/or in the sludge treatment chain as demonstrated in Figure 1-3. The processes most focus on:

a) Mechanical disintegration by ultrasound treatment.
b) Chemical oxidation disintegration by ozone treatment.
c) Physical disintegration by thermal treatment.
d) Biological disintegration by enzymatic lysis treatment.

New technologies for reducing the sludge production of municipal or industrial WWTP have been appeared during the last few years. These pre-treatments cause the lysis or disintegration of sludge cells (Weemaes *et al.*, 1998; Delgenès *et al.*, 2003). Intracellular matter is released and becomes more accessible by anaerobic micro-organisms.

The aim of these treatments is to lyse the flocs, reducing the particle size (organic compounds and especially refractory compounds) and solubilize the intra and extra cellular material to make them more easily biodegradable (Bougrier *et al.*, 2006).

The objective of sludge minimization is to optimise the activated sludge biomass growth and/or to enhance the biodegradation of the residual biomass. It will therefore always be the association of a process for organic matter hydrolysis and/or a process for biomass stress together with a biological process, either aerobic or anaerobic.

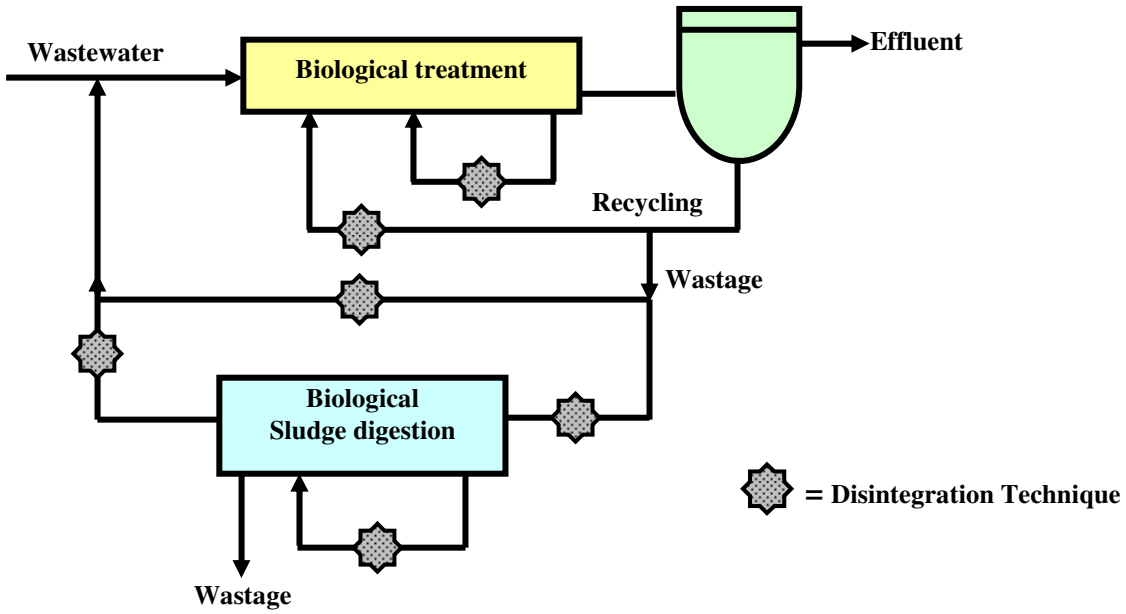

Figure 1-3: Various places in a biological process where disintegration techniques may lead to reduction in ESP. (Paul and Salhi, 2003)

The aim of $PRSP_S$ is to optimise growth of the biomass and/or its biodegradation. They combine an organic matter hydrolysis process and/or a stress process, with a biological treatment (aerobic or anaerobic). The two principles are detailed below:

2.1 Sludge minimization processes

The biological sludge production in conventional wastewater treatment plants can be minimized in a number of ways. In fact, there are a high number of different processes by which sludge reduction can be achieved.

It has been preferred to categorize the different processes according to the place of the plant where the minimization takes place. Three main strategies are identified: in the wastewater line, in the sludge line, or in the final waste line (Table 1-4). Any existing processes for sludge minimization can be placed in one of these strategies (Pérez-Elvira *et al.,* 2006).

2.1.1 Processes in the water line

It consists of reducing sludge production in the biological wastewater treatment. The idea is to reduce sludge production in the wastewater treatment rather than the post-treatment of sludge after generation. This can be achieved with two kind of processes: those that reduce the yield coefficient (e.g. ozonation, chemical un-coupler, oxic-settling-anaerobic process called OSA, etc), or those with an intrinsic lower yield coefficient (e.g. anaerobic–aerobic processes).

2.1.2 Processes in the sludge line

The idea is to reduce excess sludge production by enhanced treatment of the sludge. The aim in these processes is to reduce the final stream of sludge to be disposed of. Due to the high organic fraction of sewage sludge, anaerobic fermentation is the standard process in sludge treatment for reducing and stabilizing the wastewater solids. The anaerobic digestion process is composed of three steps: hydrolysis, acidogenesis and methanogenesis. The rate-limiting step in the overall process is the hydrolysis reaction, which makes the degradation of waste activated sludge especially low. Some technologies are being investigated in order to enhance the anaerobic digestion of sludge, some of them are pre-treatment processes prior to the anaerobic reactor (mechanical disintegration, thermal pre-treatments, biological hydrolysis with enzymes, etc), and others are changes in the reactor itself (temperature phased anaerobic digestion, anoxic gas flotation called AGF, etc).

Table 1-4: Sludge minimization processes. (Pérez-Elvira *et al.,* 2006)

Processes in the water line	Processes that reduce the yield coefficient	Lysis cryptic growth	Chemical oxidation	Ozonation	FS
				Chlorination	FS
			Integration of chemical and heat treatment		FS
			High purity oxygen process		FS
			Enzymatic reaction		FS
		Maintenance metabolism	Membrane bioreactor		EM, IN
		Uncoupling metabolism	Chemical uncoupler		EM
			Oxic-settling-anaerobic process(OSA)		IN, FS
		Predation on bacteria	Two-stage system		EM
			Oligochaetes (worms)		EM
	Processes with low yield coefficient		Anaerobic/aerobic system		EM, IN
Processes in the Sludge line	Pre-treatment processes prior to anaerobic digestion	Physical pre-treatment	Cavitations	High pressure homogenizers	EM, IN
				Ultrasonic homogenizers	EM, IN
			Thermal	Thermal hydrolysis	IN, FS
				Freezing and thawing	EM
			Mechanical	Impact grinding	EM, IN
				Stirred ball mills	EM, IN
				High performance pulse technique	EM, IN
				The lysat-centrifugal technique	EM, IN
			Radiation	Gamma-irradiation	EM
		Chemical pre-treatment	Acid or alkaline hydrolysis		EM, IN
			pre-treatment using ozone		EM
		Biological pre-treatment	Enzymatic pre-treatment		EM
		Combined pre-treatment	Combination of thermal, decompression and shear forces		IN, FS
			Chemically enhanced thermal hydrolysis		EM, IN
	Modified anaerobic digestion processes		Two-stage Anaerobic digestion		IN
			Temperature phased anaerobic digestion		IN
			Anoxic Gas Flotation		IN, FS
Processes in the final waste line			Incineration		FS
			Gasification and pyrolysis		FS
			Wet Air Oxidation (WAO)		FS
			Super Critical Water Oxidation (SCWO)		FS

EM: Embryonic (laboratory scale).
IN: Innovative (demonstration and limited use).
FS: Full-scaled (tested in several full-scale operations).

2.1.3 Processes in the final waste line

These last technologies aim to treat the sludge produced to get a final stable, dewatered and pathogen free residue. They do not represent a minimization strategy, but a post-treatment to dispose of the sewage solids. All are based on energy recovery such as incineration, gasification and pyrolysis, wet air oxidation or WAO, supercritical water oxidation or SCWO (Pérez-Elvira *et al.,* 2006).

Some valuable reports about sludge minimization technologies have been published by Liu and Tay, (2001); Odegaard *et al.* (2002); Wei *et al.* (2003); and Odegaard, (2004).

2.2 Action on bacterial growth

In order to improve the overall process performance, one approach is to use a lyse pre-treatment. Some methods for sludge disintegration can be considered: mechanical, thermal, chemical or biological treatments (Müller, 2000-b & 2001) in order to facilitate degradation in an aeration tank or in a sludge digester. In this chapter, we present the techniques that can be applied in the water line, to disintegrate particles in an activated sludge process scheme. When the treated sludge is returned to the biological reactor, degradation of the secondary substrate generated form the sludge pre-treatment takes place, hence resulting in a reduction in the sludge production.

This involves stressing the micro-organisms so as to reduce sludge production by encouraging the consumption of pollution by bacteria for their maintenance and not for their multiplication (biosynthesis). During the stress period, the micro-organisms draw on their reserves (endogenous respiration) and must then replenish their stocks, to the detriment of their replication. This stress is already used today both in low-load treatment plants and in membrane bioreactors (BIOSEP® type, Vivendi Water system process) where the sludge concentration and implicitly the age of the sludge are high. This is because fresh sludge produces bacteria that are highly viable and uses the energy of the catabolism for biosynthesis (anabolism), whereas old sludge encourages the appearance of bacteria that are not very viable and use the same energy for cell maintenance.

This stress can be achieved in different ways, by physico-mecanical means (ultrasound) in the zone away from the transmitters, by chemical means (low chlorination, low ozonation) or by biological means (increasing the age of the sludge, extended aeration/low load processes,

anoxia stage). A PRSP can also involve a combination of the two phenomena referred to above (Chauzy *et al.,* 2002).

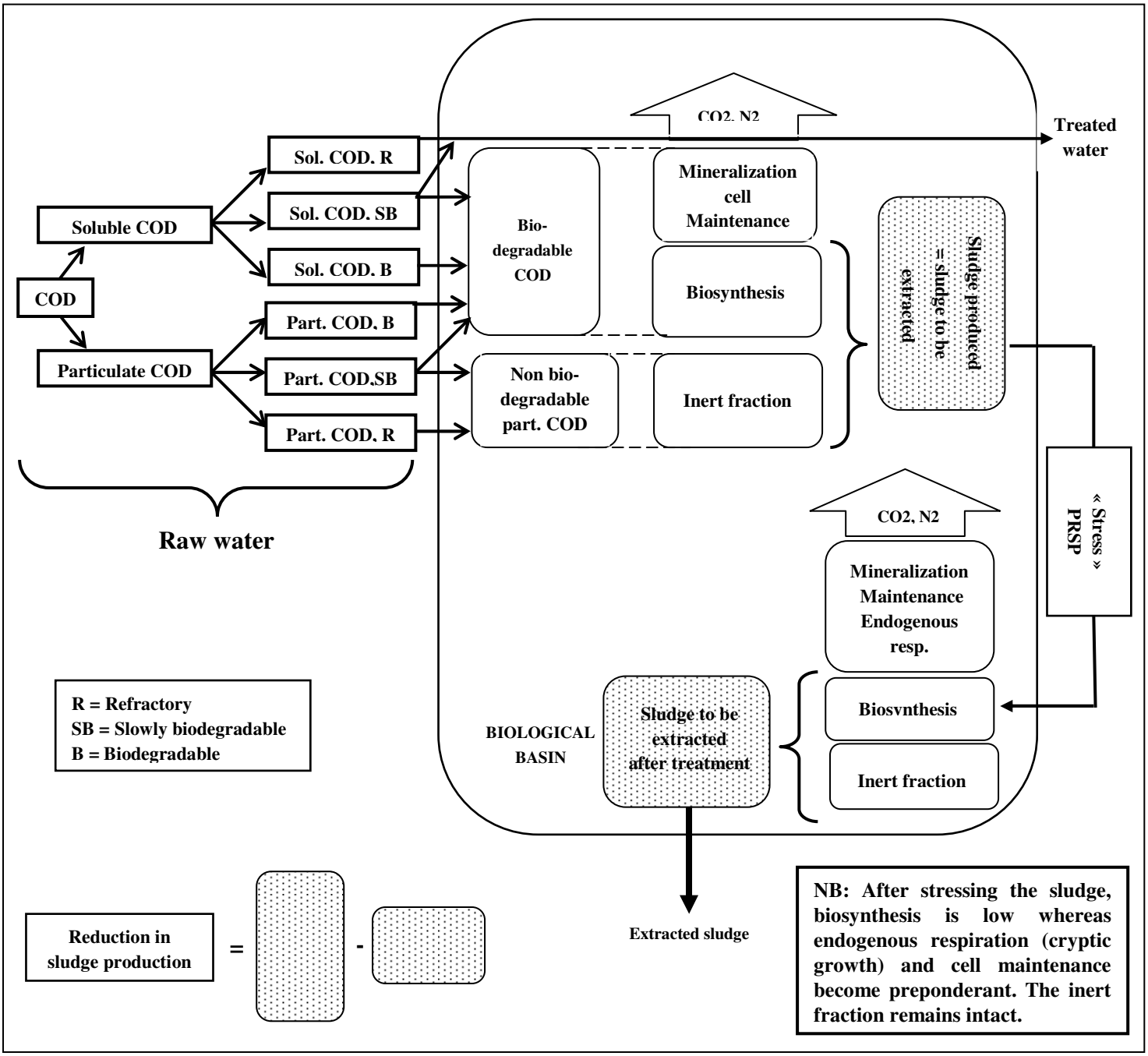

Figure 1-4: Principle of bacterial stress processes. (Chauzy et al., 2002)

It is imperative to reduce the generation of sewage sludge. This can be achieved within the wastewater treatment plant. For this, there are several possibilities.

One way to do is to control the residence time of the sludge in the aeration basin (age of sludge θ_c). Indeed, by increasing the age of sludge, it is possible to significantly reduce the production of sludge. It has been shown, through modeling that the sludge production decreases by 30% by

increasing the age of sludge from 5 to 30 days (Salhi, 2003). However, the increase in the age of sludge results in a higher concentration of bacteria in the aeration basin. In an age of sludge over 25 days, the concentration exceeds $5g.L^{-1}$ (Salhi, 2003). This creates problems for clarification and sludge losses can occur in the treated effluent (Metcalf and Eddy, 1991).To solves this problem of clarification, it is possible to work with fixed biomass processes: the hydraulic retention time (HRT) and the sludge residence time (SRT) are decoupled. This could reduce the production of sludge in half (Paul and Buffière, 2001).

2.2.1 Lysis-cryptic growth

When certain external forces are applied, microbial cells undergo lysis or death during which cell contents (substrates and nutrients) are released into the medium, providing an autochthonous substrate that is used in microbial metabolism (Mason *et al.,* 1986). The biomass growth due to this substrate is termed as cryptic growth (Mason & Hamer 1987). These results lead to a reduction of the overall biomass production. There are two stages in lysis-cryptic growth: lysis (which is the rate-limiting step) and biodegradation.

Previous laboratory studies have demonstrated that the net biomass growth could be reduced under cryptic conditions (Canales *et al*., 1994; Yausi *et al*., 1994). Researches show that microbial cell lysis can be amplified by prolongation of sludge retention time (SRT) or through physicochemical treatments of sludge, such as thermal, alkaline or acid. (Rocher, 1999). Based on these findings, it is hypothesized that cryptic growth phenomenon may be a feasible approach to achieve the goal of reducing sludge production (He *et al*., 2006). Indeed, the traditional treatments can hardly absorb the wastewater products.

There are two stages in lysis-cryptic growth: lysis and biodegradation. The rate-limiting step of lysis-cryptic growth is the lysis stage, and an increase of the lysis efficiency can therefore lead to an overall reduction of sludge production.

2.2.2 Maintenance and endogenous metabolism

According to Pirt (1965), part of energy source is used to maintain living functions of micro-organisms, which is so-called maintenance metabolism. The maintenance energy includes energy for turnover of cell materials, active transport, motility, etc. Note that the substrate consumption associated with maintenance of the living functions of micro-organisms is not synthesised of new cellular mass. Thus, the sludge production should be inversely related to the activity of maintenance metabolism (Chang, 1993). On the other hand, to account for the

decrease in biomass production that is usually observed when the specific growth rate decreases, Herbert *et al.* (1956) postulated that the maintenance energy requirement could be satisfied through endogenous metabolism. In this case, part of cellular components is oxidized to produce the energy for maintenance functions. The purpose is to reach conditions that naturally balance cell growth and decay.

Endogenous respiration is the auto-digestion of biomass. The major advantage of the endogenous metabolism is that the incoming substrate could be finally respired to carbon dioxide and water, while results in a lower biomass production (Gaudy, 1980; Martinage and Paul, 2000). It should be realized that the control of endogenous respiration would have as much practical significance as the control of microbial growth and substrate removal in wastewater treatment processes. Increasing the biomass concentration (controlling sludge retention time or sludge loading rate it would be theoretically possible to reach a situation in which the amount of energy provided equals the maintenance demand. Employing a membrane bioreactor, Canales *et al.* (1994) demonstrated that higher sludge ages increased the biomass viability.

2.2.3 Uncoupling metabolism

Metabolism is the sum of biochemical transformations, including interrelated catabolic and anabolic reactions. The yield of cells is directly proportional to the amount of energy (ATP) produced via catabolism (oxidative phosphorylation). The uncoupling approach is to increase the discrepancy of energy level between catabolism and anabolism so that the energy supply to anabolism would be limited. As a result, the growth yield of biomass decreases, and the production of sludge can be reduced. Uncoupled metabolism is observed under some conditions such as existence of inhibitory compounds or heavy metals, abnormal temperature, excess energy source, limitation of nutrients, and alternative aerobic anaerobic cycle (Tsai, 1990; Mayhew, 1998; Liu, 2000).

In an environmental engineering sense, the concept of energy uncoupling can be extended to the phenomenon in which the rate of substrate consumption is higher than that required for growth and maintenance. As a result, under energy uncoupling conditions the observed growth yield of activated sludge would be reduced markedly.

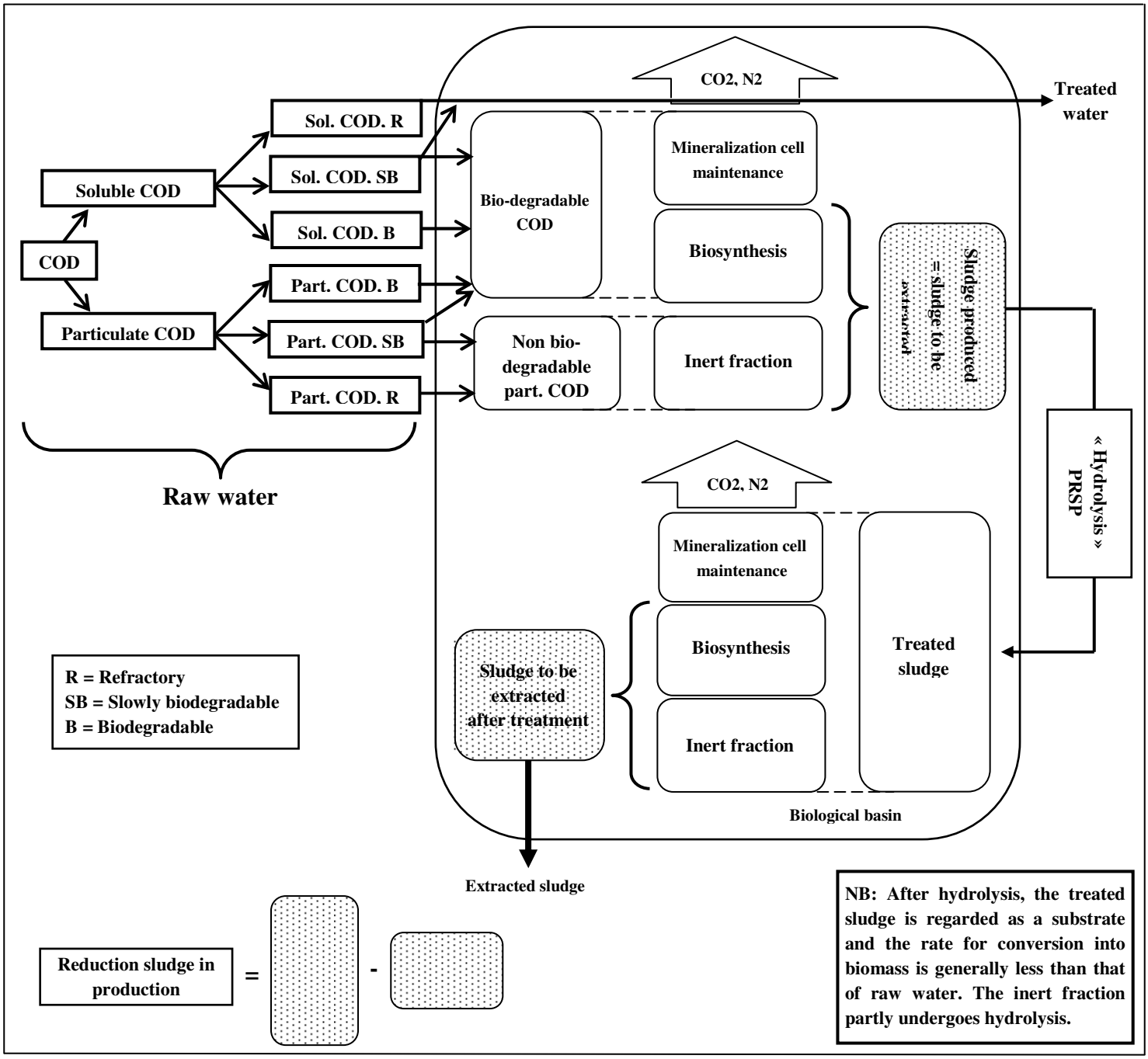

Figure 1-5: Principle of hydrolysis processes. (Chauzy *et al.,* 2002)

In theory, reduction in the growth yield means that sludge production can be cut down by an equivalent percentage. This is a promising way to reduce excessive sludge production by controlling metabolic state of micro-organisms in order to maximize dissociation of catabolism from anabolism.

2.3 Improvement of biodegradability and solubilization of organic matter

Organic matter (including part of the matter that is not or is hardly biodegradable and known as "inert") into soluble organic matter that can easily be assimilated by the biomass in the biological tank. This transformation is performed firstly by cell hydrolysis of the bacteria (destruction of bacteria by elimination of the cell wall, and release of the cell content) and secondly by reducing the size of molecules. Its aim is to increase the biodegradable fraction of sludge and therefore optimize overall mineralization of organic pollution entering the plant. The efficiency of converting cell lysis products into bacteria (biosynthesis) is usually lower than that applied to municipal effluent. The mineralization and maintenance phenomena are therefore proportionally grater.

This transformation can be mechanical (pressure/decompression, grinding of sludge, ultrasound in the zone near the transmitters), chemical (acid/base treatment, oxidation by H_2O_2, ozone), biochemical (enzyme), thermal or a combination of several parameters (Chauzy *et al.,* 2002).

In most biological wastewater treatment processes such as activated sludge process, though they have been recognized to be effective for organic wastewater treatment, a large amount of excess sludge derived from microbial growth has been problematic. Such excess sludge produced from the biological process has been generally digested either aerobically or anaerobically. To enhance the biodegradability of sludge cells, it is necessary to solubilize or hydrolyze the sludge cells prior to aerobic or anaerobic sludge digestion.

The solubilization techniques proposed so far include mechanical disintegration, (Jung *et al.,* 2001) chemical or thermo-chemical treatment based on acidic or alkaline conditions (Lin *et al.,* 1998; Rocher *et al.,* 1999; Saiki *et al.,* 1999) and oxidative treatments using ozone (Huysmans *et al.,* 2001; Sakai *et al.,* 1997). However, these techniques need high running cost. Obligate aerobic and anaerobic micro-organisms are to be dead by the change of microbial growth environments, resulting in their solubilization under alternated anaerobic and aerobic environments, respectively. The organic substances derived from the solubilized micro-organisms are expected to be utilized as substrate for another bacterial growth (Jung *et al.,* 2006).

2.4 Reduction of sludge production

Excess sludge treatment and disposal currently represents a rising challenge for wastewater treatment plants due to economic, environmental and regulation factors. The treatment of the excess sludge may account up to 65% of the total plant operation cost. An ideal way to solve sludge-associated problems is to reduce sludge production during the wastewater purification process rather than the treatment of sludge afterwards.

Micro-organisms satisfy their maintenance energy requirements in preference to producing additional biomass, and this recognition has revealed possible methods for sludge reduction during biological wastewater treatment. To reduce the production of biomass, wastewater processes must be engineered such that substrate is diverted from assimilation for biosynthesis to fuel exothermic, non-growth activities. It is well known that increasing sludge retention time or reducing sludge loading rate, which is the idea of membrane bioreactor (MBR), will lead to the reduction of the biomass.

Several methods have been applied for sludge disintegration so far: (i) thermal treatment (Kepp *et al.,* 2000; Barjenbruch *et al.,* 1999), (ii) chemical treatment (Tanaka *et al.,* 1997), (iii) mechanical disintegration (Tiehm *et al.,* 1997**;** Chu *et al.,* 2001), (iv) biological hydrolysis with enzyme addition (Guellil *et al.,* 2001), (v) advanced oxidation processes (Weemaes *et al.,* 2000), and (vi) combination ways such as thermo-chemical treatment (Neyens *et al.,* 2003), combination of alkaline and ultrasonic treatment (Chiu *et al.,* 1997).

Sludge lysis and subsequently cryptic growth could be promoted by mechanical, physical, chemical and combined ways in order to reduce sludge production.

3. Processes of sludge reduction

Recently, a lot of interest has been devoted to sludge disintegration and solubilization techniques in order to cope with the biological limitations of particulate matter degradation. We can consider combined processes where the disintegrated sludge is fed back to a biological step for further biodegradation. The disintegration processes are based on mechanical, electrical, thermal, thermo/chemical, biological and oxidative techniques.

Table 1-5: Sludge disintegration processes. (Odegaard, 2004; Gary R. Krieger *et al.,* 2001; Antoni A. Garcia, 1999)

Mechanical	Physical	Chemical	Biological
Stirred ball-mill	Freezing	Acid or base hydrolysis	Enzymatic Lysis
Homogenizer (high-pressure)	Thawing	Oxidation with H_2O_2, O_2	Autolysis
Ultrasound cavitations	Osmotic shock	Chlorination	
Lysat-centrifuge	Thermal treatment	Ozonation	
Impact grinding	High-yield pulse technology		

Various sludge disintegration technologies for sludge minimization are used, including mechanical methods (focusing on stirred ball-mill, high-pressure homogenizer, and ultrasonic disintegrator), chemical methods (focusing on the use of ozone), physical methods (focusing on thermal hydrolysis) and biological methods (focusing on enzymatic processes).

3.1 Sludge disintegration by use of mechanical pre-treatment

The mechanical disruption process involves the action of externally applied stress or pressure on the cells. Cells are disrupted when the external pressure exceeds the cell internal pressure. Mechanical disruption of sludge has gained acceptance due to its various successful industrial scale applications. As shown in Table 1-5, there are several mechanical disintegration technologies that may be used. Good reviews of the various disruption methods have been given by ATV (2000, 2001). In this study we have only focused on the most important disintegrators.

3.1.1 The stirred ball mills

This device consists of a cylindrical grinding chamber (up to 1 m^3 volume) almost completely filled with grinding beads. An agitator forces the beads into a rotational movement. The micro-organisms are disintegrated between the beads by shear- and pressure- forces.

Main research has been done by Kunz and Wagner (1994); Müller (1996); Baier and Schmidheiny (1997); Lehne *et al.* (2001); Müller (2001); Winter (2002); and Müller and winter (2004). Positive and negative aspects of stirred ball mills are summarized in Table 1-6 (Pérez-Elvira *et al.,* 2006).

Table 1-6: Positive and negative aspects of stirred ball mills.

Positive	Negative
Reliability of operation (high degree of research and development)	**The degree of disintegration of the sludge is lower compared to other techniques**
No odour generation	**High energy friction losses**
	Clogging problems
	Huge erosion in the grinding chamber

3.1.2 The high pressure homogenizers

These units consist of a multi-step high-pressure pump and a homogenizing valve. The pump compresses the suspension to pressures up to several hundred bars. When passing through the homogenizing valve, the pressure drops below the vapour pressure of the fluid, and the velocity increases up to 300m/h. The formed cavitation bubbles implode, inducing into the fluid temperatures of several hundred degrees Celsius, which disrupt the cell membranes.

The patented Micro-Sludge process (Stephenson and Dhaliwal, 2000) utilizes alkaline pre-treatment to weaken cell membranes and reduce viscosity. Main research has been done by Kunz and Wagner (1994); Müller (1996); Baier and Schmidheiny (1997); Müller (2000-a and b); Lehne *et al.* (2001); Theodore *et al.* (2003); and Stephenson *et al.* (2004). Table 1-7 shows the positive and negative aspects of high pressure homogenizers (Pérez-Elvira *et al.,* 2006).

Table 1-7: Positive and negative aspects of high pressure homogenizers.

Positive	Negative
No odour generation	**Low reduction of pathogens**
Easy to implement in a WWTP	**Clogging problems caused by coarse and fibrous particles**
Better dewaterability of the final sludge	**High tensions and erosion in the pump and homogenizing valve**

3.1.3 The ultrasonic disintegrator

The application of ultrasound for treating sludge prior to anaerobic digestion has been recognized by Chiu *et al*. (1997) and Tiehm *et al*. (1997, 2001-b). Ultrasound is the term used

to describe energy waves at frequencies above the normal hearing range of humans (>20 kHz) propagated via a compression/rarefaction mechanism. Low power ultrasound technologies have been known and used for a long time in non-destructive applications. High power ultrasound is applied for sludge disintegration.

Table 1-8: Positive and negative aspects of ultrasonic homogenizers.

Positive	Negative
Reliability of operation (high degree of research and development)	**Negative energy balance due to the high energy consumption of the equipment**
No odour generation	**Erosion in the sonotrode**
No clogging problems	
Easy to implement in a WWTP	
Better dewaterability of the final sludge	

At sufficiently high power densities, the rarefaction cycle will exceed the attractive forces of the molecules of the liquid and bubbles will form. These will grow until they implode creating localized extreme pressure and temperature conditions (cavitation) resulting in cell lysis (Odegaard, 2004). Table 1-8 presents the positive and negative aspects of ultrasonic homogenizers (Pérez-Elvira *et al.,* 2006).

Table 1-9 summarizes the state of the art of the most well known mechanical methods ATV (2001).

Table 1-9: Experiences with the most established mechanical disintegration technologies. (Odegaard, 2004)

Extent of operational experience	The stirred ball-mill	The high-pressure homogenizer	The ultrasonic disintegrator
Lab	**++**	**++**	**++**
Pilot-Plant	**++**	**++**	**++**
Full-scale	**+**	**-**	**+**
Long term operation	**-**	**--**	**-**
Operational stability	**+/-**	**--**	**++**
Technical state of the art	**+**	**--**	**+**

++ very much/very (good), + much/(good), - little/(poor), -- very little/very (poor)

3.1.4 Sonication treatment

Ultrasonic treatment is a suitable method to disintegrate sewage sludge and to overcome the slow biological sludge hydrolysis. Ultrasound is already widely used to break the structure of bacterial flocs, disrupt cell walls and finally to extract exo-polymers (Chu *et al.,* 2001).

These devices consist of three components: A generator which supplies a high frequent voltage, a piezo-electrical material that transforms electrical into mechanical impulses which are transmitted by a sonotrode into the fluid and a probe (sonotrode). Cavitations bubbles are created by alternating over-pressure and under-pressure. When imploding, they generate a great amount of energy that causes cell disruption.

Ultrasound may be generated by two different methods, magnetostrictive and piezoelectric. The former uses electric energy, passing through a magnetic coil attached to the vibrating piece to produce the mechanical energy, or vibration. The latter uses electrical energy, converted to high frequency electric energy, which is applied to piezoelectric crystals that vibrate at the same frequency. The crystals are attached to the vibrating piece (known as the sonotrode, probe or horn), causing the vibration to be transferred to the liquid. Magnetostrictive systems typically have a longer life, but lower energy efficiency as the electrical energy applied is converted to magnetic energy prior to being converted to mechanical energy. For wastewater applications it appears that the economics favour the use of piezoelectric systems due to the high energy intensity required to lyse the cellular material in the sludge.

There are differences in the ultrasound systems available for wastewater treatment. Each manufacturer uses a unique shape for the vibrating ultrasound piece. For example Ultra-waves uses short rod shaped sonotrodes that project into the flow path, while Sonico uses ring shaped horns that sit within a pipe spool. Ultra-waves treat a smaller portion of the flow for a longer retention time, while Sonico typically treats a greater portion of the sludge flow for a considerably shorter retention time. Each probe in the Ultra-waves system is rated for 2 kW power input, but typically operates at 1 kW. Sonico has 3 kW and 6 kW horns, with the latter as their standard unit, operating at 50 to 60 percent of rated power.

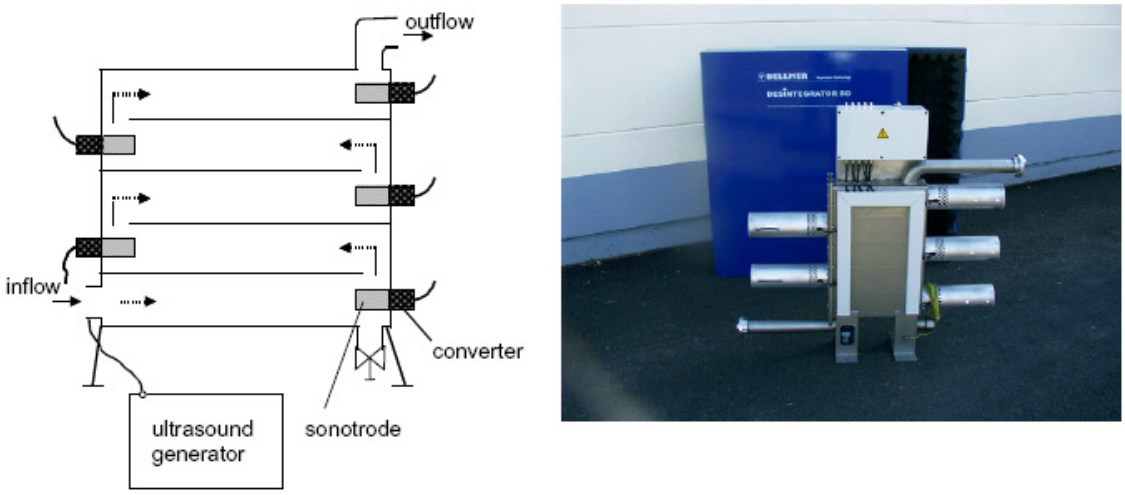

Figure 1-6: Scheme and side view of the full-scale ultrasound reactor (ULTRAWAVES Water and Environmental Technologies, Hamburg, Germany) (Nickel and Neis, 2007).

The majority of ultrasound applications to date have been for WAS pre-treatment prior to anaerobic digestion. However, both Ultra-waves and Sonico have European installations on return activated sludge (RAS) streams within the waste activated sludge process (Roxburgh *et al.,* 2006).

3.1.5 Effect of ultrasound on physicochemical characteristic of sludge

Particle size analysis, microscopic image and sludge dewaterability are some of the techniques adopted to judge the effectiveness of ultrasonic disintegration. Physical evaluation, especially particle size distribution and microscopic image analysis, has been widely employed for simplicity as qualitative measures of sludge disintegration (Khanal *et al.,* 2007).

Ultrasonic pre-treatment also modifies the physicochemical characteristics of sludge. For instance, Ultrasound affects turbidity phenomena, by increasing supernatant turbidity. According to Bougrier (2005), turbidity increases linearly by increasing specific energy. In fact, an augmentation of SE leads to disintegration of flocs, thus increases average amount of colloidal material ($\varnothing < 1$ µm) in supernatant.

pH decreases slightly during the sonication. In Zhant *et al.* (2007) studies pH of the sludge decreased by less than 0.5 in all sonication experiments and was not adjusted. The cause of pH decrease during the sonication can be considered to be fat destruction and thus production of volatile organic acids.

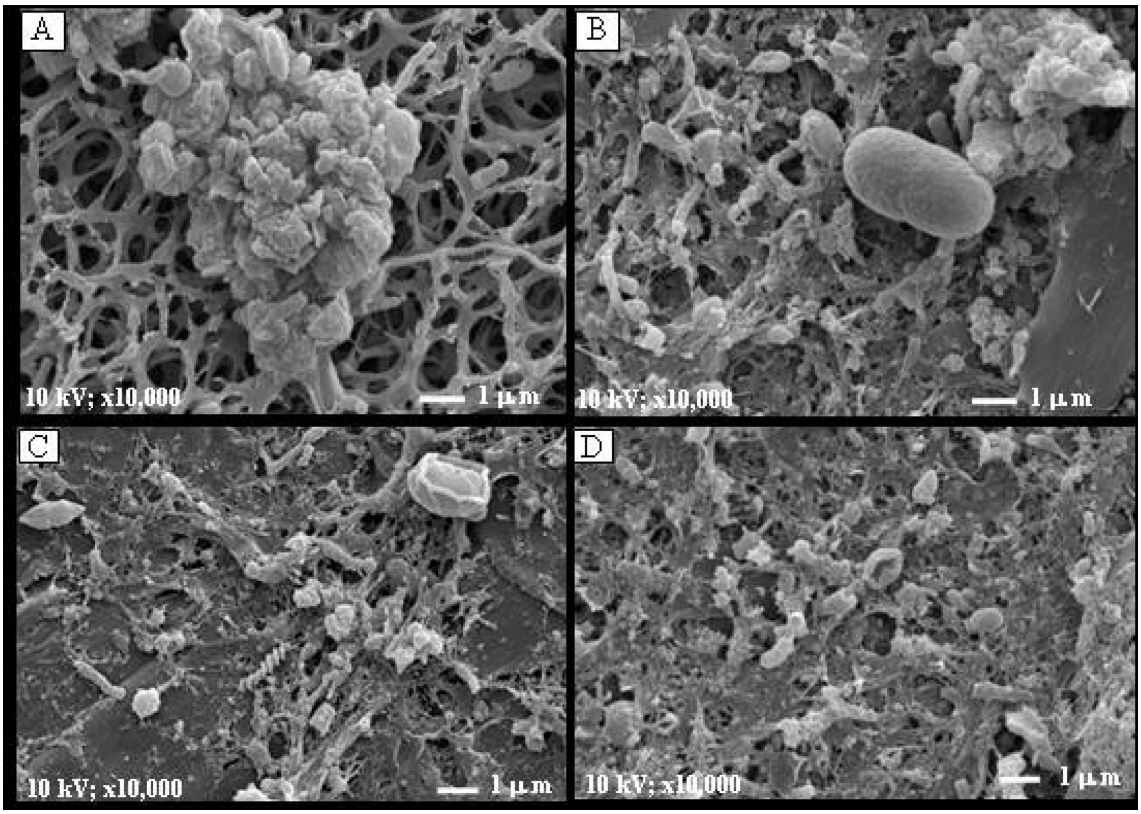

Figure 1-7: Scanning electron micrographs (SEM) images of undigested WAS at different sonication duration with constant power input of 1.5 kW and frequency of 20 kHz: (A) 0 min (control); (B) 2 min; (C) 10 min; and (D) 30 min. (khanal *et al.,* 2007)

Scanning electron micrographs (SEM) provide more thorough information on sludge disintegration particularly at the cellular level as depicted in Figure 1-7. Prior to sonication, flocs entangled within large numbers of filaments can be observed (Figure 1-7-A). This filament-like structures are essentially organic debris (with diameter less than one-fourth of a micron) attached to the flocs. During 2 minuets of sonication, the structural integrity of flocs as well as filaments will be significantly disrupted without appreciable destruction of bacterial cells as seen in Figure 1-7-B. At a longer sonication duration, such as 10 minutes, nearly complete disintegration of flocs and filament-like structures with a very few scattered bacterial cells can be observed (Figure 1-7-C). When the sludge is sonicated for 30 minutes, more or less complete break-up of cell walls will be observed with several punctured cells (Figure 1-7-D) (Khanal *et al.,* 2007).

3.1.6 Reaction Mechanisms of ultrasonic

Hoffmann *et al.* (1996), Gonze *et al.* (1997), and Tiehm *et al.* (2001-a) have studied the mechanisms related to the use of ultrasound applied to sludge. Ultrasound is sound above the

range of human hearing, with frequencies between 20 kHz and 10 MHz. Figure 1-8 shows the relative frequencies of sound waves.

Above certain intensity the attractive forces of the liquid can be overcome during rarefaction and a small bubble is formed. This phenomenon is called acoustic cavitation (Tiehm *et al.,* 1997; Petrier *et al.,* 1998). The cavitation bubbles collapse within microseconds and give rise to strong hydromechanical shear forces (Tiehm *et al.,* 2001-b). Cavitation occurs more readily at a frequency of 20–40 kHz.

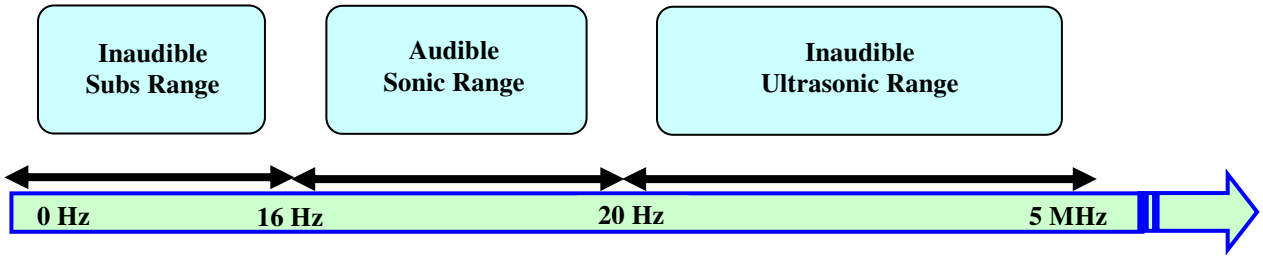

Figure 1-8: Nomenclature of sound waves at different frequencies. (Khanal *et al.,* 2007)

When the ultrasound wave propagates in a medium such as sludge, it generates a repeating pattern of compressions and rarefactions in the medium. The rarefactions are regions of low pressure (excessively large negative pressure) in which liquid or slurry is torn apart. As a result of reduced pressure, micro-bubbles are formed in the rarefaction regions. These micro-bubbles also known as cavitation bubbles, essentially containing vaporized liquid and gas that was previously dissolved in the liquid. As the wave-fronts propagate, micro-bubbles oscillate under the influence of positive pressure, thereby growing to an unstable size before violently collapsing. Cavitation is the phenomenon as a result of which micro-bubbles are formed in the aqueous phase and expand to unstable size, and then rapidly collapse (Khanal *et al,.* 2007).

At the lower end of this range the compaction (high pressure) and rarefaction (low pressure) waves generated by ultrasound lead to the formation of cavitations bubbles in the fluid, which implode creating high mechanical shear forces. The implosions create localized hot spots with conditions similar to the sun, reaching temperatures up to 5000°K and pressures up to 500 bar (7,250 psig). Jet streams caused by the implosions can have speeds up to 400 km/hr (250 miles/hr). These forces can be used for disintegrating solids in the fluid (Roxburgh *et al.,* 2006). High frequencies (500 kHz) encourage radical reactions, (Tiehm, 2001) while low frequencies (20-40 kHz) favour the formation of cavitation bubbles (Tiehm *et al.,* 1997).

Studies have shown that particularly low frequency and high intensity ultrasonic treatments (low intensity ultrasound can not break up the cell wall but accelerates the cell hydrolysis) are well suited to disrupt the sludge flocs and to lyse the bacterial cells. (Zhang *et al.,* 2007-a).

Regarding micro-organisms, Tsukamoto *et al.* (2004) reported that the ultrasounds have a bacteriostatic effect (which prevents cell division) on micro-organisms. Indeed, the explosion of cavitations bubbles can isolate the bacteria and make them more fragile. The toxic compounds can penetrate more easily in the cells and inactivate them. In fact, hydrophobic organic compounds are more volatile and thus can be more easily degraded by ultrasonic than non-volatile hydrophilic compounds (Gonze *et al.,* 1999).

For wastewater applications it has been shown that ultrasound is most beneficial when applied on biological secondary solids, where rapid hydrolysis can be induced, releasing the nutrients in the cells for consumption in the activated sludge or anaerobic digestion process (Roxburgh *et al.,* 2006).

Mechanisms of reaction of ultrasonic initialization of radical are done by sonolyse of water. Mechanisms of reaction take place during three steps (Chitra *et al.,* 2004; Bernal-Martinez, 2005):

Table 1-10: Mechanisms of reaction of ultrasonic initialization.

1) Initiation	2) Propagation	3) Termination
$H_2O \rightarrow H^{\bullet} + HO^{\bullet}$ $O_2 \rightarrow 2O^{\bullet}$	$H^{\bullet} + O_2 \rightarrow HOO^{\bullet}$ $O^{\bullet} + H_2O \rightarrow 2OH^{\bullet}$ $RH + OH^{\bullet} \rightarrow R^{\bullet} + H_2O$ $R^{\bullet} + O_2 \rightarrow ROO^{\bullet}$ $RH + OOH^{\bullet} \rightarrow R^{\bullet} + H_2O_2$	$2HOO^{\bullet} \rightarrow H_2O_2 + O_2$ $2HO^{\bullet} \rightarrow H_2O_2$ $R^{\bullet} + OH^{\bullet} \rightarrow ROH$ $R^{\bullet} + OOH^{\bullet} \rightarrow ROOH$

There are four paths for disintegration mechanisms which are responsible for the ultrasonic activated sludge disintegration:

- Hydro-mechanical shear forces;
- Oxidizing effect of $^{\bullet}OH$, $^{\bullet}H$, $^{\bullet}N$, and $^{\bullet}O$ produced under the ultrasonic radiation;
- Thermal decomposition of volatile hydrophobic substances in the sludge;
- Increase of temperature during ultrasonic activated sludge disintegration.

If the sludge temperature is improved, the lipid on the cytoplasmic membrane can be decomposed, which results in the generation of little holes on the membrane. The intracellular substances can release through the holes, which causes the increase of S_{COD} in the supernatant (Wang *et al.,* 2005).

3.1.7 Performances of ultrasonic treatment

Ultrasound as a pre-treatment method has been investigated on laboratory, pilot and full-scale levels. Reports in the literature tell of floc-size reduction, (Chu *et al.,* 2001 & 2002; Bougrier *et al.*, 2006), cell lysis (Tiehm *et al.,* 1997; Chu *et al.,* 2001; Brown *et al.,* 2003; Odegaard, 2004; Bougrier *et al.,* 2005; Zhang *et al.,* 2007-a), increased concentration of soluble chemical oxygen demand COD_S (Tiehm *et al.,* 1997 & 2001-b; Chu *et al.,* 2001; Lafitte-Trouqué and Forster, 2002; Brown *et al.,* 2003; Grönroos *et al.,* 2005; Bougrier *et al.,* 2005 & 2006; Akin *et al.,* 2006), increased volatile solids VS (Tiehm *et al.,* 1997 & 2001-b; Brown *et al.,* 2003; Rooksby, 2001; Nickel and Neis*,* 2007), and increased biogas production (Tiehm *et al.,* 2001-b; Chu *et al.,* 2002; Rooksby, 2001; Brown *et al.,* 2003; Grönroos *et al.,* 2005; Bougrier *et al.,* 2005; Braguglia *et al.,* 2006). Likewise, main research has been done by (Kunz and Wagner, 1994; Müller, 1996; Schwedes, 1996; Baier and Schmidheiny, 1997; Bien and Wolny, 1997; Chiu *et al.,* 1997; Clark, 1998; Ma and Lin, 1998; Clark and Nujjoo, 2000; Neis *et al.,* 2000; Onyeche *et al.,* 2001; Gonze *et al.*, 2003; Mesas, 2003; Bien *et al.,* 2004; Hogan *et al.,* 2004; Yin *et al.,* 2004; Yoon *et al.,* 2004; De Silva and Nickel, 2004; Wang *et al.,* 2005; Braguglia *et al.,* 2006; Zhang *et al.,* 2007-b).

Table 1-11 presents the main results published on the homogenization by ultrasound. However, it is quite difficult to compare these results, because of the great diversity of sludge used and the little information about their composition.

Table 1-11: Summary of previous work done on ultrasonic treatment of waste activated sludge.

Reference	Condition of treatment	Results	Scale
Tiehm *et al.,* (1997)	f = 31 kHz, t = 64 sec, P = 3.6 kW	Reducing the particles size. Increasing of soluble COD. (72.2%) Increased degradation of organic matter. (45.8 – 50.3%) Reduction the residence time.	Pilot
Tiehm *et al.,* (2001-b)	f = 41 kHz, t = 30 min	Degree of disintegration. (DD_{COD} = 85%) The VS reduction. (21.5 – 33.7%) Increased volume of biogas production. Increasing of soluble COD.	Lab
Chu *et al.,* (2001)	f = 20 kHz, t = 120 min, P = 0.33 kW/ml	Reducing the size of flocs. Increasing of soluble COD. (0.5 – 20% of total COD) Increased ratio BOD/COD. (66 – 80%) Reduction of total coliforms. (97%) Heterotrophic bacteria. (56%) Increased volume of biogas production.	Lab
Lehne *et al.,* (2001)	f = 200 kHz, SE = 30000 kJ/kg-TS	Reducing the size of flocs. (80%) Degree of disintegration. (DD_{COD} = 66%)	Lab
Chu *et al.,* (2002)	f = 20 kHz, t = 20 min, P = 0.33 W/ml	Inactivation partial sludge. Decrease the size of flocs. Increased production biogas. (104%)	Lab
Lafitte-Trouqure and Forster, (2002)	f = 23 kHz, t = 90 sec, P = 0.47 W/ml	Increasing of soluble COD. (+354%) No statistical significance in biogas production.	-
Rooksby,(2001)	f = 20 kHz, T = 1.5 sec, P = 5.3 kW	The VS reduction. (46 - 78.7%) Increased production biogas. (+25 – 50%)	Full
Brown *et al.,* (2003)	F = 20 kHz, T = 1.5 sec, P = 5.3 kW	Increasing of soluble COD. Increased production biogas. (340 – 550 ml/g VS)	Full
Gonze *et al.,* (2003)	f = 20 kHz, t = 10 min, P = 260 W	Reducing the particles size. Degree of disintegration. (DD_{COD} = 12%)	-
Bien *et al.,* (2004)	f = 20 kHz, t = 1 min, P = 180 W	Increased production biogas. (24%) Increased degradation of organic matter. (40 – 47%) Decreasing the concentration of AGV. (78%)	-
Grönroos *et al.,* (2005)	f = 27 kHz, t = 30 min, P = 300 W/L	Increased volume of biogas production. (10 – 20%)	Lab
Bougrier *et al.,* (2005)	f = 20 kHz, SE = 10000 kg/kJ-TS	Solubilization of COD. (8 – 35%) Degree of disintegration. (DD_{COD} = 14 – 55%) Solubilization of TS. (25 – 32%) Increased production biogas.	Lab
Akin *et al.,* (2006)	f = 20 kHz, t = 240 sec, P = 2.2 kW	Reducing the particles size. Increasing of soluble COD. Decreasing of degree of inactivation of sludge. (60%)	Lab
Zhang *et al.,* (2007-a)	f = 25 kHz, t = 30 min, P = 0.5 W/ml	Increased the S_{COD}, supernatant proteins and nucleic acids by 690%, 560% and 1640%, respectively. The DD_{COD}, VS reduction, and nucleic acids increase were almost linear with the sonication time.	Lab

3.1.8 Solubilization

Ultrasonic energy can be applied as pre-treatment to disintegrate sludge flocs and disrupt bacterial cells' walls, and the hydrolysis can be improved. The break-up of microbial cell walls leads to the release of intracellular organic compounds into the sludge water phase. Therefore, one commonly used method to quantify the extent of cell disintegration is to determine the increase of the chemical oxygen demand (COD) in the sludge supernatant (Nickel and Neis, 2007; Schneider *et al.*, 1998).

"COD solubilization" represents in fact the transfer of COD from the particulate fraction of the sludge (solids after centrifugation) to the soluble fraction of the sludge (supernatant after centrifugation). The same definitions will be used for matter and nitrogen solubilization (Bougrier *et al.,* 2005).

In Bougrier works, for each experiment, while the energy input increased, total COD was constant. During the experiments, the soluble/particulate COD repartition varied: soluble COD (CODs) increased whereas particulate COD (CODp) decreased. Cells underwent lysis and organic compounds were released into the liquid phase. CODs increased strongly for specific supplied energy between 0 and 10,000 kJ.kg-TS^{-1}, CODs ratio (that is to say CODs divided by total COD) increased from 4 to 32%. For higher specific energies applied, CODs and CODp were quite constant (Bougrier *et al.,* 2005).

For specific energies under 1000 $kJ.kg^{-1}$, Solubilization and degree of disintegration were low, (S_{COD} = 8% and DD_{COD} = 14%) for supplied energy over 1000 kJ.kg-TS^{-1}, Solubilization and degree of disintegration rose strongly; for SE = 15000 kJ.kg-TS^{-1}, S_{COD} = 35% and DD_{COD} = 55% (Bougrier *et al.*, 2005). These values are similar to those obtained by other authors, Lehne *et al.* (2001); Müller and Pelletier (1998).

Bougrier reported that for all treatments sludge solubilization increased with the treatment (ultrasonic specific applied energy). In all cases, solubilization of matter was focused on organic solids: mineral solids solubilization was lower than organic solids solubilization.

She stated that using ultrasound did not change total matter quantity. Total solids concentration (TS) was constant. The total mineral solid content and the total organic solids content were constant. Thus ultrasound did not induce a mineralization phenomenon. However, the solid content of soluble (supernatant of centrifugation) and particulate (solids of centrifugation) parts varied with specific supplied energy. Soluble matter concentration increased, whereas

particulate matter concentration decreased. Thus, ultrasound led to a solubilization phenomenon of organic solids but also of mineral solids (Bougrier *et al.*, 2005).

On the other hand according to Tiehm's works, sludge disintegration was most significant at low frequencies. Low-frequency ultrasound creates large cavitations bubbles which upon collapse initiate powerful jet streams exerting strong shear forces in the liquid. The decreasing sludge disintegration efficiency observed at higher frequencies was attributed to smaller cavitations bubbles which do not allow the initiation of such strong shear forces. Short sonication times resulted in sludge floc deagglomeration without the destruction of bacteria cells. Longer sonication brought about the break-up of cell walls, the sludge solids were disintegrated and dissolved organic compounds were released (Tiehm *et al.,* 2001-b).

3.1.9 Energetic balance

The ultrasound pre-treatment also faces several challenges. One of the major issues is the high capital and operating costs of ultrasound units. The cost may go down as the technology becomes mature. At the same time, long-term performance data of full-scale ultrasound systems are still limited. This discourages design engineers to recommend ultrasound systems for full-scale applications.

Roxburgh *et al.* (2006) investigated Sonico's ultrasound systems. For these systems the investment costs ranged from around 320,000 € to 580,000 €. Electricity and maintenance costs were about 7 € per tons of dry solid. For the same systems total savings (natural gas offset and boisolid management saving) due to sonication was 34 € per tons of dry solids, suggesting a 27 € net operation value per tons of dry solids for the system.

3.1.10 Conclusion on ultrasonic treatment

The ultrasonic treatment consists of several stages. At the first stage of sonication at a power input exceeding the critical level the porous floc can be readily deteriorated into compact flocculi, while the dewaterability of sludge is markedly deteriorated. In the second stage, although the floc size has remained almost unchanged, both heterotrophic bacteria and total coliform are effectively disinfected. The COD_S (soluble COD) value increases accompanied with the reduction in the microbial density levels. In the final stage, if the bulk temperature has been controlled, ultrasonic treatment has essentially no effects on the sludge characteristics. However, the raised bulk temperature of sludge could induce continuous transformation of solid-state organic compounds into a soluble form (Chu *et al.,* 2001).

Ultrasonic process leads to cavitation bubble formation in the liquid phase (Gonze, 2000). These bubbles grow and then violently collapse when they reach a critical size. Cavitational collapse produces intense local heating and high pressure on liquid–gas interface, turbulence and high shearing phenomena in the liquid phase. Because of the extreme local conditions, $OH^{\bullet}$, $HO2^{\bullet}$, $H^{\bullet}$ radicals, and hydrogen peroxide can be formed.

Sonication leads to a decrease in particles size, in apparent viscosity and in filterability, and leads to little solubilization of sludge, which allows to enhance the particulate fraction biodegradability (Bougrier *et al.*, 2006).

Fermentation studies demonstrate that ultrasonic cell disintegration is a suitable method to overcome the slow biological sludge hydrolysis. Consequently the fermentation rate is significantly increased. Higher removal rates allow shorter sludge residence times. A decrease in sludge residence time from 16 to 4 days (Neis *et al.,* 2000), showed no loss in degradation efficiency.

Ultrasound treatment of waste activated sludge is a reliable method to reduce the necessary volume of sludge digesters. Higher removal rates lead to higher degree of volatile solids degradation. An increased production of biogas is also observed.

In ultrasound processes for specific supplied energies lower than 1000 $kJ.kg\text{-}TS^{-1}$, energy is used in order to reduce flocs size. Then, supplementary energy is used to break flocs or cells. This results in the release of organic substances into the liquid phase (Bougrier *et al.,* 2005).

3.2 Sludge disintegration by used of chemical pre-treatment

Chemical oxidation is widely used in the production of potable water for destroying micro-pollutants organic, to combat the problems of tastes and odours associated with the development algae and especially as a means of disinfection. However, in Europe, the oxidation is not used in wastewater, and even less about the sludge.

Chemical pre-treatment at ambient temperatures using low levels of alkali was evaluated by Rajan *et al.* (1989) and Ray *et al.* (1990) on its effects on solubilization and gas production. Solubilization rates of more than 45% of particulate COD were achieved at $30meq.L^{-1}$ NaOH and the gas production increased by 112% over control.

The main oxidants are the chlorine, hydrogen peroxide and ozone. Among chemical processes, the treatment using ozone is of special interest, because no chemicals are added.

3.2.1 The ozonation disintegrator

The aim of ozone pre-treatment is partial oxidation and hydrolysis of the organic matter. A complete oxidation is avoided and larger molecules are cracked into smaller ones instead. Barely degradable compounds are transferred into more easily degradable ones (Déléris *et al.,* 2000; Déléris *et al.,* 2002).

Table 1-12: Positive and negative aspects of ozone treatment.

Positive	Negative
No significant accumulation of inorganic solids occurred in the aeration tank at optimal ozone dose rates	Metals present in the initial sludge (Fe, Zn, Ag, Cu), are transferred to the liquid phase that should be purified
The sludge settle-ability in terms of SVI was highly improved as compared with control test without ozonation	Sludge ozonation causes TOC slight increase in the effluent (although mainly composed of proteins and sugars, which should be harmless for the environment)
Better dewater-ability of the final sludge	High energy consumption
Successful full-scale experience	Consumption of ozone in the degradation of other possible organic materials that may be present
	High costs involved in ozonation

Several authors (Mustranta and Viikai, 1993; Scheminski *et al.,* 1999; Liu *et al.,* 2001) have considered that the recommended ozone dose is between 0.05 and 0.5gO_3.g-TS^{-1}. The optimum dosage for each operation depends on the type of sludge. Table 1-12 presents the positive and negative aspects of ozone pre-treatment: (Pérez-Elvira *et al.,* 2006)

3.2.2 Ozonation treatment

Ozone (O_3) is a very powerful oxidizing agent that has the potential to treat and reduce the quantity of sludge produced at WWTPs.

The sludge ozonation system consists of ozone generator, air generator, exsiccator, cylindrical shape ozone contactor and reflux pump. Ozonation reactor was a glass cylindrical column with 12 cm of inner diameter and 30 cm of height. Ozone dose was defined as the ratio of the mass of ozone introduction into the ozonation reactor to the mass of the sludge before ozonation.

3.2.3 Effect of ozonation on physicochemical characteristic of sludge

Ozonation pre-treatments lead to modification of the physicochemical characteristics of sludge. For instance, ozonation modifies the turbidity of supernatant. This modification depends on

injected ozone dosage. According to Bougrier, (2005) and Park *et al.* (2003), if we increase ozone dosage from zero the turbidity of supernatant will increase until a certain point. Then, if we increase ozone dosage further more, the turbidity will slightly decrease due to mineralization of disintegrated solids to carbon dioxide.

Further mores, ozonation decreases pH. This can be explained by formation of acidic compounds. In fact during ozone pre-treatment, fats degrade and volatile organic acids are formed which will cause pH to decrease. It is clear that ozonation can reduce pH more efficiently than sonication.

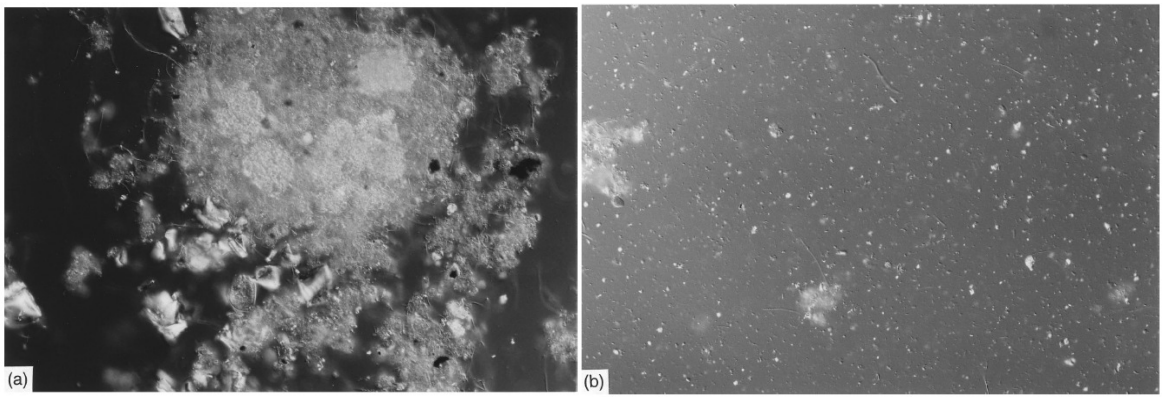

Figure 1-9: Microscopic observation of the sludge before and after ozonation (800×), microscopic observation of the sludge before ozonation (a) and microscopic observation of the sludge after ozonation (b) (Weemaes *et al.,* 2000).

A microscopic view of the sludge before and after ozonation is given in Figure 1-9. The pictures show a destruction of the sludge flocs by ozonolysis. Microscopic observations indicated that the sludge flocs were dispersed. This dispersion of flocs causes filter clogging which complicates the dewatering operation.

Obviously, the treatment subsequent to ozonation has to be aimed at coagulation and flocculation of the fine particles (Weemaes *et al.,* 2000).

3.2.4 Ozonation reaction mechanisms

Ozone is a molecule that consists of three negatively charged oxygen atoms. The ozone molecule is very unstable and has a short half-live, causing it to fall back into its original form after a while, according to the following reaction mechanism:

$2O_3 \longrightarrow 3O_2$

Ozone is a strong chemical oxidant and unstable in aqueous media. It is a compound allotropic (different forms of resonance), high reactivity, with the properties of a dipole. As a result, ozone thus has a great capacity to attack organic compounds and metals, with the exception of gold, platinum and iridium. Ozone is an unstable gas if it is compressed, so it is extremely necessary to produce at the place of consumption. Ozone is produced from oxygen:

$3O_2 \longrightarrow 2O_3$

This is an endothermic reaction ($\Delta Hr° = 142.1$ kJ.mol^{-1} O_3), it is necessary to provide energy. The solution lies in the use of electric shocks. These are not selective. Indeed, other molecules can be oxidized (water, nitrogen). The oxidation of nitrogen led to a corrosive compound and the oxidation of water to hydroxyl radicals. So it is better to use pure and dry oxygen (Bernal-Martinez, 2005).

Ozone reacts in two different ways: (1) Direct reactions of ozone and (2) Indirect reaction of secondary oxidators, such as free OH-radicals. Both reactions occurring simultaneously, the indirect reaction is based on the high reactivity of hydroxyl radicals which do not react specifically, whereas the direct reaction rate with ozone depends more on the structure of the reactants.

In practice, both direct and indirect oxidation reactions will take place. One kind of reaction will dominate, depending on various factors, such as temperature, pH and chemical composition of the water (Bernal-Martinez, 2005; Bougrier, 2005 and Gunten, 2003).

3.2.4.1 Direct reactions

Based on the structure of ozone that was represented and known, ozone can act as a 1, 3-dipole, an electrophilic agent and a nucleophilic agent during reactions (Doré, 1989). These three types of reactions usually occur in solutions that contain organic pollutants. Here, we discuss these three types of reaction mechanisms.

a) Cyclo addition (Criegee mechanism)

Consequentially to its dipolar structure, an ozone molecule can undergo a 1-3 dipolar cyclo addition with saturated compounds (double or triple bonds). This leads to the formation of a compound called ‘ozonide’.

b) Electrophilic reactions

Electrophilic reactions occur in molecular solutions that have a high electronic density and mainly in solutions that contain a high level of aromatic compounds. Aromatic compounds that are substituted by electron donors (such as OH and NH_2), have a high electronic density on the carbon compounds in ortho and para position. Consequentially, in these positions aromatic compounds react actively with ozone.

c) Nucleophilic reactions

Nucleophilic reactions mainly take place where there is a shortage of electrons and particularly at carbon compounds that contain electron-retreating groups, such as –COOH and $–NO_2$. For electron-retreating groups, the reaction speed is much lower.

From the above-mentioned data, it appears that direct oxidation of organic matter by ozone is a quite selective reaction mechanism, during which ozone reacts quickly with organic matter that contains double bonds, activated aromatic groups or amines (Gunten, 2003). It is also stated that ozone reacts quicker with ionized and dissociated organic compounds than with the neutral (non-dissociated) type.

For most inorganic compounds in drinking water, the reaction speed is relatively high. The main reaction mechanism for oxidation of inorganic compounds is determined by transfer of the extra oxygen atom of ozone to the inorganic compounds. For inorganic compounds, reaction speed is also higher for ionized and dissociated compounds.

Summarized, ozone oxidizes organic compounds selectively and partly. A large number of inorganic compounds are oxidized fast and completely.

3.2.4.2 Indirect reactions

Contrary to those of ozone, OH-radical reactions are largely non-selective. Indirect reactions in an ozone oxidation process can be very complex. In fact, an indirect reaction takes place in the following steps:

a) Initiation

The first reaction that takes place is accelerated ozone decomposition by a type of initiator. This can be an OH-molecule, see reaction 1:

1: $O_3 + OH^- \longrightarrow {}^{\bullet}O_2^- + HO_2^{\bullet}$

This radical has an acid/base equilibrium of $pK_a = 4.8$. Above this value, this radical no longer splits, because it forms a super-oxide radical, (see reaction 2):

2: $HO_2^{\bullet} \longrightarrow {}^{\bullet}O_2^- + H^+$ ($pK_a = 4.8$)

b) Radical chain-reaction

Now, a radical chain-reaction takes place, during which OH^- radicals are formed. The reaction mechanism is as follows:

3: $O_3 + {}^{\bullet}O_2^- \longrightarrow {}^{\bullet}O_3^- + O_2$

4: ${}^{\bullet}O_3^- + H^+ \longrightarrow HO_3^{\bullet}$ ($pH < \approx 8$)

The OH-radicals that have been formed react with ozone according to the following reaction mechanism:

5: $OH^{\bullet} + O_3 \longrightarrow HO_4^{\bullet}$

6: $HO_4^{\bullet} \longrightarrow O_2 + HO_2^{\bullet}$

During the last reaction, $HO_2^{\bullet}$ radicals are formed, which can start the reaction all over again (see reaction 2). As a result, a chain-reaction develops, which is maintained by so-called promoters. Promoters are substances that transform OH-radicals to super-oxide radicals.

c) Termination

Terminal reactions are:

7: $2HO_2^{\bullet} \longrightarrow H_2O_2 + O_2$

8: $HO_2^{\bullet} + HO^{\bullet} \longrightarrow H_2O + O_2$

Ozone has been commonly used in water disinfection process. Ozonation-assisted sludge reduction process is based on the idea that part of activated sludge is mineralized to carbon dioxide and water, while part of sludge is solubilized to biodegradable organics that can be biologically treated. Many research works have been conducted with respect to the ozonation-assisted sludge reduction process (Yasui and Shibata, 1994; Sakai *et al.,* 1997; Kamiya and Hirotsuji, 1998; Egemen *et al.,* 1999 & 2001; Ahn *et al.,* 2002; Böhler and Siegrist, 2004; Bernal-Martinez, 2005; Bougrier, 2005; He *et al.,* 2006).

Ozonation-combined activated sludge process would be a useful technology for reducing excess sludge production and further improving sludge settleability, but there are still some problems associated with this technique. Ozone is not a selective oxidant, it can react with other reducing materials, and this may lower the oxidation efficiency of activated sludge, while refractory organic carbon can be released into the effluent after ozonation. Sometimes, the toxicity of those released refractory organic carbon might pose problem to effluent receptor.

This technology is already established in full-scale plants (Yasui *et al.,* 1996). Biolysis®O is the process developed by Ondeo-Degrémont to reduce sludge generation using ozone. In this process, liquor extracted from the activated sludge basin is contacted with ozone in a reactor and returned to the activated sludge tank. A demonstration of Biolysis®O in France produced sludge reductions of between 30% and 80% (Pérez-Elvira *et al.,* 2006).

During sludge pre-treatment, the aim of ozone is to cause the hydrolysis and partial oxidation of the organic matter. A complete oxidation is avoided.

Due to its strong oxidative properties, ozone has been used for water and wastewater treatment. During sludge ozonation, because of the complex composition of sludge, ozone decomposes itself into radicals and reacts with the whole matter: soluble and particular fractions, organic or mineral fractions (Cesbron, *et al.,* 2003; Salhi, 2003). Using ozone for sludge reduction has been widely studied. Optimal consumed ozone dose ranges from 0.05 and 0.5grO_3.gr-TSS^{-1} of total solid: there is a phenomenon of mineralization for higher ozone doses (Goel, *et al.,* 2002; Yeom *et al.,* 2002). Moreover, ozonation modifies viscosity and settlement of sludge (Battimelli, *et al.,* 2003).

Table 1-13: Redox potential of oxidizing agents. (Gunten, 2003)

Substance	Potential(V)
Fluorine (F)	**2.87**
Hydtoxyradical(OH)	**2.86**
Oxygen atom (O)	**2.42**
Ozone molecule (O_3)	**2.07**
Hydrgen peroxide (H_2O_2)	**1.78**
Chlorin (Cl)	**1.36**
Chlorine dioxide (ClO_2)	**1.27**
Oxygen molecule (O_2)	**1.23**

An ozone process is always based on the effect of direct and indirect reaction mechanisms. This is consequential to the disintegration of ozone in water, into OH-radicals. These radicals are very short-living compounds that have an even stronger oxidation mechanism than that of ozone (Gunten, 2003).

When the number of OH-radicals in a solution rises, one speaks of an Advanced Oxidation Process (AOP). This unique process causes dissolved solids to be oxidized by both ozone (direct) and OH-radicals (indirect). The ozone oxidation process is represented schematically in Figure 1-10.

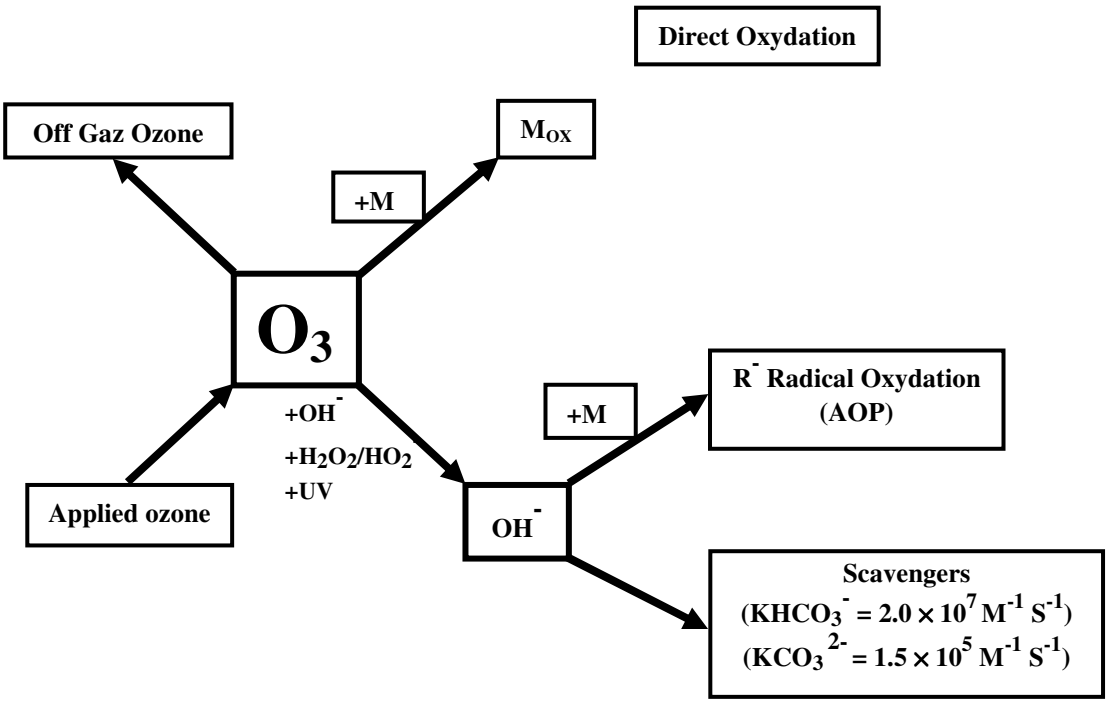

Figure 1-10: reactions of ozone and dissolved solids. (Gunten, 2003)

Ozone is a strong cell lysis agent. When sludge is kept in contact with ozone in the ozonation unit, most activated sludge micro-organisms would be killed and oxidized to organic substances. There is evidence that more than 50% of the carbon obtained after ozonation is readily biodegradable (Deleris *et al.,* 2000). This is the reason why those organic substances produced from the sludge ozonation can then be degraded in the subsequent biological treatment.

3.2.5 Performances of the treatment with ozone

In recent years, several novel sludge treatment processes such as thermal, mechanical, chemical, and oxidation pre-treatment have been commonly practiced to improve the recycling and reuse of wastewater sludge (Yasui and Shibata, 1994; Yasui *et al*., 1996; Sakai *et al*., 1997; Muller *et al*., 1998; Scheminski *et al*., 2000; Weemaes *et al*., 2000; Muller, 2000; Deleris *et al.,* 2000; Dignac *et al.,* 2000; Ried *et al*., 2002; Yeom *et al.,* 2002; Ahn *et al*., 2002; Park *et al.,* 2003; Liu, 2003; Böhler and Siegrist, 2004; He *et al.,* 2006; Bougrier *et al.,* 2006; Carballa, *et al.,* 2007; Bernal-Martinez *et al.,* 2007). Two of the strongest oxidizing agents in wastewater and sludge treatment are ozone and hydroxyl radicals.

Sludge ozonation was referred to as one of the most cost effective technologies with the highest disintegration capability (Müller, 2000-b; Park *et al.,* 2003). Furthermore, ozonated sludge could be effectively utilized as an additional carbon source in a biological nitrogen removal process saving a great deal of cost for external carbon source (Ahn *et al.,* 2002). Sludge disintegration by ozone was well described with the sequential decomposition processes of floc disintegration, solubilization and mineralization (Ahn *et al.,* 2002). The floc disintegration and solubilization generate a large amount of micro-solids and soluble organic matter that can be easily decomposed by micro-organisms. Improvement of the ozonated sludge biodegradability has also been confirmed by several researchers (Scheminski *et al.,* 2000; Weemaes *et al.,* 2000; Yeom *et al.,* 2002).

The feasibility of the activated sludge system coupled with ozonation process was verified through the full scale plant operations without excess sludge production (Yasui and Shibata, 1994; Yasui *et al.,* 1996).

The ozone disrupts the cell, the cell content is released to the bulk solution and the ozone partly oxidizes the solubilized organics. The ozone oxidation of the recycled sludge may have other benefits in addition to sludge reduction – like reduced bulking and internal carbon source production and many of the studies are more oriented towards these goals than towards sludge minimization. An overview of ozonation studies is given in Liu (2003).

On the other hand, treatment of wastewater sludge by ozone has been investigated under aspects of controlling sludge bulking problems in the aeration tank and in the digester (Collignon *et al*., 1994) and improving the settling characteristics (van Leeuwen, 1992). An interesting ozone application to wastewater sludge was studied in Japan (Yasui *et al*., 1996;

Sakai *et al*., 1997). They developed the activated sludge system combined with ozone treatment in sludge recycle stream and zero sludge growth obtained in full-scale plant. Studies on ozonation of excess sludge were followed by several other research groups (Deleris *et al.*, 2000; Huymans *et al*., 2001) and they investigated further sludge solubilization/mineralization and the cost effectiveness of ozone dosage.

Table 1-14: Summary of previous studies on ozonation pre-treatment of waste activated sludge.

Reference	Condition of treatment	Results	Scale
Yasui *et al.,* (1996)	0.05 $gO_3.g\text{-}SS^{-1}$	Sludge reduction. (100%) Increased of TOC in the effluent.	full
Sakai *et al.,* (1997)	0.02 $gO_3.g\text{-}SS^{-1}$	Sludge reduction. (100%) Slight increased of BOD in the effluent.	full
Kamiya and Hirotsuji,(1998)	10 $mgO_3.g\text{-}MLSS^{-1}\ d^{-1}$ (aeration tank)	Excess sludge production was reduced. (50%) Sludge volumetric index (SVI) was highly improved.	full
Scheminski *et al*., (2000)	0.5 $gO_3.g\text{-}DS^{-1}$	Solubilization of protein, lipid, and polysaccharide.	Pilot
Weemaes *et al.*, (2000)	0.1 g O3.g-COD^{-1}	Solubilization of COD. (26%) Mineralization of COD. (11%) Increased production Biogas. (111%) Increased of matter degradation. (36% to 64%)	Pilot
Yeom *et al.*, (2002)	0.1 g $O_3.g\text{-}TSS^{-1}$	Solubilization of matter. (24%) Biodegradability is 2 to 3 times greater, compared to the raw sludge.	lab
Ried *et al*., (2002)	0.052 $gO_3.g^{-1}SS$	Reduction of the excess sludge production. (30%)	full
Park *et al.,* (2003)	0.1-0.5 $gO_3.g\text{-}DS^{-1}$	Mass reduction. (70%) Volume reduction. (85%) Deterioration of filterability Biomass loss by mineralization increased. (5% to 20%)	Pilot
Battimelli *et al.*, (2003)	0,16 g $O_3.g\text{-}TSS^{-1}$ post-treatment et re-circulation 25%	Solubilization of matter. (22%) Deterioration of COD. (66%) Deterioration of matter. (55%)	Pilot
Goel *et al.*,(2003)	0,05 g $O_3.g\text{-}TS^{-1}$	Solubilization of matter. (37%) Mineralization of matter. (5%) Increased degradation organic matter. (35% to 65%) Increased of methane production. (120-250 L/kg-VSS)	lab
Lee *et al.,* (2005)	0.05 kg $O_3.kg\text{-}SS^{-1}$	Solubilization of COD. (22%) Mineralization of COD. (8%) Residuals based on COD. (70%)	Pilot
Bougrier *et al.,* (2006)	0.1-0.16 $gO_3.g\text{-}TS^{-1}$	Solubilization of COD and TS. (20-25%) Ozonation did not seem to affect particles size. Biodegradability of COD. (70% to 78%) Methane production. (246 to 272 ml $CH_4/g\text{-}COD_{added}$)	Pilot
He *et al.,* (2006)	0.16 kg $O_3.kg\text{-}SS^{-1}$	Increased the contents of N & P soluble in the solution Increased the amounts of soluble organic in the solution Filamentous bacteria were squeezed and bundled after ozonation. SVI decreased with ozonation time.	lab
Wang *et al.,* (2007)	Ozone contact time (1-5 min)	Removal rate of TOC. (50.2%)	Pilot

Table 1-14 presents literature data of lysis-cryptic growth (ozonation) for reducing excess sludge production, but it is quite difficult to compare these results.

3.2.6 Solubilization

Ozonation has been used as sludge pre-treatment in order to improve the sludge stabilization by anaerobic digestion. The use of this process leads to an improved COD solubilization, thus increasing the biogas production and the soluble organic matter removal efficiency during anaerobic digestion. However, the elimination of solids and total COD remains in the same range. The digested sludge characteristics, except the dewatering properties which were deteriorated after ozonation, indicate that it is suitable for final disposal or application as agricultural fertilizer (Carballa *et al.,* 2004).

Sludge solubilization and reduction depend strongly on the ozone dosage (Yasui and Shibata, 1994; Déléris *et al*., 2000; Camacho *et al*., 2002; Ried *et al*., 2002, Böhler and Siegrist, 2004).

Results from a 10-month full scale ozonation-activated sludge system loaded with 550 kg $BOD.d^{-1}$ showed that no excess sludge was produced, and the accumulation of inorganic solids in the aeration tank is negligible, while effluent total organic carbon was slightly higher than under the conventional activated sludge process (Yasui *et al.,* 1996).

Results showed that the excess sludge production was reduced by 50% at an ozone dose of 10 $mg.g^{-1}$ mixed liquor suspended solids (MLSS).d^{-1} in aeration tank. When the ozone dose was kept as high as 20 $mg.g^{-1}$MLSS.d^{-1}, no excess sludge was produced. It had been reported that the sludge settleability in terms of sludge volumetric index (SVI) was highly improved compared to control test without ozonation (Kamiya and Hirotsuji, 1998). In the study of Egemen *et al.* (1999), a similar technical approach was used.

Müller (2000-b) reported that ozonation of sludge was the most cost effective and reached the highest degree of disintegration among several developing disintegration methods. The effects of ozone on waste activated sludge are explained by the destruction of the bacteria cell membrane.

Scheminski *et al*. (2000) reported that sludge particulates were transformed into soluble composition regarding protein, lipid, and polysaccharide at an ozone dose of $0.5gO_3.g\text{-}DS^{-1}$.

Ried *et al*. (2002) measured a nearly 30% reduction of the excess sludge production in the ozonated lane of a two-lane full-scale activated sludge plant (SRT = 15 days) by treating daily

10% of the activated sludge with an ozone dosage of $0.052gO_3.g\text{-}SS^{-1}$ ($0.08gO_3.g\text{-}SS^{-1}$ initial excess sludge).

Salhi (2003) showed that a portion of mineral matter (20%) was solubilized with Ozonation at the basin aeration (transfer of solid phase to soluble phase). However, an ozone treatment is not as effective on the mineralization of Organic matter.

The other experimental results, showed that mass reduction of 70% and volume reduction of 85 % compared with the control sludge was achieved through the sludge ozonation at a dose of $0.5gO_3.g\text{-}DS^{-1}$. It is also interesting to note that the filterability deteriorates up to ozone dose of $0.2gO_3.g\text{-}DS^{-1}$ and then improves considerably at a higher ozone dose (Park *et al.,* 2003).

Böhler and Siegrist (2004) found a nearly linear increase of the sludge reduction with increasing ozone dosage up to an optimal dosage of $0.05gO_3.g\text{-}SS^{-1}$, where 25–35% sludge reduction is reached. If the ozonated sludge is recycled to the activated sludge system new biomass will grow on the solubilized degradable organic fraction. But also an inert soluble organic fraction is produced.

Transferred ozone dose on the digested sludge was equal to 0.1 $grO_3.g\text{-}TS^{-1}$, according to the optimal dose determined in Bernal-Martinez (2005). The optimum dosage for each operation depends on the type of sludge.

According to article published by Bougrier *et al.* (2006), Ozonation allowed a weak solubilization and a weak biodegradability compared with ultrasound and thermal treatments.

Carballa *et al.* (2007) showed that during ozonation, about 1 % and 8 % of volatile solids were mineralized and solubilized, respectively. These results were similar to those obtained by Goel *et al.* (2003) during the ozonation of activated sludge. Besides, the soluble COD concentration increased from 6 to $16g.L^{-1}$, which leads to a COD solubilization efficiency of approximately 60%. No COD mineralization was observed during ozone treatment. The ozone dose was set approximately at 20 $mgO_3.g\text{-}TSS^{-1}$ in the reactor.

3.2.7 Energetic balance

Ozonation-combined activated sludge process would be a useful technology for reducing excess sludge production and further improving sludge settleability, but there are still some problems associated with this technique. Apparently, both operation and capital costs of the ozonation activated sludge process should be high due to energy required for ozone production.

However, economical estimate suggests that the operation costs of the whole process was lower than that of conventional activated sludge process if the costs of sludge dewatering and disposal were taken into account (Yasui *et al.,* 1996).

The cost of ozonation increases almost linearly with the plant capacity because of operational and maintenance cost. Therefore it is estimated that a large plant is not favourable to ozone treatment.

Goel *et al.* (2003) reported that a sample ozonation pre-treatment requiring 50 kg of ozone per day (90 €/d), reduced total sludge to be disposed of from 3600 $kg.d^{-1}$ to 2450 $kg.d^{-1}$ resulting in saving 140 € per day. Thus for this sample system the net value could be estimated at about 50 euro per day.

3.2.8 Conclusion on ozonation treatment

Ozone is a powerful oxidant that preferentially oxidizes electron rich moieties containing carbon–carbon double bonds and aromatic alcohols (Karnik *et al.,* 2005). It can break the structure of natural organic matter and enhance the transformation of higher molecular weight compounds into lower MW ones, such as carboxylic acids, hydrophilic acids, carbohydrates, amino acids, etc. (Yavich, 2004 and Saroj, 2005). Upon ozonation of natural organic matter, the total organic carbon (TOC) was either reduced, or unchanged (Saroj, 2005).

Previous reports (Yasui *et al*., 1996) on full-scale applications of ozone treatment aiming to completely eliminate excess sludge production from full-scale activated sludge treatment plants signify the role that ozone can play in sludge hydrolysis and enhancement of biodegradability.

Considering this, ozonation was also considered as an attractive pre-treatment for solid hydrolysis before aerobic and anaerobic digestion (Goel *et al.,* 2003).

Due to ozonation, the cell walls are disintegrated and inner cell products can be released. In addition, ozone reacts with organic compounds that are less biodegradable, oxidizing them to smaller compounds which are more bio-available (Weemeas *et al.,* 2000).

Recent laboratory scale studies indicate that the proposed process can reduce the waste sludge production by 40 to 60%. However, the ozonation process needs to be studied in depth in order to increase the feasibility of the process (Egemen *et al.,* 2001).

Ozonation also leads to a decrease in apparent viscosity and filterability, but has no effect on particles' size. In terms of anaerobic biodegradability, pre-treatment leads to an enhancement of

biogas production. Nevertheless, for ozonation, this enhancement is low, but raw sludge biodegradability was very high (Bougrier *et al.,* 2006).

Based on the observations, it can be concluded that ozone treatment of sludge combined with the biodegradation process can greatly reduce the amount of sludge production.

3.3 Sludge disintegration by used of physical pre-treatment

Physical disruption of sludge has gained acceptance due to its various successful industrial scale applications. As shown in Table 1-5, there are several mechanical disintegration technologies that may be used. In this study we focused on the thermal hydrolysis disintegrator.

3.3.1 Thermal hydrolysis

Thermal pre-treatment destroys the cell walls and makes the inside of the cell accessible for biological degradation. Thermal treatment of sludge may be used alone or together with chemical reaction for many different purposes in addition to sludge minimization. The method involves heating the sludge to a temperature at which cells disintegrate and lysis takes place.

One may differentiate between processes that take place under 100ºC in which disintegration may take place under normal pressure and those at higher temperatures up to 250ºC for which a pressure reactor is needed (Odegaard, 2004). Lower temperature processes have mainly been investigated with the aim to improve aerobic and anaerobic digestion (Hiraoka *et al*., 1984). A 15% increase in methane production was demonstrated by Li and Noike (1992) at a pre-treatment temperature of 80ºC. Much stronger effects are reported, however, at higher temperatures.

Main research has been done by Haug *et al.* (1983); Pinnekamp, (1989); Li and Noike, (1992); Tanaka *et al.* (1997); Kepp *et al.* (2000); Prechtl *et al.* (2001); Kepp and Solheim, (2001); Guibelin, (2002); Carballa *et al.* (2004). There are some full-scale operating plants, through the Cambi patented thermal hydrolysis (Kepp *et al.,* 2000; Weisz *et al.,* 2000; Kepp and Solheim, 2001). Table 1-15 shows the positive and negative aspects of thermal hydrolysis (Pérez-Elvira *et al.,* 2006).

Table 1-15: Positive and negative aspects of thermal hydrolysis.

Positive	Negative
Most effective treatment, according to energetic considerations **Very good dewater-ability of the final sludge** **Best sludge disinfection**	**Fouling of the heat exchangers** **Possible bad odour if gas streams are not treated**

3.3.2 Thermal treatment

A number of pre-treatment processes have been developed and investigated in order to improve and enhance the disintegration and solubilization of sludge solids and are reviewed by Müller (2001). Thermal pre-treatment is suitable for the improvement of stabilization, enhancement of sludge dewatering, reduction of the numbers of pathogens and could be realized at relatively low costs (Müller, 2001).

Brooks (1970) observed solubilization of organic matter from samples of WAS as well as a mixture of primary sludge and WAS when the treatment temperature is 170°C. Experiments with municipal sewage sludge show that the highest yield of hydrolysis can be achieved at 165–180°C.About 60% of sludge reduction was achieved when the returned sludge passed through a thermal treatment loop, 90°C for 3 hr (Canales *et al.,* 1994).

3.3.3 Effect of thermal pre-treatment on physicochemical characteristic of sludge

Thermal treatment leads to the modification of sludge composition: organic compounds are directly affected by treatment. In fact, it seems that lipids are degraded in order to form volatile fatty acids, which decreases the pH (Bougrier, 2003). pH decreases with thermal treatment. This can be explained by the formation of acidic compounds.

Thermal treatment leads to an increase in the sludge volume. On the other hand, thermal treatment leads to particles agglomeration. This could suggest that the rise in temperature leads to the creation of chemical bonds (Bougrier *et al.,* 2006).

Thermal treatment also leads to the release of more water by breaking the sludge structure. The reached temperature can have an effect on hydrogen bonds which give structure to sludge. By

modifying this structure, it is possible to release a part of the initial bound water. Moreover, thermal treatment was initially used as a dewatering pre-treatment (Haug *et al.,* 1978).

The photographs given in Figure 1-11 illustrate that heating to 100°C does not destroy flocs. On the contrary, the flocs appear greater at 95°C with a fluffy structure.

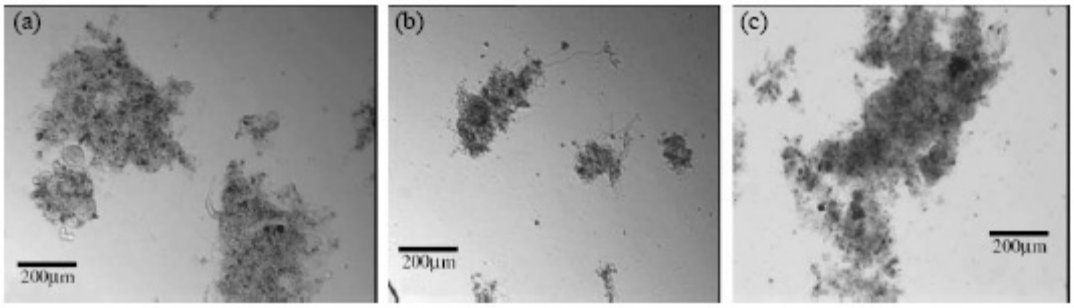

Figure 1-11: Photographs of representative flocs of AS after a treatment at: (a) ambient temperature; (b) 65°C; and (c) 90°C for a contact time of 10 h. (Paul *et al.,* 2006)

3.3.4 Reaction mechanisms thermal treatment

Thermal pre-treatment has been studied to improve anaerobic sludge digestibility and dewatering properties. Heat energy applied during thermal treatment acts by disrupting the chemical bonds of the cell wall and membrane, thus releasing the cell components into solution (Cacho Rivero, 2005) on the other hand, thermal treatment led to the release of more water, by breaking the sludge structure (Bougrier *et al.,* 2006).

Heating treatment is an interesting candidate to apply to reduce the excess sludge production (ESP) when associated with a conventional biological process, an activated sludge or a digestion process (Paul *et al.,* 2006). Through pre-treatment of the sludge, which leads to the destruction of micro-organisms and to the liberation of cell contents (disintegration), the carbon can be microbially converted better and faster. Moreover, effects on digestion can be expected (Barjenbruch and Kopplow, 2003).

With thermal pre-treatment, cells are broken due to pressure differences. These treatments also have the advantage of sanitization the sludge and enhancing its dewatering properties (Haug *et al.,* 1978). In heating pre-treatment, while the carbohydrates and the lipids of the sludge are easily degradable, the proteins are protected from the enzymatic hydrolysis by the cell wall (Kepp, *et al.,* 2000, Barjenbruch *et al.,* 1999). Thermal pre-treatment in the temperature range from 60 to 180°C destroys the cell walls and makes the proteins accessible for biological degradation (Neyens, and Baeyens, 2003).

High temperature is provided in order to allow cell lysis and the release of biodegradable cell components into solution (Giovanni B, D.F., 2005).

However, this pre-treatment faces several major difficulties: Odour problems, clogging of heat exchangers and corrosion and economic cost expensive (Kepp *et al.,* 2000).

The performance of heat treatment is linked to several parameters: (Bougrier, 2005)

- Influence of temperature
- Influence of the nature of sludge
- Influence of contact time

3.3.4.1 High temperature thermal treatments

Thermal pre-treatment has been studied using a wide range of temperatures ranging from 60 to 270°C (Climent *et al.,* 2007). More studies focus on thermal process as a pre-treatment stage of WAS. These studies include thermal pre-treatment in the moderate temperature range of 60–100°C (Hiraoka, 1984; Li and Noike, 1992), in the medium temperature range of 100–175°C (Haug *et al.,* 1978), and in a high temperature range of 175–225°C (Haug, 1983).

In high temperature thermal treatments, treatment time appeared to have less effect compared to that of temperature, with common values in the range 30–60 min (Valo *et al.,* 2004). High temperature treatments are usually applied to sludge by heat exchangers or by steam injection (Müller, 2000-b). Valo *et al.* (2004) reported increments in COD_S of around 25% and 60% after thermal treatment of secondary sludge at 130 and 170°C, respectively. These authors also evaluated the biogas production of the thermally treated sludge in batch tests at mesophilic temperatures and observed increments of respectively 21% and 45% in biogas production, compared to untreated sludge. The most significant drawback of this treatment is the high requirement of energy that it involves. Some authors have pointed out that the energetic expense can be balanced due to the increment in sludge biodegradability and to the use of sludge residual heat in the maintenance of digester temperature (Haug *et al.,* 1983).

An autoclave is a pressurized device designed to heat aqueous solutions above their boiling point to achieve sterilization. It was invented by Charles Chamberland in 1879.

Thermal pre-treatment was carried out by maintaining the sludge under different combination of temperature (from 110 to 134°C), time (from 10 to 120 min) and pressure (1 – 1.5 atm) in an autoclave reaction conditions (that is, high temperatures and pressures).

3.3.4.2 Low temperature thermal treatments

Low temperature thermal treatment has been pointed out as an effective treatment for increasing biogas production from both primary and secondary sludge (Skiadas *et al.,* 2004). However, few references are found in the literature although this treatment implies lower energy consumption. Some authors have concluded that thermal treatment applied at temperatures around 70°C enhances biological activity of some thermophilic bacteria population with optimum activity temperatures in the high values of the thermophilic range (Nielsen *et al.,* 2004). Thus, low temperature thermal treatment may be considered as a pre-digestion step.

Thermal treatment at temperatures lower than 100°C applied to conventional biological system (activated sludge) allows for significant reduction of excess sludge production (ESP). Indeed, by applying a thermal treatment at 95°C to an activated sludge from a primarily settled urban wastewater treatment (Camacho *et al.,* 2003), and from a synthetic wastewater treatment (Canales *et al.,* 1994), a 50% reduction in the ESP was observed. Very few studies characterised the effect of temperature below 100°C on sludge degradability (Camacho, 2001). There is a need for data to understand by which mechanism the treatments at low temperature act on sludge.

3.3.5 Performances of the thermal treatment

It has been known for many years that a thermal pre-treatment gives an improvement in the dewater-ability of sludge. Several methods to treat the WAS prior to biological process have been studied to accelerate the solubilization of substrate in aerobic and anaerobic digestion sludge.

Thermal pre-treatment prior to digestion sludge may result in net energy production from the system because of increased biodegradability and reduced digester heating requirements.

Li and Noike (1992) found the best conditions for pre-treatment of waste activated sludge to be: (i) 170°C; (ii) between 30 and 60 min holding time; and (iii) a hydraulic retention time of 5–10 days based on both gas production and studies on microbial populations of various species of methanogens. They observed that the hydrolysis effect was greater on carbohydrates and proteins than on lipids. Activated sludge consists of 60% carbohydrate and protein. The biochemical pathway for methanogenic fermentation of proteins and carbohydrates suggests that these are hydrolyzed to monomers, deaminated for amino acids and undergo acetic acid

fermentation for sugar monomers. Hydrolysis is the rate limiting step for this pathway. This is not the case with lipids which undergo two carbon decarboxylations to produce acetic acid from long chain fatty acids. They also observed that volatile fatty acids were present in high levels in the digester feed and converged to a common value which was slightly higher than the control. They concluded that this was evidence that there was little or no refractory effects at the temperatures used.

Other researchers like Elbing and Dünnebil (1999) investigated the effects of thermal hydrolysis on mesophilic digestion of waste activated sludge. After pre-treatment at 135°C, the volatile solids destruction in the digester increased to 135 and 235% above the reference level at an increasing 12 and 15 days retention time, respectively.

Other conclusions/observations were: (Brooks, 1970; Fisher, and Swanwick, 1971; Hang *et al.,* 1977 & 1987 & 1983; Hiraoka *et al.,* 1984; Pinnekamp, 1989; Tanaka *et al.,* 1997; Wang *et al.,* 1999 & 1997; Kepp *et al.,* 2000 ; Camacho, 2001 & 2003; Müller, 2000-b; Chauzy *et al.,* 2002 & 2004; salhi *et al.,* 2003 ;Valo *et al.,* 2004; Nielsen *et al.,* 2004; Bougrier, 2005; Paul *et al.,* 2006; Climent *et al.,* 2007).

The aim of these treatments is to solubilized (i.e. to make a transfer from the particles to the liquid fraction) organic compounds and especially refractory compounds, in order to make them more biodegradable (Bougrier *et al.,* 2006). Table 1-16 presents the main results published in thermal treatment.

The holding time (10–30 min) has little influence on the result. The dissolved components are readily degradable in a digestion process. In addition the dewater-ability is increased.

Fisher and Swanwick, (1971) reported on the effect of high temperature treatment of sewage sludge. They showed that for a wide range of sludge, dewaterability was improved at temperatures above 150°C. Most of the work was above 180°C where the effect became more pronounced. Unfortunately at these higher temperatures they also reported on the formation of refractory COD compounds (the chemical oxygen demand, COD, is the amount of oxygen required to chemically destroy the organic compounds of wastewater). As part of the study they looked at some selected liquors and concluded that about a third of the liquor COD was not treatable.

Haug (1997) and Haug *et al.* (1978 & 1983), worked on heat treatment at lower temperatures to combine some of the benefits of dewaterability with improved digestibility and at the same

time avoid the problems that occurred with higher temperature heat treatments. Haug (1997) and Haug *et al.* (1978 & 1983), showed that it was possible to obtain an improvement in dewater-ability of undigested and digested sludge and that the temperature of 175°C was about the limit for digestibility before digestion was inhibited (presumably because of the formation of inhibitory and/or refractory compounds). They showed that the largest effect on digestibility was for activated sludge but that all sludge tested dewatered better at 175°C.

At that temperature, digestion of the thermally pre-treated sludge resulted in an increase of 60 – 70% in methane production over not pre-treated sludge. Higher temperatures resulted in decreased gas production. Thermal hydrolysis as pre-treatment has hence given very good results on digester performance. The homogenization of the material goes further than in a mechanical process. The total surface of the particles is significantly increased, enhancing biological degradability.

Table 1-16: Summary of previous studies on thermal pre-treatment of waste activated sludge.

Reference	Condition of treatment	Results	Scale
Haug *et al.,* (1977, 1987, 1983)	T = 100°C – 250°C t = 30 min	Reduction of energy production compared to conventional digestion. (25%) Solubilization of COD. (40%) Increased in methan production.(60% to 70% at 175°C)	full
Hiraoka *et al.,* (1984)	T = below 100°C t = high	An increase of more than 30% in gas production.	Pilot
Pinnekamp, (1989)	T = 120°C & 220°C t = 45 min	VS reduction varying from10% to 55% for WAS. VS reduction varying from7% to 34% for primary sludge. Maximum gas yield was observed at 140°C.	
Li and Noik, (1992)	T = 120°C - 175°C t = 30 & 60 min SRT = 5 – 10 day	Increased of COD (30% to 60%) Increase of VSS degradation efficiency. (30% to 60%) Increased in Biogas production. (100%)	full
Tanaka *et al*., (1997)	T = 180°C t = 60 min	Solubilization of matter organic. (30%) Increased of biogas production. (90%)	Pilot
Kepp, *et al.*, (2000)	T = 130°C - 180°C t = 30 min	Saving in digester volume. (50%) Increase in solids reduction. (23%) Increase in mass reduction. (50%)	full
Fjordside, (2001)	T = 160°C HRT = 15 day	Abatement of the matter. (20%) Increased of Biogas production. (60%)	
Camacho *et al*., (2002)	T = 40°C and 120°C	Maximum soluble COD release of 30 – 35% at 95°G. Maximum total COD release of 30 ± 7% at autoclave. Mineralization of the organic fraction was obtained for higher temperature.	full
Jeongsik *et al.,* (2003)	T = 121°C t = 30 min P = 1.5 Atm	Soluble COD removal efficiency. (36.7%) VS reduction. (36.1%) Increases in methane levels averaged. (35.2%)	Lab
Carballa *et al.*, (2004)	T = 130°C t = 60 min HRT = 20 day	Solubilization of COD. (60%) Increasing in matter reduction. (58% to 66%)	Pilot
Valo *et al.*,(2004)	T = 170°C t = 60 min	Solubilization of COD. (57%) Increasing in matter reduction. (27% to 59%) Increased of biogas production. (45% to 54%) Solubilization of matter. (50%)	lab
Graja *et al.,* (2005)	T = 175°C t = 40 min HRT = 3 day	Reduction of TSS. (65%) Solubilization of Nitrogen. (32%) Average solubilization of TSS. (16%) Average solubilization of COD. (12%)	Pilot
Paul *et al.,* (2006)	T = 95°C t = 40 min	Biodegradability of the released organic matter. (30% to 50%)	lab
Bougrier *et al.,* (2006, 2007)	T = 135°C – 190°C t = 30 – 60 min	Increase of COD removal yield. (52% to 64%) Decrease of sludge production. More than 30% Degradation yields of lipids and carbohydrates. (up to 82%) were higher than protein ones. (up to 46%) Increase methane production. (25%) Solubilization of COD & TS. (40% to 45%)	Pilot
Climent *et al.,* (2007)	High temperature (T = 134°C , t = 90min) Low temperature (T = 70°C , t = 9hr)	Increment of FVS/TVS :914 ±5 Increment of FVS/TVS : 751 ± 36 Increment in biogas production. (70%)	Lab

3.3.6 Solubilization

Li and Noike (1989) reported that the optimum temperature and contact time for the WAS were 170°C and 60 min, respectively.

Carballa *et al.* (2004) studied the effect of chemical and thermal pre-treatment in a mixture of primary and activated sludge (70:30 v/v). They also evaluated posterior anaerobic digestion of the treated sludge under mesophilic and thermophilic conditions.

The chemical pre-treatment considered the addition of lime (CaO) until pH above 12 for 24 hours. Thermal pre-treatment was carried out by maintaining the sludge at 130ºC for 60 min in an autoclave. Chemical pre-treatment achieved a COD solubilization ranged between 65 and 85% while thermal pre-treatment achieved only 50 to 65% COD solubilization (Cacho Rivero, 2005).

3.3.7 Energetic balance

Although thermal hydrolysis of sludge requires energy, the need for electrical energy is very low. The consumption of heat energy can be optimised so that the total energy balance is positive compared to conventional sludge treatment.

For a system pre-treating sludge by thermal hydrolysis with electrical heaters before digestion, Haug *et al.* (1983) calculated a 25 % reduced energy production compared to conventional digestion (without pasteurisation). Pinnekamp (1989) gave a prognoses of a 40 % increased electricity production for a similar system if the exhaust gases from biogas combustion in a combined heat and power plant are used to sustain the thermal pre-treatment.

Total investment cost of a sample thermal pre-treatment system (Thélys + Turbo digestion) is estimated to be between 1.5 and 2.5 M€ while the running costs of such system are between 60 and 70 € per treated ton of MS (personal information).

3.3.8 Conclusion on thermal treatment

Sludge heating has been studied to improve sludge dewatering, to produce an available carbon source for biological nutrient removal (Henze and Harremoës, 1990; Barlindhaug and Odegaard, 1996) or to increase the methanogenic potential of the sludge. Hygienisation is an additional benefit of sludge thermal treatment processes. When sludge heating is performed in order to reduce sludge production, sludge Solubilization would be required. In that case, two

main temperature brackets are to be considered: temperatures either higher or lower than 150°C (Camacho, 2001; Paul *et al.,* 2006). Temperatures around 160–200°C are necessary to obtain liquidised sludge (Haug *et al.,* 1978; Li and Noike, 1992; Tanaka *et al.,* 1997).

The thermal pre-treatment allows a significantly reduced footprint of the methaniser, while biogas production – and hence sludge reduction – is enhanced (Graja *et al.,* 2005). At the same time, thermal treatment leads to a strong decrease of apparent viscosity, a strong increase in filterability and an increase in particles diameter (Bougrier *et al.,* 2006).

Influence of temperature and contact time in the efficiency of high temperature thermal treatment has also been systematically studied using the experimental design technique (Climent *et al.,* 2007).

Thermal treatment results in the breakdown of the gel structure of the sludge and the release of intracellular bound water (Weemaes and Verstraete, 1998). Therefore, this treatment allows a high level of Solubilization, an improvement in biogas production, modification in sludge characteristics (increase in filterability and viscosity reduction) and reduction of pathogen micro-organisms (Haug *et al.,* 1978; Valo *et al.,* 2004; Odegaard *et al.,* 2002). The main parameter for thermal treatment is temperature: time of treatment has less influence (Li and Noike, 1992; Haug *et al.,* 1978; Barlindhaug and Odegaard, 1996).

3.4 Conclusion

All techniques lead to solids Solubilization and to aerobic and anaerobic biodegradability enhancement. However different techniques lead to different sludge solubilization and biodegradability efficiencies depending on different conditions such as sludge type, pre-treatment conditions, operational conditions, economical expenses, etc. It means that according to pre-treatment technique and pre-treatment conditions (intensity, power, time, dosage, etc), different solubilization rates and consequently sludge biodegradabilities will be obtained.

Table 1-17 compares different pre-treatment methods in terms of COD Solubilization, sludge removal, biogas production percentages and etc.

Table 1-17: Comparison of pre-treatment technologies. (Pérez-Elvira *et al.,* 2006)

Pre-treatment method	COD solubilization (%)	Sludge removal (%)	Biogas production %)	Pathogen reduction	Influence on the dewatering results
High Pressure homogenizers	18 – 20	23 – 64	Up to 300	Low	High
Ultrasonic homogenizers	6	40 – 70	10 – 60	Low	High
Thermal hydrolysis	10 – 20	60 – 80	Up to 400	Total	Very high
Freezing and thawing	–	–	–	–	High
Impact grinding	10	5 – 9	10 – 36	No	High
Stirred ball mills	15	40 – 60	10	No	High
High performance pulse technique	–	–	–	No	Moderate
The Lysat-centrifugal technique	–	–	Up to 25	No	High
Gamma-irradiation	–	–	–	High	–
Acid or alkaline hydrolysis	–	–	–	–	High
Pre-treatment using ozone	5	36	8	–	High
Thermal + explossivdecompression + shear forces	8 – 12	40 – 85	–	–	–

Bougrier *et al.* (2006) studied three pre-treatment techniques (ultrasound, thermal, and ozonation) and investigated apparent characteristics of sludge and concluded that sonication leads to a decrease in particles size, in apparent viscosity and in filterability, ozonation leads to a decrease in apparent viscosity and filterability, but has no effect on particles size, and finally, thermal treatment leads to a strong decrease of apparent viscosity, a strong increase in filterability and an increase in particles diameter (Bougrier *et al.,* 2006). Table 1-18 summarizes these results.

Table 1-18: Comparison of three pre-treatment. (Bougrier *et al.,* 2006)

	Ultrasound	Ozonation	Thermal
Solubilization	+	+	++
Viscosity	+	+	++
Particle size	Decrease	0	Increase
Filterability	--	-	++
Biodegradability	++	0/++	++
Mechanisms	Low solubilization and improved particulate biodegradability	?	High solubilization and little effect on particulate biodegradability
Supposed effects	Release of exo-polymers	Oxidation of the flocs molecules	Breaking cells

Negative (-), very negative (--), positive (+), very positive (++)

4. Aerobic and anaerobic stabilization

Digestion is a commonly used biological process for the stabilization of sludge from wastewater treatment plants. The stabilization of sludge results in the reduction of the pathogens concentration and reduction in volatile solids and odours. Digestion can be carried out either anaerobically or aerobically (John *et al*., 2003).

Both anaerobic and aerobic digestion has been widely used to stabilize the wastewater sludge prior to ultimate solids disposal. Reduction of volatile solids and destruction of pathogens are the primary objectives of both processes. Each digestion is processed through very different microbiological and biochemical reactions and the major difference of two digestion processes is whether digestion proceeds in the presence or absence of molecular oxygen.

4.1 Aerobic sludge digestion

4.1.1 Generalities

Aerobic digestion of excess biological sludge from a municipal waste water treatment plant (WWTP) is a continuation of the activated sludge process which occurs under endogenous conditions (Ros, 1993). When a culture of aerobic heterotrophic micro-organisms is placed in an environment containing a source of organic material, the micro-organisms will degrade and remove this material. A fraction of the removed organic material is used for the synthesis of new micro-organisms, resulting in a biomass increase. The remaining material is oxidized to carbon dioxide, water and soluble inert material, providing energy for synthesis, metabolism and maintenance of the micro-organisms' vital functions. Once the external source of organic material is exhausted, the micro-organisms will begin endogenous respiration where cellular material is oxidized to satisfy the energy requirements for life support. If such conditions are maintained over an extended period of time, the total quantity of biomass will be reduced considerably and the remaining material will exist at a low energy state and can be considered biologically stable and suitable for disposal to the environment (Zupancic and Ros, 2007). Aerobic digestion has been used primarily in plants of a size less then 5 $Mgal.d^{-1}$ (0.2 $m^3.s^{-1}$), but in recent years the process has been employed in large wastewater treatment plants (Metcalf and Eddy, 1991).

The objective of the aerobic digestion process, which can be compared with those of the anaerobic digestion process, consists of production of a stable product by oxidizing organisms and other biodegradable organics, reduction of mass and volume, reduction of pathogen organisms, and conditioning for further processing.

4.1.2 Aerobic digestion theory

The basis of aerobic digestion process is similar with activated sludge process. In the presence of molecular oxygen and nitrate, micro-organisms convert organic matter into carbon dioxide, ammonia-N, water and new biomass. As available substrate is depleted, endogenous respiration, auto-oxidation of cellular protoplasm, takes place, accounting for the destruction of volatile solids (Metcalf and Eddy, 1991).

Aerobic oxidation process is exothermic and net release of heat occurs during the process. Although the digestion process should theoretically go to completion, in actuality only 75 to 80% of the cell tissue is oxidized. The remaining 20 to 25% is composed of inert components and organic compounds that are not biodegradable (Metcalf and Eddy, 1991). The material that remains after the full completion of the digestion process exists at such a low energy state that it is essentially biologically stable. Consequently, it is suitable for a variety of disposal options (Vesilind, 2003).

The aerobic digestion process thus consists of two steps; direct oxidation of biodegradable matter, and endogenous respiration in which cellular material is oxidized. These processes can be illustrated by the following equations: (Vesilind, 2003)

$$\text{Organic matter} + NH_4^+ + O_2 \xrightarrow{Bacteria} \text{cellular material} + CO_2 + H_2O \qquad (1)$$

$$\text{Cellular material} + O_2 \xrightarrow{Bacteria} \text{digested sludge} + CO_2 + H_2O + NO_3 \qquad (2)$$

Relation (1) describes the oxidation of organic matter to cellular material. This cellular material is subsequently oxidized, producing digested sludge. The process described in relation (2) is typical endogenous respiration process and is the predominant reaction in aerobic digestion systems. Because primary sludge contains little cellular material, inclusion of primary sludge in the process can shift the overall reaction to Eq. (1), resulting in an increase of total biomass.

Consequently, the aerobic digestion process, in which the sludge mass is reduced, is only recommended for excess activated sludge. For primary sludge digestion, anaerobic digestion is recommended (Ros and Zupancic, 2003).

Simplicity of process and lower capital cost are the advantages of aerobic digestion compared to anaerobic process and because of these merits, aerobic digestion has been a popular option for the small scale WWTPs. However, high energy cost and lower pathogen inactivation could be the disadvantages of aerobic digestion (Grady *et al*., 1998).

4.1.3 Advantages and disadvantages of aerobic digestion

The major advantage of aerobic digestion is that it produces a biologically stable product suitable for subsequent treatment in a variety of processes. Volatile solids reductions similar to anaerobic digestion are possible.

As with almost all treatment processes, aerobic digestion entails both advantages and disadvantages. The most marked advantages are:

(1) Production of an inoffensive, humus-like, biologically stable end product.
(2) The stable end product has no odours; therefore, simple land disposal, such as in lagoons, is feasible.
(3) Capital costs for an aerobic system are low when compared whit anaerobic digestion and other processes.
(4) Aerobically digested sludge usually has good dewatering characteristics. When applied to sand drying beds, it drains well and re-dries quickly if rained on.
(5) The volatile solids reduction can be equal to those achieved by anaerobic digestion.
(6) Supernatant liquors from aerobic digestion have a lower BOD (generally lower than 100 ppm) than those from anaerobic digestion.
(7) There are fewer operational problems with aerobic digestion than with the more complex anaerobic from because the system is more stable. As a result, less skilled labour can be used to operate the facility.
(8) Compared with anaerobic digestion, more of the bio-solids, basic fertilizer values are recovered.

The major disadvantage associated with aerobic digestion is high power cost. Unlike anaerobic digestion, aerobic digestion requires the supply of oxygen, which is energy consumptive. At small waste water treatment plant, the power costs may not be significant but they might be so at larger plants. Experience suggests another disadvantage in that aerobically digested bio-solids dos not always settle well in subsequent thickening processes. This situation leads to a thickening tank decant having a high solids concentration. Two other disadvantages associated

with aerobically digested bio-solids are that bio-solids dose not dewater easily by vacuum filtration and the variable solids reduction efficiency changes with varying temperature. An additional disadvantage is that a useful by-product such as methane is not recovered. In cases where separate sludge digestion is considered, aerobic digestion of biological sludge may be an attractive application (Metcalf and Eddy, 1991; Spellman, 1996).

4.1.4 Environmental factors in aerobic digestion

Parameters that must be considered in aerobic digesters include: (1) temperature, (2) solids reduction, (3) rate of oxidation, (4) energy requirements for mixing, and (5) process operation (Metcalf and Eddy, 1991).

4.1.4.1 Temperature

Because the majority of aerobic digesters are open tanks, digester liquid temperatures are depended on weather conditions and can fluctuate extensively. As with all biological systems, lower temperatures retard the process, whereas higher temperatures accelerate it. In considering temperature effects, heat losses should be minimized by using concrete instead of steel tanks, placing the tanks below grade instead of above grade or providing insulation for above-grade tanks, and using subsurface instead of surface aeration. In extremely cold climates, consideration should be given to heating the sludge or the air supply, covering the tanks, or both.

a) Thermophilic aerobic digestion

Thermophilic aerobic digestion of wasted bio-mass is exothermic and can therefore be auto-thermal with appropriate heat retention and heat exchange. Thermophilic temperatures induce lysis of those cells less tolerant to heat and promote the biodegradation of certain compounds that are recalcitrant in less extreme environments. Also the thermophilic temperatures may pasteurize the biomass reducing the content of pathogenic organisms (Drier and Obma, 1963).

Mason and Hamer (1987) sought to identify optimal conditions for the digestion of cell lysis products by a mixed thermophilic bacterial population.

Thermophilic digestion without external heat input can be achieved by using the heat released during microbial oxidation of organic matter to heat the sludge. It has been estimated that more than 25 $kcal.L^{-1}$ of heat energy are realized in the aerobic digestion of primary and secondary sludge (between 2 and 5 percent solids).

Aerobic thermophilic digestion has also been used extensively in Europe as a first stage in the dual digestion process. The second stage is anaerobic digestion. Residence time in the aerobic reactor range typically from 18 to 24 hr, and the reactor temperature ranges from 55 to 65°C. The advantages of using aerobic thermophilic digestion in dual digestion are (1) increased levels of pathogen kill, (2) improved overall volatile solids destruction, (3) increased methane gas generation in the anaerobic digester, and (4) less organic material in and fewer odours produced by the stabilized sludge (Metcalf and Eddy, 1991).

b) Mesophilic (cryophilic) aerobic digestion

The operation of aerobic digestion systems at lower temperature ranges (less than 20°C) has been investigated to provide better operational control for small package-type treatment plants. Researchers in British Columbia (Canada) have found that the sludge age must be increased as the operating temperatures decrease so as to maintain an acceptable level of suspended solids reduction. The product of operating temperature (°C) and sludge age (days) should be maintained in the range of 250 to 300 degree-days for operating liquid temperature ranges between 5 and 20°C to ensure acceptable volatile solids reduction (Metcalf and Eddy, 1991).

4.1.4.2 Solids reduction

One primary objective of the aerobic digestion process is to reduce the volatile solids concentration in order to minimize the handling cost of the residual sludge. While achieving volatile solids reduction, pathogen and vector-attraction contact is reduced. Volatile solids reduction typically falls within the range of 35 to 50 percent.

The change in biodegradable volatile solids can be represented by a first-order biomechanical reaction:

$$\frac{dM}{dt} = -k_d M \qquad \underline{Eq.1}$$

With *dM/dt* denoting rate of change of biodegradable volatile solids per unit of time (Δ mass/time)

K_d = reaction-rate constant (time^{-1})

M = concentration of biodegradable volatile solids remaining at time t in the aerobic digester (mass/volume)

The time *t* is the sludge age or the solids residence time in the aerobic digester. Depending on how the aerobic digester is being operated, time *t* can be equal to or considerably greater than the theoretical hydraulic residence time.

The reaction rate term, K_d, is a function of the sludge type, temperature, and solids concentration. Representative values for the decay coefficient K_d may range from 0.05 d^{-1} at 15°C to 0.14d^{-1} at 25°C for waste activated sludge. Because the reaction rate is influenced by several factors, it may be necessary to confirm decay coefficient values by bench-scale or pilot-scale studies (Metcalf and Eddy, 1991).

4.1.4.3 Rate of oxidation

The oxygen requirements that must be satisfied during aerobic digestion are those of the cell tissue and, with mixed sludge, the BOD_5 in the primary sludge. The oxygen requirement for the complete oxidation of the BOD_5 contained in primary sludge varies from about 1.6 to 1.9 kg/kg destroyed. The oxygen residual should be maintained at 1 $mg.L^{-1}$ or above, under all operating conditions.

4.1.4.4 Energy requirements for mixing

To ensure proper operation, the contents of the aerobic digester should be well-mixed. In general, because of the large amount of air that must be supplied to meet the oxygen requirement, adequate mixing should be achieved; nevertheless, mixing power requirements should be checked.

4.1.4.5 Process operation

Depending on the buffering capacity of the system, the pH may drop to a low value (5 ± 0.5) at long hydraulic detention time. This could be due to the increased presence of nitrate ions in solution and the lowered buffering capacity due to air stripping (Fischer *et al.*, 1997). Filamentous growths may also develop at low pH values. The pH should be checked periodically and adjusted if found to be excessively low. Dissolved-oxygen levels and respiration rates should also be checked to ensure proper process performance (Metcalf and Eddy, 1991).

Other factors affected in Aerobic digestion are: (1) tank volume (hydraulic retention time), (2) loading rate, (3) system oxygen requirements, (4) bio-solids age (sludge retention time), and (5) solids characteristics.

4.2 Anaerobic sludge digestion

4.2.1 Generalities

Anaerobic digestion is a very complex process and various groups of micro-organisms in the absence of oxide molecules and nitrate are involved in reciprocal relationship. Conversion of organic matter into methane after several steps of biochemical reactions accounts for removing COD of feed sludge in anaerobic digestion.

Anaerobic digestion is one of the oldest and most widely used processes for wastewater sludge stabilization for plants with average flows greater than $20000 m^3.d^{-1}$ (5 mgd). Its history can be traced from the 1850_S with the development of the first tank designed to separate retain solids. One of the first installations in the United States using separate digestion tank was the wastewater treatment plant in Baltimore, Maryland. A net reduction in the quantity of solids and destruction of pathogenic organisms are also accomplished in the anaerobic digestion process (Turovskiy and Mathai, 2006).

The process transforms organic solids in sludge, in the absence of oxygen, to gaseous end products such as methane and carbon dioxide and to innocuous substances. In very general terms however, it is possible to simplify the overall biochemical reaction to:

Organic material $\longrightarrow$ $CH_4 + CO_2 + H_2 + NH_3 + H_2S$

It must also be borne in mind that some organic materials, for example, lignin, effectively do not digest, nor obviously, do non-organic inclusions within the waste (Evans, 2001).

It is widely considered that there are three effective temperature ranges for anaerobic digestion, each of which has its own favoured group of bacteria and its own set of characteristic advantages and disadvantages. Bacteria may be classified as Psychrophilic (also called Cryophilic), Mesophilic or Thermophilic.

4.2.2 Anaerobic digestion theory

Anaerobic digestion involves several successive stages of chemical and biochemical reactions involving enzymes and a mixed culture of micro-organisms.

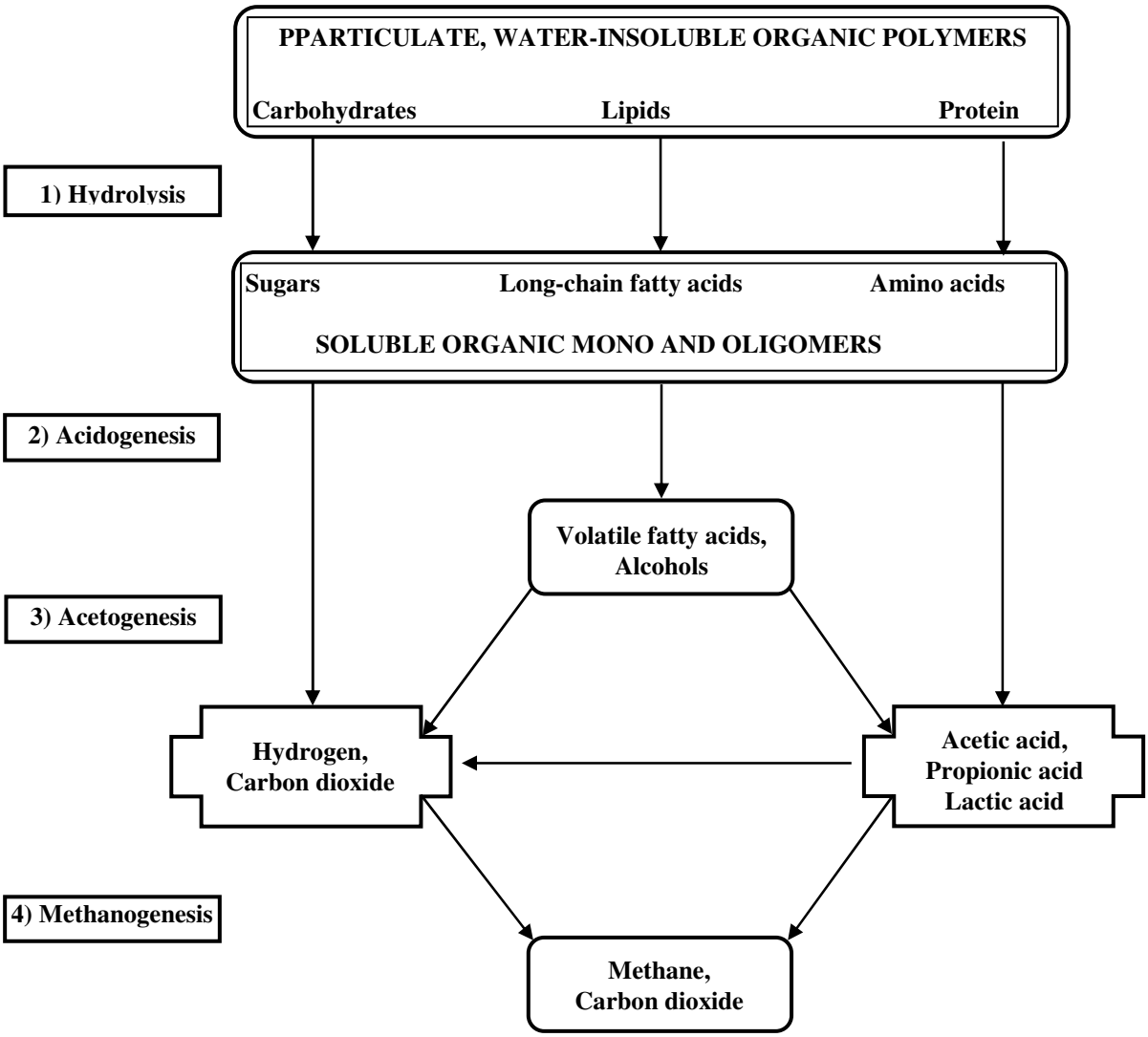

Figure 1-12: Schematic of reaction in anaerobic digestion.

The process comprises four general degradation phases: hydrolysis, acidogenesis, acetogenesis, and methanogenesis. Figure 1-12 is a simplified representation of the reactions involved in anaerobic digestion. There are several groups of bacteria that perform each step, once different species are needed to degrade completely a heterogeneous stream.

4.2.2.1 Hydrolysis

In the first step, hydrolysis, insoluble organic matter and large molecular organic compounds are hydrolyzed to soluble and smaller size of organic compounds. For WSA (wastewater activated sludge) degradation, the rate-limiting step is the hydrolys (Bougrier *et al.*, 2006; Li and Noike**,** 1992). For example, the reaction of hydrolysis of cellulose is:

$$(C_6H_{10}O_5)_n + nH_2O \longrightarrow nC_6H_{12}O_6$$

4.2.2.2 Acidogenesis

Acidogenesis sometimes split into *acidogenesis* and *acetogenesis*. In acidogenesis (also known as fermentation), anaerobic micro-organisms break down the products of first step into hydrogen molecule and simple organic acids such as volatile fatty acids and acetic acid. The main products of this stage are acetic, lactic and propionic acids and the pH fall as the levels of these compounds increase. The reactions of degradation of glucose are:

$$C_6H_{12}O_6 \longrightarrow CH_3(CH_2)_2COOH + 2H_2 + 2CO_2$$
$$C_6H_{12}O_6 + 2H_2 \longrightarrow 2CH_3CH_2COOH + 2H_2O$$
$$C_6H_{12}O_6 + 2H_2O \longrightarrow 2CH_3COOH + 4H_2 + 2CO_2$$

4.2.2.3 Acetogenesis

In acetogenesis, the products from the acidogenesis are used for the production of acetates, carbon dioxide and hydrogen. In this process, two types of acetogenic bacteria may be distinguished, namely the hydrogen producing bacteria and the hydrogen consumption bacteria.

$$CH_3CH_2COOH + 2H_2O \longrightarrow CH_3COOH + 3H_2 + CO_2$$
$$CH_3(CH_2)_2COOH + 2H_2O \longrightarrow 2CH_3COOH + 2H_2$$

a) Hydrogen producing bacteria

This bacteria promotes the anaerobic oxidation of the volatile fatty acids in acetates (acetic acid). The reactions are not spontaneously, since they only occur when the partial pressure of hydrogen is in reduced levels. The reactions are shown in Table 1-19.

Table 1-19: Some reactions of the hydrogen producing bacteria.

Substrate	Reaction
Ethanol	$CH_3CH_2OH + H_2O \longrightarrow CH_3COOH + 2H_2$
Proponic acid	$CH_3CH_2COOH + 2H_2O \longrightarrow CH_3COOH + 3H_2 + CO_2$
Butyric acid	$CH_3CH_2CH_2COOH + 2H_2 \longrightarrow 2CH_3COOH + 2H_2$

b) Hydrogen consuming bacteria

This type of bacteria is able to produce acetate from CO_2 and H_2, contributing for the maintenance of the desirable hydrogen partial pressure in the system.

4.2.2.4 Methanogenesis

In the final step of anaerobic digestion, known as methanogenesis, methanogenic bacteria convert acetic acid and hydrogen into methane and carbon dioxide.

In fact, methane is produced from a number of simple substrates: acetic acid, methanol or carbon dioxide and hydrogen (Evans, 2001). Methanogens are strictly anaerobic Archaea that can be sub-divided into two groups: (i) hydrogenophilic or hydrogenotrophic species, which form methane by the reduction of H_2/CO_2 and (ii) acetoclastic or acetotrophic methanogens, which generate methane by acetate decarboxylation (Ferry, 1999). Acetoclastic methanogens are considered the more important methanogenic species, as 70% of the total methane generated during anaerobic digestion of domestic sewage is via this pathway (Grotenhuis 1992; Lettinga 1995).

$$CH_3COOH \xrightarrow{\textit{Acetotrophic methanogenes}} CH_4 + CO_2$$

Methane-forming bacteria may also use methanol:

$$CH_3OH + H_2 \xrightarrow{\textit{Methanophilic}} CH_4 + H_2O$$

Or carbon dioxide and hydrogen:

$$CO_2 + 4H_2 \xrightarrow{\textit{Hydrogenotrophic species}} CH_4 + 2H_2O$$

Methanogens are strict anaerobes and have very slow growth rate. Consequently, their metabolism is usually considered rate-limiting and long detention time is required (Metcalf and Eddy, 1991).

The anaerobic digestion can reduce dry matter of about 50% (OTV, 1997) and the production of biogas, consisting primarily of methane (55-70%) and dioxide carbon (25-40%) (Degrémont, 1989). Methane can be valued in the form of energy (boiler producing heat or electricity). At the same time, according to Trably (2002), the anaerobic micro-organisms consume little energy, which leads to a limited production of sludge (3 to 20 times less than aerobic treatment). Indeed, anaerobic micro-organisms use only about 10 to 15% of the energy of the substrate to grow (Edeline, 1997), the rest being used for the production of biogas. Lastly, anaerobic digestion allows for a reduction of pathogenic micro-organisms.

4.2.3 Advantages and disadvantages of anaerobic digestion

Anaerobic digestion offers several advantages over the other methods of sludge stabilization.

The benefits of anaerobic digestion of sludge are:

(1) About 50% of reduction in the sludge solids (Degrémont, 1989).
(2) Production of a recoverable gas in the form of energy (heat, electricity cogeneration).
(3) Reduction of the number of pathogenic micro-organisms (Elissalde, 1994).
(4) Agronomic interest, linked to a high concentration of nitrogen ammonium (NH_4^+), and phosphates (PO_4^{3-}) due to lysis of organic matter (Trably, 2002).
(5) An opportunity to biodegrade some xenobiotic compounds (Bitton, 2005).
(6) Lower energy demand than aerobic processes and no oxygen.

However, it also has some drawbacks. The principal disadvantages of anaerobic sludge digestion are the following:

(1) A high sensitivity to variations in organic loads and toxic compounds.
(2) Slower degradation than aerobic processes (Bitton, 2005).
(3) Lack of nitrogen treatment (nitrogen flow returns at the top of the station are to be considered in the sizing).
(4) Start-up with long installation.
(5) Important investment costs.
(6) A fall in the calorific value of sludge (to consider whether the sludge is incinerated).

This study is limited to physicochemical treatment cell lysis: enzymatic processes will not be considered.

4.2.4 Environmental factors in anaerobic digestion

Important environmental factors that affect the rates of the three phases of anaerobic reactions are: (1) temperature, (2) hydraulic retention time (HRT), (3) Solids retention time (SRT), (4) pH, (5) Alkalinity, and (6) the presence of inhibitors (Bitton, 2005; Turovskiy, and Mathai, 2006).

4.2.4.1 Solids and Hydraulic Retention Times

The most important factor in sizing the anaerobic digester is that the bacteria be given sufficient time to reproduce and metabolize volatile solids. The key parameters in providing

sufficient time are the solids retention time (SRT), which is the average time the solids are held in the digester, and the hydraulic retention time (HRT), which is the average time the liquid sludge is held in the digester. They can be defined operationally as follows:

- SRT, in days, is equal to the mass of solids in the digester (kg) divided by the mass of solids withdrawn daily ($kg.d^{-1}$).
- HRT, in days, is equal to the volume of sludge in the digester (m^3) divided by the volume of digested sludge withdrawn daily ($m^3.d^{-1}$).

For digestion systems without recycle, HRT can be calculated based on either the sludge feeding rate or the removal rate. For such a system, SRT and HRT are equal. The three reactions in an anaerobic digestion system are directly related to SRT (or HRT). An increase in SRT increases the extent of reactions. Similarly, a decrease in SRT decreases the extent of reactions (Turovskiy and Mathai, 2006).

4.2.4.2 Temperature

Temperature has an important effect on bacterial growth rates and, accordingly, changes the relationship between SRT and digester performance. Most anaerobic digesters are designed to operate in the mesophilic temperature range 30 to 38°C (85 to 100°F), 35°C (95°F) being the most common. Some digesters are designed to operate in the thermophilic range 50 to 57°C (122 to 135°F). It is important that a stable operating temperature be maintained in the digester. Sharp and frequent fluctuations in temperature affect the bacteria, especially methanogens. Process failure can occur at temperature changes greater than 1°C/d. Changes in digester temperature greater than 0.6°C/day should be avoided (Turovskiy and Mathai, 2006).

a) Thermophilic anaerobic digestion

A group of micro-organisms, called *thermophilic* bacteria, grow in the temperature range 49 to 57°C (120 to 135°F). These temperatures are suitable conditions for thermophilic bacteria. Thermophilic anaerobic digestion has been studied since the 1930s, at both the laboratory and plant scales (U.S. EPA, 1979).

In general, advantages claimed for thermophilic anaerobic digestion over mesophilic digestion are:

- Faster reaction rates, which permit increased volatile solids destruction.

- Increased sludge-processing capability.
- Improved sludge dewatering.
- Increased bacterial (pathogens) destruction.

Disadvantages of thermophilic anaerobic digestion include:

- Higher energy requirements for heating.
- Lower-quality supernatant, containing large quantities of dissolved materials.
- Higher odour potential.
- Poorer process stability because thermophilic bacteria are more sensitive than mesophilic bacteria to temperature fluctuations.
- Poor dewaterability.

Because of these disadvantages, application of thermophilic digestion has been limited. U.S. federal regulations controlling land application of sludge classify thermophilic digestion, along with mesophilic digestion, as a process to significantly reduce pathogens (PSRP). That is, although there may be greater reduction of pathogens levels in thermophilic digestion, it is not classified as a process to further reduce pathogens (PFRP). Therefore, single-stage thermophilic digestion is limited in its application (Turovskiy and Mathai, 2006; Metcalf and Eddy, 1991).

b) Mesophilic anaerobic digestion

The optimum temperature ranges are the mesophilic, 25 to 40°C. Most high-rate digesters are operated in the range 30 to 38°C (86 to 100°F). Bacteria that grow in this temperature range are called *mesophilic*. Most researchers have considered mesophilic anaerobic sludge to be good inoculums for thermophilic anaerobic sludge, because it is grown in a similar anaerobic environment. However, some researchers have also shown the same or better activity from other sources.

4.2.4.3 pH and Alkalinity

Methane-producing bacteria are extremely sensitive to pH. Optimum pH for methane formers is in the range 6.8 to 7.2. Volatile acids produced in the acid-forming phase tend to reduce the pH. The reduction is normally countered by methane formers, which also produce alkalinity in the form of carbon dioxide, ammonia, and bicarbonate. In the anaerobic digestion process, the carbon dioxide–bicarbonate relationship is very important. The best way to increase pH and buffering capacity in a digester is by the addition of sodium bicarbonate. Lime will also

increase bicarbonate alkalinity but may react with bicarbonate to form insoluble calcium carbonate, which promotes scale formation (Turovskiy and Mathai, 2006).

4.2.4.4 Presence of toxic materials

Although many materials are toxic to the bacteria in an anaerobic digester, heavy metals, light metal cations, ammonia, sulphides, and some inorganic materials are of concern. Toxic conditions normally occur from overfeeding and excessive addition of chemicals. Toxic conditions can also occur from industrial wastewater contributions with excessive toxic materials to the plant influent.

Heavy metal toxicity has frequently been cited as the cause of anaerobic digestion failures, although trace amounts of most heavy metals are necessary for cell synthesis. Domestic wastewater sludge normally has low concentrations of light metal cations (sodium, potassium, calcium, and magnesium). However, significant contributions can come from industrial discharges and from the addition of alkaline material for pH control. Ammonia, produced during the anaerobic digestion of proteins and urea, may reach toxic levels in highly concentrated sludge. Ammonia nitrogen concentrations of more than 1000mg.L^{-1} can be highly toxic. When wastewater sludge contains high concentrations of sulphide, it can cause a problem in anaerobic digestion because the sulphate-reducing bacteria reduce sulphate to sulphide, which is toxic to methanogens at concentrations over 200mg.L^{-1}. This can be controlled by precipitating the sulphide as iron sulphide by adding iron salts to the digesters at controlled amounts (Turovskiy, and Mathai, 2006).

4.3 Improvement of digestion after PRSP

In order to improve hydrolysis and anaerobic digestion performance, one possibility is to use lysis pre-treatments. As stated in above sections, several pre-treatments can be considered: mechanical, thermal, chemical or biological treatments (Weemaes and Verstraete, 1998). The aim of these treatments is to solubilize (i.e. to make a transfer from the particles to the liquid fraction) organic compounds and especially refractory compounds, in order to make them more biodegradable. In fact, a linear relation between Solubilization and biodegradation has been shown (Bougrier *et al.,* 2006). Final quantity of residual sludge and time of digestion can be reduced and biogas production can be increased (Tiehm *et al.,* 1997; Haug *et al.,* 1978; Goel *et al.,* 2003). For example, a thermal pre-treatment led to 60% enhancement of performance of sludge anaerobic digestion with an increase of CH_4 production from 115 to 186mL.g^{-1} COD_{feed}

(Haug *et al.,* 1978). Besides, an ultrasound pre-treatment (64 sec at 31 kHz) allowed to reduce the sludge retention in the digester from 22 to 8 days while volatile solids removal yields did not change (44%), (Tiehm *et al.,* 1997). Results obtained from the researches of Bougrier *et al.* (2006) with ozone treatment were surprising. At the end of the experiments (day 24), biogas volume produced from a sample of sludge treated with an ozone dose of 0.16 $gO_3.g\text{-}TS^{-1}$ was only 1.25 times higher than volume produced with untreated sludge.

4.3.1 Ultrasonic treatment

Mechanisms of the ultrasonic process are influenced by three factors: supplied energy, ultrasonic frequency and nature of the influent. Cell disintegration is proportional to supplied energy (Lehne *et al.,* 2001; Müller and Pelletier, 1998). High frequencies promote oxidation by radicals, whereas low frequencies promote mechanical and physical phenomena like pressure waves (Gonze *et al.,* 1999). With complex influents, radical performance decreases. It has been shown that degradation of excess sludge is more efficient using low frequencies (Tiehm *et al.,* 2001-b).

Ultrasounds were shown to have an effect on sludge biodegradability and on biogas production during batch anaerobic digestion of sonicated sludge. COD, matter and nitrogen Solubilization increased with supplied energy. In the same time, biogas production also increased. During Bougrier's experiments, for each ultrasonic pre-treatment, biogas production was higher than that for untreated sludge: minimum increase of 25% in biogas volume was obtained with ultrasonic pre-treatments. These volumes were always lower than those obtained for a completely biodegradable substrate like ethanol. Ultrasound led to an increase of sludge biodegradability, but they were not fully biodegradable. For specific supplied energies of 660 and 1350 $kJ.kg\text{-}TS^{-1}$, biogas production was the same (Bougrier *et al.,* 2005 & 2006). This can be explained by variation in particle size. Indeed, these energies were very close to the minimal energy necessary (1000 $kJ.kg^{-1}$). Energy was used to reduce flocs size, not to break cells. Organic compounds were not released in the liquid phase, but matter was much more available.

4.3.2 Ozonation treatment

Yasui and Shibata, (1994) developed a new process for reducing excess sludge production in the activated sludge process. The process consists of a sludge ozonation stage and a biodegradation stage, in which a fraction of recycled sludge passes through the ozonation unit and then the treated sludge is decomposed in the subsequent biological treatment. The

ozonation of sludge results in both solubilization (due to disintegration of suspended solids) and mineralization (due to oxidation of soluble organic matter), and the recycling of solubilized sludge into the aeration tank will induce cryptic growth (Wei *et al.,* 2003).

The ozonation improves biodegradability of extremely refractory compounds. Déléris *et al.* (1999) showed that for activated sludge treated with a dose of ozone of $0.1gO_3.g\text{-}VSS^{-1}$, batch aerobic biodegradability tests lead to a COD biodegradable efficiency of 60 % in the easily biodegradable fraction.

Regarding to the anaerobic biodegradation, Goel *et al.* (2003) have shown that, following an ozonation to $0.05gO_3.g\text{-}MS^{-1}$, the anaerobic degradation of synthetic activated sludge (Reactor was fed with yeast extracts and fructose) was improved by 90% (SRT = 28 days).

Weemaes *et al.* (2000) observed an alteration of the organic matter up to 67% during bio-solids ozonation. Yeom *et al.* (2002) reported the effects of ozone treatment on the biodegradability of municipal sludge in anaerobic and aerobic biodegradation experiments. Solubilization increased with ozone dosage up to $0.5gO_3.g\text{-}SS^{-1}$ and decreased at higher dosages.

In anaerobic experiments, biodegradation increased with ozone dosage up to $0.2gO_3.g\text{-}SS^{-1}$. Further increase of ozone treatment did not improve the biodegradation. In the aerobic condition, about 77% of the ozonated sludge at $0.1gO_3.g\text{-}SS^{-1}$ could be biodegraded after 15 days and is compared with 36 % degradation of the untreated sludge. The biodegradation of the ozonated sludge mostly occurred within 5 days while the raw sludge was steadily biodegraded for more than 15 days, indicating the conversion of sludge into readily degradable substrate by ozone treatment. The biodegradation enhancement of ozonated sludge was also confirmed in batch denitrification experiments (Yeom *et al.,* 2002).

4.3.3 Thermal treatment

Indeed, sludge lysis pre-treatments can be used either to maximize biogas production (to minimize residual sludge amount) or to accelerate sludge anaerobic digestion and to treat more sludge in a given digester by reducing sludge retention time (SRT). Treatments also permit to accelerate sludge degradation (Bougrier *et al.,* 2006).

Odorous compounds normally associated with heat treatment are significantly reduced during digestion of thermally pre-treated sludge. Pinnekamp (1898) found optimum conditions for all types of sludge when pre-treated at 135–170°C and digested under mesophilic conditions.

Hiraoka *et al.* 1984 investigated the thermal pre-treatment at temperatures below 100°C and revealed an increase of more than 30% in gas production at lower temperatures such as 60 and 80°C, but the low temperature pre-treatment necessitated a longer contact time than the high temperature treatment.

Haug *et al.* (1983) calculated a 25% reduced energy production compared to conventional digestion. This conclusion has been confirmed by 3 years operation of a full-scale plant (80,000 inhabitant equivalent) at Hamar, Norway. The biogas was used to produce both electricity, covering 65% of the plant electrical demand, and heat (100% of the plant requirements).

Haug *et al.* (1977, 1978 and 1983) thermally pre-treated the WAS at l00-250°C for 30 minutes. Digestion of the thermally pre-treated sludge at 175°C resulted to an increase of 60-70% in methane production over unpretreated sludge, but higher temperatures resulted in decreased gas production. Pinnekamp (1989) also confirmed that at temperatures below 170°C the gas yields were lower than those obtained at 170-180°C, but the gas yields sharply decreased above 180°C.

5. Conclusion and objectives of the study

The treatment and disposal of excess sludge is one of the most serious problems in biological wastewater treatment due to environmental, economic, social and legal factors.

Sludge minimization technologies have been available for several decades; however recent developments have brought some sludge minimization technologies to the forefront. All of the technologies utilize one or more of three basic approaches to minimize the amount of waste activated sludge produced by an activated sludge process: cell lysis, cyclic oxic environments, and long solids retention time.

In order to improve aerobic and anaerobic digestion performance, one possibility is to use cell lyse pre-treatments. Several pre-treatments can be considered: mechanical, physical, chemical or biological treatments.

In Bougrier works, pre-treatments led to modification of the physicochemical characteristics of sludge. For instance, pH decreased with ozonation or thermal treatment. For sonication, pH was not modified. Another modification due to pre-treatment was particles size. For the applied energies, sonication decreased median diameter. On the contrary, thermal treatment led to an

increase in the diameter. Ozonation did not seem to affect particles size. In the same time, thermal treatment led to a strong decrease of apparent viscosity, ozonation and sonication led to a decrease in apparent viscosity.

Sonication and ozonation increased strongly the capillary suction times (CST) value, whereas, thermal treatment decreased it (Bougrier *et al.*, 2006; Chu *et al.,* 2001).

Pre-treatments led to a modification of the repartition of the solids. For all treatments, total mineral solids concentration was almost constant: sonication, ozonation or thermal treatment did not lead to a mineralization phenomenon in those conditions. Treatment led to a transfer from particles to supernatant.

For each technique, COD Solubilization and TS Solubilization are increased and can be totally different according to used technique.

Indeed, sludge lysis pre-treatments can be used either to maximize biogas production (or to minimize residual sludge amount) or to accelerate sludge anaerobic digestion and to treat more sludge in a given digester by reducing sludge retention time (SRT).

In general, pre-treatment leads to a modification of the reparation of the solids, increases solubilization, increase biodegradability percentage (biogas production enhancement), accelerate sludge degradation and treatment, and also have an effect on rheology of sludge.

In this study, we focused on ultrasound, ozonation, and thermal (low temperature) pre-treatments.

The aim of these treatments is to lyse the flocs, reducing the particle size (organic compounds and especially refractory compounds) and solubilize the intra and extra cellular material to make them more easily biodegradable. These treatments can be applied at different places on the wastewater lines or sludge. The use of a pre-treatment coupled to cell lysis aerobic and anaerobic digestion can offer some advantages:

1) The co-treatments allow solubilization of organic particulate matter, or even mineral (Salhi, 2003), and better biodegradability. This leads to an increased volume of produced biogas and a reduction of sludge production.
2) The digestion time (Nah *et al.,* 2000) or size reactors (Li and Noike, 1992) can be reduced compared to conventional digesters.
3) Some techniques allow partial hygienic (sanitation) sludge (Müller, 2001).

4) Treatment may, in some cases, improve the qualities of settling (Battimelli *et al.,* 2003), dehydration (Anderson *et al.,* 2002), or to eliminate the problems abundance related to filamentous bacteria (Müller, 2000-a).

5) The final dry cake can be increased by using a pre-treatment (Kopp *et al.,* 1997; Chauzy *et al.,* 2004).

6) However, it should be noted that the establishment of co-treatment has the following drawbacks.

7) The co-treatment cell lysis can induce side effects, as the formation of refractory compounds and creation of odours. This is particularly true for thermal treatment (Müller, 2001).

8) The installation of a technique causes investment and running cost. Depending on technique, it may be necessary to purchase a new apparatus (ultrasonic grinder, heat exchanger, etc) to provide a high amount of energy (heat or electricity) and to maintain thr device in good conditions. Moreover, in some cases, we must take into account the reagents and mixing cost (Weemaes and Verstraete, 1998).

9) The co-treatments can cause foam problems (ozone, peroxide hydrogen), scaling (thermal) and corrosion of reactors (oxidation) or devices pre-treatment (mechanical) (Weemaes and Verstraete, 1998; Müller, 2001).

10) Some treatments coupled to an anaerobic digestion can cause problems during the dehydration and require more amount of polymers (Winter and Müller, 2002).

Chapter 2

Material and methods

Chapter 2: Material and methods

In this chapter, all of the materials and methods used are presented. Thus, the origin of the sludge, experimental devices to lyses cellular and aerobic & anaerobic digestion and all the analytical methods used are exposed.

1. Experimental

1.1 Characteristics of waste activated sludge

The activated sludge was sampled from the municipal wastewater treatment plant of Limoges-France. WWTP had a capacity of 285000 people equivalent. This plant treats domestic and a very small fraction of industrial wastewater (about 10 percent) and operates advanced activated sludge treatment with an output of 47000 m^3 per day in dry weather and 81000 m^3 during rain (wastewater 47000 m^3 per day and run off 34000 m^3 per day).

The sampled sludge from the return line of WWTP had an initial concentration of 3.5 to 5$g.L^{-1}$. Before pre-treatment and digestion processes, the sludge was concentrated. The sludge was stored in 3 to 5 litre containers under the laboratory conditions. The water on the top of sludge was withdrawn (usually by means of a syringe) every few hours and as a result solid concentration increased. This operation was performed 6 times and after 24 to 36 hours, the sludge was completely concentrated and ready for experiments. Activated sludge was medium concentrated up to 14.53$g.L^{-1}$ of Total Solids (TS), with standard deviation = 3.58$g.L^{-1}$ and volatile solids (VS) content was 72.95% TS (S.D = 2.77%). Sludge was stored at 4°C. Table 2-1 shows the characteristics of none treated sludge used for each series of tests.

1.2 Pre-treatment condition

Pre-treatment is a step of digestion of waste activated sludge that break up of cell walls and disintegration of sludge flocs. A pre-treatment step would render hydrolysis less difficult, thus giving a more efficient process.

Table 2-1: Characteristics of raw sludge.

Parametrs	Mean (X)	Standard Deviation (S.D)
pH	6.88	0.14
BOD_T (mg $O_2.L^{-1}$)	6240	784.5
BOD_S (mg $O_2.L^{-1}$)	150	41.3
COD_T (mg $O_2.L^{-1}$)	15210	2979
COD_S (mg $O_2.L^{-1}$)	818	173.2
$Nitrogen_T$ ($mg.L^{-1}$)	982	253.1
$Nitrogen_S$ ($mg.L^{-1}$)	161	20.95
$Phosphorus_T$ ($mg.L^{-1}$)	870	140
$Phosphorus_T$ ($mg.L^{-1}$)	196	34.57
$Protein_T$ ($mg.L^{-1}$)	3460.8	734.36
$Protein_S$ ($mg.L^{-1}$)	135.2	18.26
$Carbohydrate_T$ ($mg.L^{-1}$)	2448.3	281.66
$Carbohydrate_S$ ($mg.L^{-1}$)	70.3	12.22
Total Suspended Solids (TSS) ($g.L^{-1}$)	13.75	3.14
Volatile Suspended Solids VSS ($g.L^{-1}$)	10.45	2.54
Total Solids TS ($g.L^{-1}$)	14.53	3.58
Volatile Solids VS ($g.L^{-1}$)	10.60	2.77

Examples of pre-treatment methods presented in the literature are ultrasound, thermal pre-treatment, enzyme addition, ozonation, chemical solubilization by acid or base addition and mechanical disintegration.

In this study, three kinds of pre-treatment were considered: mechanical (US), thermal (Bain-marie and Autoclave), and Oxidative (O_3).

1.2.1 Ultrasonic setup

The ultrasonic equipment consisted of a generator, a converter and a sonotrode, supplied by Alpha Ultrasonic. The generator supplies alternating current to a piezo-ceramic crystal; located at the extremity of the sonotrode. The amplitude and thus the intensity of the ultrasound waves can be varied. The maximal energy output is 1kW. A maximum ultrasonic efficiency is obtained when steady waves with large pressure amplitude are generated. The sonotrode is positioned eccentrically in the reactor to limit damp-down effects. The frequency is set at 20 kHz in accordance with literature recommendations. The sound frequency of 20 kHz was selected because sludge disruption is most effective at low frequencies. Ultrasound horns magnify the amplitude and they were made thermally stable and corrosion resistant.

The used ultrasonic apparatus is a Sonopuls Ultrasonic Homogenisers (BANDELIN – HD 2200).This apparatus is equipped with a probe TT 13 and worked with an operating frequency of 20 kHz and a supplied power of about 200 W and volume range 5 – 900 mL. The probe used is a standard probe 12.7mm in diameter (Figure 2-1).

For each sonication experiment, 100 mL of sludge is filled in a stainless steel beaker and the ultrasonic probe is dipped 2 cm into the sludge. The range of the specific supplied energy was 5000, 50000, 100000 and 200000 kJ.kg-TSS^{-1} for different durations (from 2 to 80 min) and powers (50, 100 and 200 W).Power density ranging from 0.5 to 2 W/mL were investigated in order to optimize the enzymatic activities. During sonication, the sludge lead to increase of temperature and this temperature was controlled with icebound and maintained at 20°C to prevent possible temperature effects.

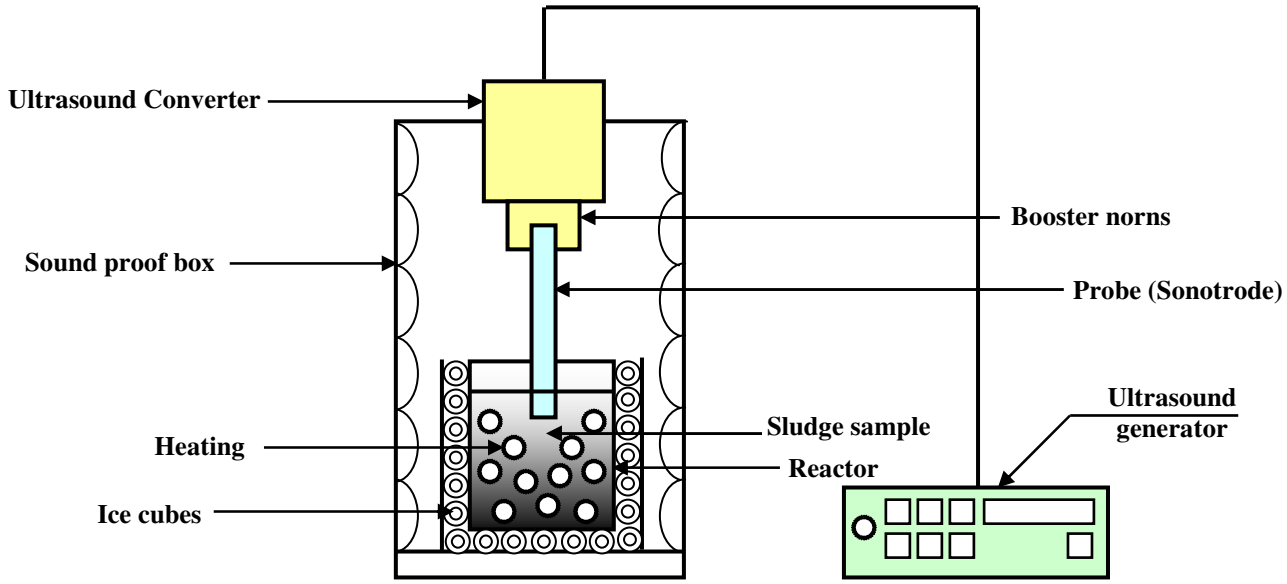

Figure 2-1: Scheme of ultrasonic activated sludge disintegration.

❁ Specific energy

Specific supplied energy has been chosen in order to compare results. The specific energy input is a function of the energy, concentration in the matter and volume of the sample and is defined as the ratio of energy (J) on the concentration of suspended solids (g.L^{-1}) multiplied by the volume of the test (L)

This Specific Energy (SE) can be defined by using ultrasonic power (P), ultrasonic time (t), sample volume (v) and initial total solid concentration (TS_0) as follows: (Bougrier *et al*. 2006)

$$\text{Specific energy} = SE = \frac{P_{(W)} \times t_{(Sec)}}{C_{(g/l)} \times V_{(L)}} \qquad \underline{Eq.2}$$

where:

SE = specific energy (kJ.kg^{-1}-TSS) [L^2T^{-2}]

P = power supplied (W) [ML^2T^{-3}]

T = time of treatment (s) [T]

V = volume of the sample (L) [L^3]

C = concentration of total solids (g.L^{-1}) [ML^{-3}]

In this study, ultrasonic parameters are used as defined by Hua and Hoffmann (1997), (Khanal *et al.,* 2007):

- **Ultrasonic dose**: This is the amount of energy supplied per unit volume of sludge and is expressed as Ws/L or kWs/L (J/L or kJ/L) [$ML^{-1}T^{-2}$]. However, it does not account for the TS content in the calculation. The ultrasonic dose for sludge with certain TS content cannot be directly compared to another with a different TS content. As long as the TS content remains fairly constant, the ultrasound dose is a practical method of expressing the energy input for the disintegration of sludge on a volume basis.

- **Ultrasonic density**: This relates to the power supplied per unit volume of sludge and has a unit of W/L or kW/L or W/mL [$ML^{-1}T^{-3}$]. Ultrasound density also relates power input to the volume of sludge, similar to ultrasound dose. However, ultrasound density does not take into account the sonication duration.

- **Ultrasonic intensity**: This is defined as power supplied to sludge per unit of converter area and is expressed as W/cm^2 [MT^{-3}]. Ultrasonic intensity therefore reflects the power-generating capacity of the converter. The higher the amplitude, the higher is the ultrasonic intensity that the system will be able to produce.

1.2.2 Ozonation system

Ozonation method was investigated as chemical means of oxidation from the activated sludge. Ozone has many properties desirable for the treatment of the wastewater. Firstly, it is a powerful oxidant capable of oxidative degradation of many organic compounds and also results in oxidation products which are more biodegradable. Ozone also results in the formation of highly reactive hydroxyl radical in the system, which has higher oxidation potential as compared to ozone itself. Ozonation has been used for the disinfection, oxidation of inorganic and organic compounds, including taste, odour, colour and particle removal.

The ozonation reactor consists of an ozone generator (TRAILIGAZ OZONE SAS), an ozone analyzer (964 BT), an oxygen cylinder for oxygen supply, a contact column (1800 mm high water column), and an ozone destructor (supplied by TRAILIGAZ). An air pump and a tail gas adsorption flask with potassium iodide inside. A pre-calibrated rota-meter with a regulating valve for gas flow adjustment and an output control scale was mounted in front of the generator assembly. Piping and valves are made of polypropylene (for water flow) and PTFE (for ozone flow), and the contact column is made of PVC (opaque in the base of column and transparent in the top of column). The power of the ozone generator and the oxygen flow and air pressure were set in all the tests at 180 Watt (from 50 to 200 W) and 600 NL. h^{-1} (from 300 to 800 NL/hr), and 0.7 bar (from 0.0 to 1 atm) respectively, ensuring a constant supply of O_3 to the contact column. Ozone generation was determined by measuring the gas flow rate. Maximum ozone production was 50 g/N m^3. Residual ozone has been measured at the outlet of the contact column during all the tests (Figure 2-2 shows ozonation system).

All the experiments were conducted at room temperature and in a semi-batch mode by sparging the ozone into the sludge sample. The sludge ozonation lead to decreased of pH and after ozonation the pH was readjusted to 7.0 – 7.2 with using of NaOH.

For each ozonation experiment, 700 mL of sludge was ozonated in a cylindrical glass contactor with 2 lit effective volume (φ = 120mm and H = 300mm). Ozone consumption ratio was calculated from difference between amount of ozone at inlet and outlet of the ozone contactor per amount of initial ozonated sludge indicated as TSS since dissolved ozone was not detected.

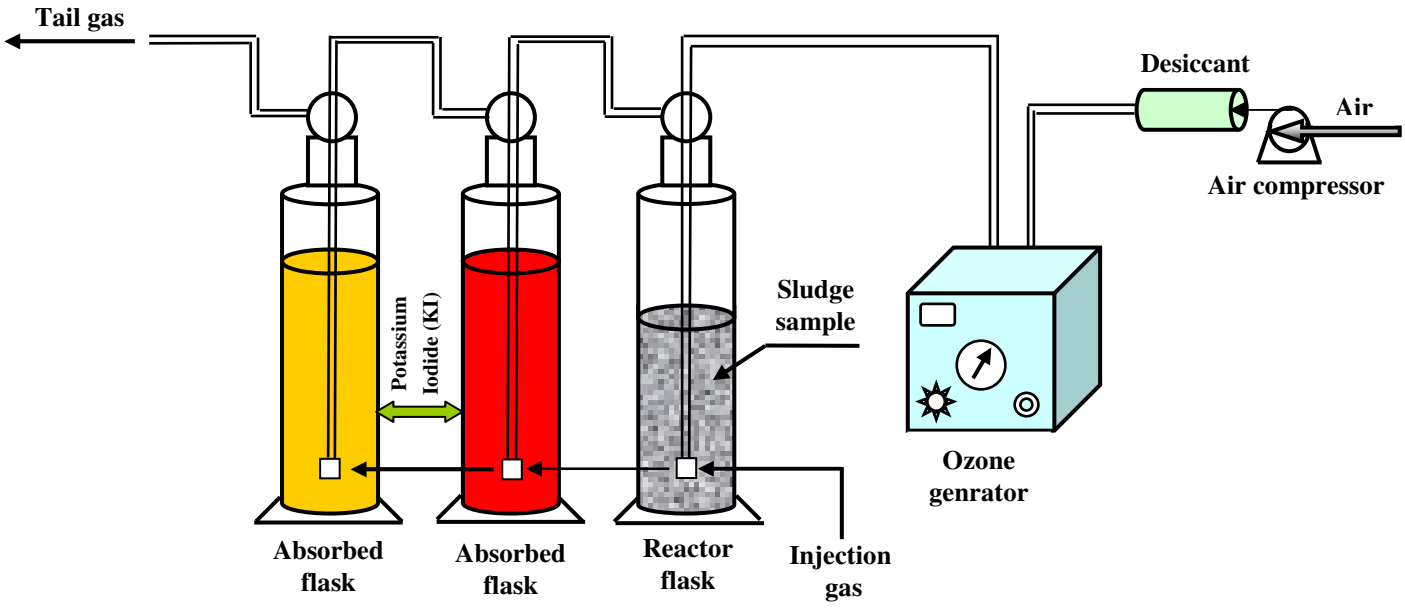

Figure 2-2: Photo of ozonation apparatus and ozonated sample.

Ozone was determined by an iodometric titration method. The iodometric method was used to determine ozone concentration in feed and exhaust gas and in the solvents. In iodometric method, ozone is absorbed by the Alkaline Potassium Iodide solution, and by acidifying it, releases iodine. The iodine concentration can be measured by sodium thiosulfate. The reaction is:

$$O_3 + 2KI + H_2O \rightarrow I_2 + 2KOH + O_2$$

$$I_2 + 2Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2NaI$$

We know that 2 moles of thiosulfate corresponds to 1 mole of I_2 and that 1 mole of I_2 corresponds to 1 mole of O_3, therefore: 2 moles thiosulfate corresponds to 1 mole O_3.

After ozonation the containing of both KI bottles are mixed in a beaker up to a total volume of two liters. The mixture is titrated using one molar sodium thiosulfate. Before titration, we add 200 ml of sulfuric acid 4.5 molar into KI sample. The volume of consumed thiosulfate is noted as $V_{Thiosolfat}$ (V_1). The distilled water undergoes the same procedure and the consumed thiosulfate volume is noted as $V_{Distillated\ Water}$ (V_2). Ozone consumption is calculated using the difference between these two volumes by applying equation (3).

$$M_{O3} = \frac{N \times (V_2 - V_1) \times X}{V_S \times C} \qquad \underline{Eq: 3}$$

where:

M_{O3} = masse of ozone used (gO_3/g-TSS)
N = normality of thiosulfate (mol/L)
V_1 = volume of thiosulfate solution used in sample (L)
V_2 = volume of thiosulfate solution used in Distillated Water (L)
V_S = volume of sludge (L)
X = 0.5 mole Ozone (24 gO_3/mol)
C = Concentration of sludge (g-TSS/L)

Using this method, the measurement uncertainty is about ±1% and we can measure concentrations ranging from 2 to 160 $mgO_3.L^{-1}$.

1.2.3 Thermal pre-treatment apparatus

Heat supply effects a change in the sludge structure. Through destruction of the cell membranes of the micro-organisms, the water-soluble cell contents are set free; chemical and physical reactions then lead to a change in the substances liberated to a gel-like structure.

In this study, thermal destruction of the sludge was studied. Two different thermal treatments have been investigated: Autoclave and Bain Marie. Autoclave Reactor was Préciclave n° 942 (Autoclave France) with power of 6000 W that controlled in 121°C, and 1.5atm pressure for 15 minutes and sample volume was 0.7 L. Bain- Marie reactor was Isotemp 120 with a supplied power of about 1000 W that controlled at low temperature (from 0 to 100°C) and different time (from 10 to 480 min). Sludge cooled to ambient temperature and cooling time was about 1.5 hr (see Figure 2-3).

Figure 2-3: Photo of Bain- Marie reactor for thermal treatment.

2. Degree of disintegration, solubilization rate and removal efficiency

2.1 Degree of disintegration

In order to get the results and compare them, the degree of disintegration was introduced. This definition was used in the bibliographic data and was determined based on measuring chemical oxygen demand (COD). The degree of disintegration was defined by Müller and Pelletier (1998) as the comparison between pre-treatment process (e.g. ultrasonic) and a maximum soluble chemical demand COD_{NaOH} obtained by alkaline hydrolysis: (Tiehm *et al.*, 1997, Lehne *et al.*, 2001, Gonze *et al.*, 2003, Bougrier *et al.*, 2005)

Degree of disintegration has been determined by the following formula Equation (4). (Tiehm *et al*., 1997, Müller, and Pelletier, 1998**,** Lehne *et al*., 2001, Gonze *et al*. 2003 and Bougrier *et al*, 2006).

We define a factor DD_{COD} termed "degree of disintegration" as ratio of COD-increase by pre-treatment in the sludge supernatant to the COD-increase by the chemical hydrolyzation:

$$\text{Degree of Disintegration} = DD_{COD} = \frac{COD_S - COD_{S0}}{COD_{S-NaOH} - COD_{S0}} \times 100 \qquad \underline{Eq.4}$$

where:

DD_{COD} = degree of disintegration based on the chemical oxygen demand (%)
COD_S = soluble COD in the treated sample ($gO_2.L^{-1}$)
COD_{S0} = soluble DCO in the untreated sample (initial soluble COD) ($gO_2.L^{-1}$)
$COD_{S\text{-}NaOH}$ = soluble COD in the sample disintegrated in sodium hydroxide: total supposed disintegration ($gO_2.L^{-1}$)

In this formula, according to the authors, the total disintegration is done in various ways and the word COD_{NaOH} corresponds to a treatment of alkaline hydrolysis:

- Treatment by sodium hydroxide (0.5M) for 22 h at room temperature (Tiehm *et al.*, 1997).
- By temperature together a volume of sludge with a volume of NaOH (1N) during 10 min at 90 ° C (Lehne *et al.*, 2001).
- Treatment by sodium hydroxide 1 M for 24 h at room temperature (Gonze *et al.*, 2003).
- Treatment by Supposed solubilization maximum for alkaline hydrolysis, the sludge was mixed with NaOH (1 mol/l), for 24 h, at room temperature (Bougrier *et al*, 2005).

In order to obtain the rate of $COD_{S\text{-}NaOH}$, equal volumes of sludge sample and solution of NaOH (1N) were mixed and the mixture was heated in Bain-Marie at 90°C during different times from 5 to 60 minutes. In this study, maximum $COD_{S\text{-}NaOH}$ for 90°C thermal treatment and US was achieved respectively after 40 and 30 minutes. The difference can be explained by different sludge natures and concentrations in each series of the tests. Figure 2-4 depicts the $COD_{S\text{-}NaOH}$ rate for each series.

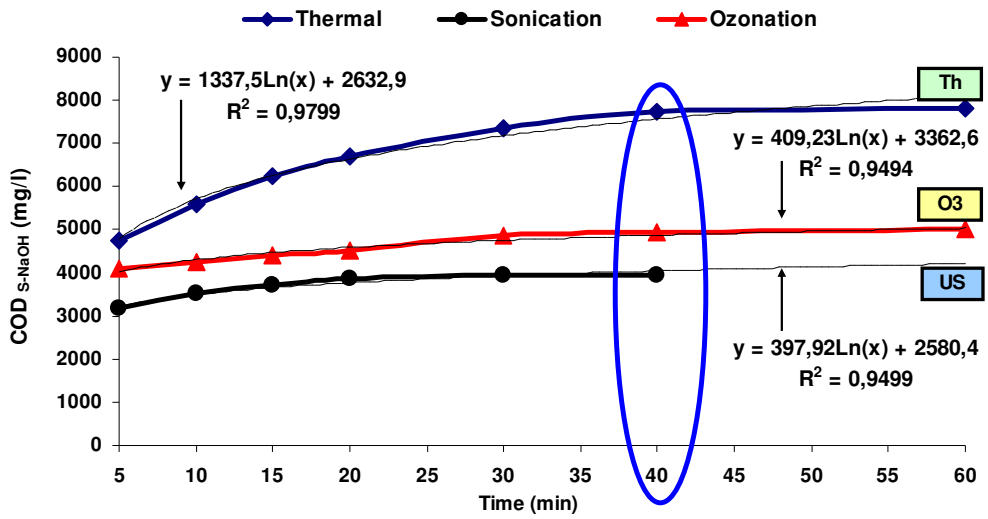

Figure 2-4: The $COD_{S\text{-}NaOH}$ rate versus time for sonication, ozonation and thermal treatment.

2.2 Solubilization evaluation

In order to determine sludge solubilization, several measurements were carried out on samples, according to Standard Methods (1992). In fact, the term "solubilization" represents the transfer (of organic or mineral matter) from the particulate fraction of the sludge (solids after centrifugation) to the soluble fraction of the sludge (supernatant after centrifugation).

COD (S_{COD}), Nitrogen (S_N), Phosphorus (S_P), Protein ($S_{Protein}$) and, Carbohydrate ($S_{Carbohydrate}$) solubilization were calculated using the difference between soluble X (X_S) and initial soluble X (X_{S0}), compared to the initial particulate X (X_{P0}) (Bougrier *et al*, 2006). X representing COD, Nitrogen, Phosphorus, Protein, and Carbohydrate concentrations (equation 5):

$$\text{Solubilization of X} = S_X = \frac{X_S - X_{S0}}{X_{P0}} \times 100 \qquad \underline{Eq.5}$$

where:

S_X = Solubilization of X (%)

X_S = Soluble X in the treated sample ($gO_2.L^{-1}$)

X_{S0} = initial soluble X ($gO_2.L^{-1}$)

X_{P0} = initial particulate X =initial total - initial soluble ($gO_2.L^{-1}$)

Measures of total and organic solids (TS and VS) were realized on sludge and on solids after centrifugation (total and volatile suspended solids: TSS and VSS). Solids concentration of the supernatant, that is to say the soluble phase, was then deduced. That led to the composition in

the different parts in the sludge. Total solids (S_{TS}) and volatile solids (S_{VS}) solubilization rates were calculated as follows: (Bougrier *et al.*, 2006).

$$\text{Solubilization of TSS} = S_{TSS} = \frac{TSS_0 - TSS}{TSS_0} \qquad \underline{Eq.6}$$

where:

S_{TSS} = Solubilization of TSS (%)

TSS = TSS in the treated sample ($g.L^{-1}$)

TSS_0 = TSS in the untreated sample ($g.L^{-1}$)

$$\text{VS solubilization} = S_{VS} = \frac{VS_0 - VS}{VS_0} \qquad \underline{Eq.7}$$

where:

S_{VS} = Solubilization of VS (%)

VS = Volatile solids in the treated sample ($g.L^{-1}$)

VS_0 = Volatile solids in the untreated sample ($g.L^{-1}$)

3. Biological digestion (aerobic and anaerobic)

In this study, the sludge samples from ultrasonic, ozonation and thermal pre-treatments and control sample underwent digestion in reactors. All experiments were conducted in batch reactor under aerobic and anaerobic digestion condition.

3.1 Aerobic digestion reactors

Aerobic digestion has been used to remove excess organic matter and the aerobic digestion of sludge was studied in four stirred tanks in order to reduce sludge production. Aerobic digestion is mostly selected for the treatment of secondary sludge such as those generated by the activated sludge and trickling filter processes and is a preferred method for treatment of dilute waste sludge.

The bioreactor (aerobic digester) was a circular vessel (cylindrical) with dimensions 130 mm and 200 mm in inner diameter and height, respectively (H/D = 1.54) and an effective volume capacity of 3 L. Air was supplied through a sparger located at the bottom of the reactor to ensure that the dissolved oxygen concentration was uniformly maintained in excess of 2 $mg.L^{-1}$

of the reactors content (Figure 2-5). The airflow rates were measured and maintained with the help of a pre-calibrated Rota-meter. The reactor was provided with a lid containing inlet-ports for bubbling of gas (air passed through a submicron air filter) and stirring and outlet-ports for sampling and venting.

The sludge provided by municipal wastewater treatment plant of Limoges-France. The wastewater treated at WWTP consists of municipal sewage and wastewater produced at local small-scale industries. The reactors were fed with 0.5L of inoculums (sludge coming from the aerobic basin) and with 2L of treated or untreated sludge. The reactor temperature was maintained at the ambient temperature.

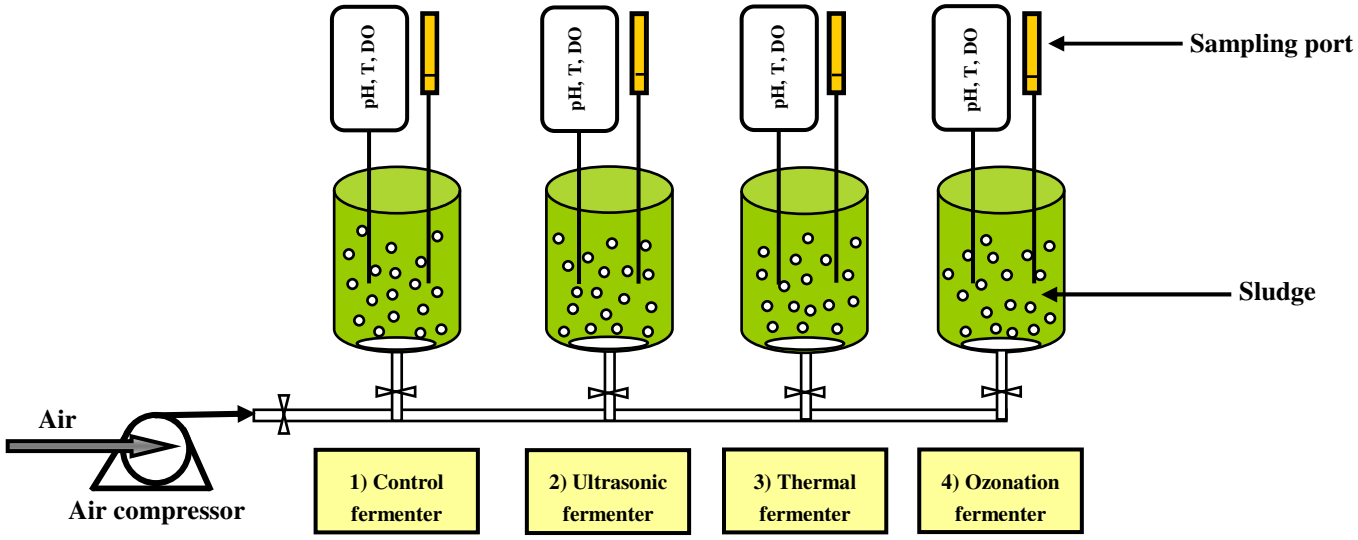

Figure 2-5: Laboratory scale aerobic fermenters (operated batch with 2500 ml WAS).

3.2 Anaerobic digestion reactors

Anaerobic digestion is an appropriate technique for the treatment of sludge before final disposal and it is employed worldwide as the oldest and most important process for sludge stabilization, reducing sludge volume and producing biogas.

The anaerobic digestion of sludge was studied in four stirred tank fermenters (water-jacketed reactors) at 35 - 37°C. The fermenters immersed in a temperature controlled, agitated water bath and Protected from 35 to 37°C. Temperature of digester was controlled by circulation warm water through water jacket (Figure 2-6). Each fermenter had a total volume of 3 litter (similar to aerobic reactors) and contained 2500 mL of sludge (pre-treated sludge = 2000 mL + inoculum (sludge from digester) = 500 mL). The digesters were operated in a magnetic agitator

(Fisher-Bioblock-France) at 10 rpm to supply a slow mix condition. At the beginning of the digestion experiments, the fermenters were filled with concentrated sludge from Limoges WWTP.

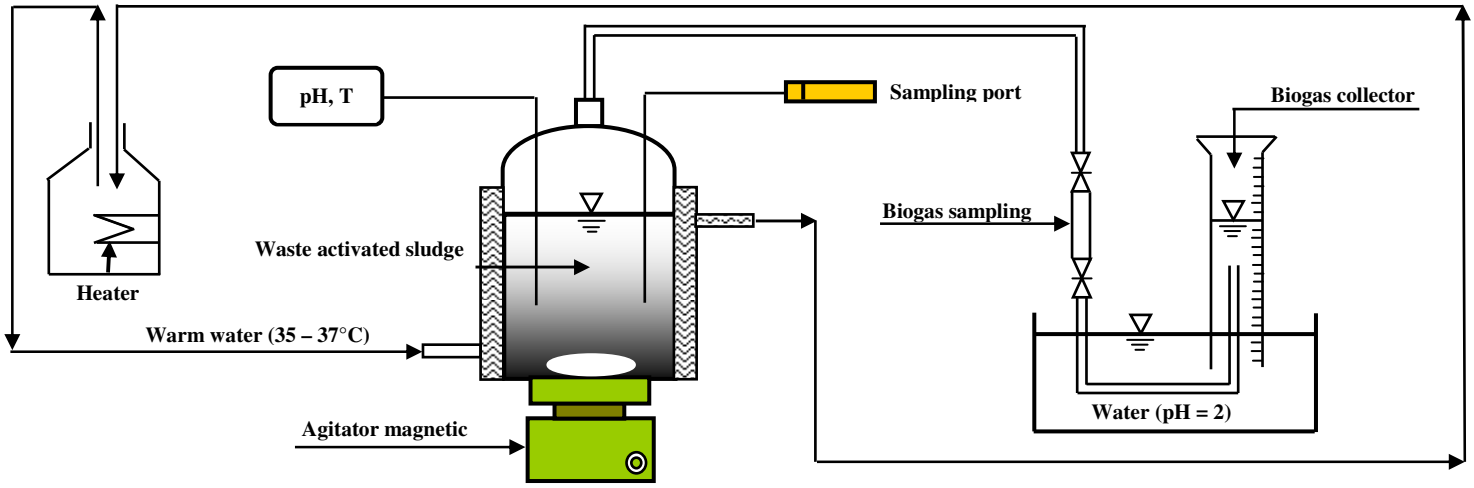

Figure 2-6: Laboratory scale anaerobic digester (4 reactors were operated batch with 2500 ml WAS).

The produced biogas was collected in calibrated glass cylinders. The cylinders were filled with deionised water and acidified with HCL (pH is about 2) to avoid losses of CO_2 due to the formation of carbonate (Figure 2-6). The biogas composition was determined by a gas chromatograph equipped with a heat conductivity detector.

3.3 Aerobic and anaerobic digestion reactors setting-up

The pilot is made of four aerobic and four anaerobic stirred reactors (Figure 2-7). Each reactor has a working volume of 3 litres. The reactors were filled with 2500 mL of sample sludge (≈15g.L^{-1} concentration) in control (non pre-treatment), sonicate (200000 kJ.kg-TSS^{-1}), thermal (40°C, 60°C and 90°C during 60min) and ozonation (0.1 gO_3.g-TSS^{-1}) reactors, respectively and 500 mL of sludge inoculum coming from limoges WWTP (sludge of aerobic tank, for aerobic reactors and sludge of digester tank, for anaerobic reactors). The aerobic digestion was carried out at room temperature. The anaerobic digestion is investigated at 35-37°C. The produced biogas was collected in calibrated glass cylinders.

The aerobic and anaerobic reactors were studied in a batch mode. Parameters that were monitored simultaneously throughout each experiment were pH, Temperature (T°C), Dissolved Oxygen (DO) and biogas volume. The pH and Temperature measurements were done using digital pH metre (Digital pH metre SUNTEX instruments, Taiwan) and dissolved oxygen were

done using digital DO meter (Mettler-Toledo, SG6, Germany). Certain parameters were measured everyday while others were measured initially every other day (until 10 days) and then every six days (see Table 2-2).

Table 2-2 : Period of different analysis performed on the sludge

Frequency	Analysis
Everyday	pH, T°C, DO, Biogas
Every 6 days	COD, BOD, TS, VS, TSS, VSS, N, P, protein, carbohydrate, anions and cations

The employed analytical procedures were in compliance with the standard analytical methods outlined in Standard Methods for the Examination of Water and Wastewater (APHA, 1992). The fermenters operated during 40 to 50 days for the first and second pilot in a batch mode. Replicate samples were analyzed for quality control.

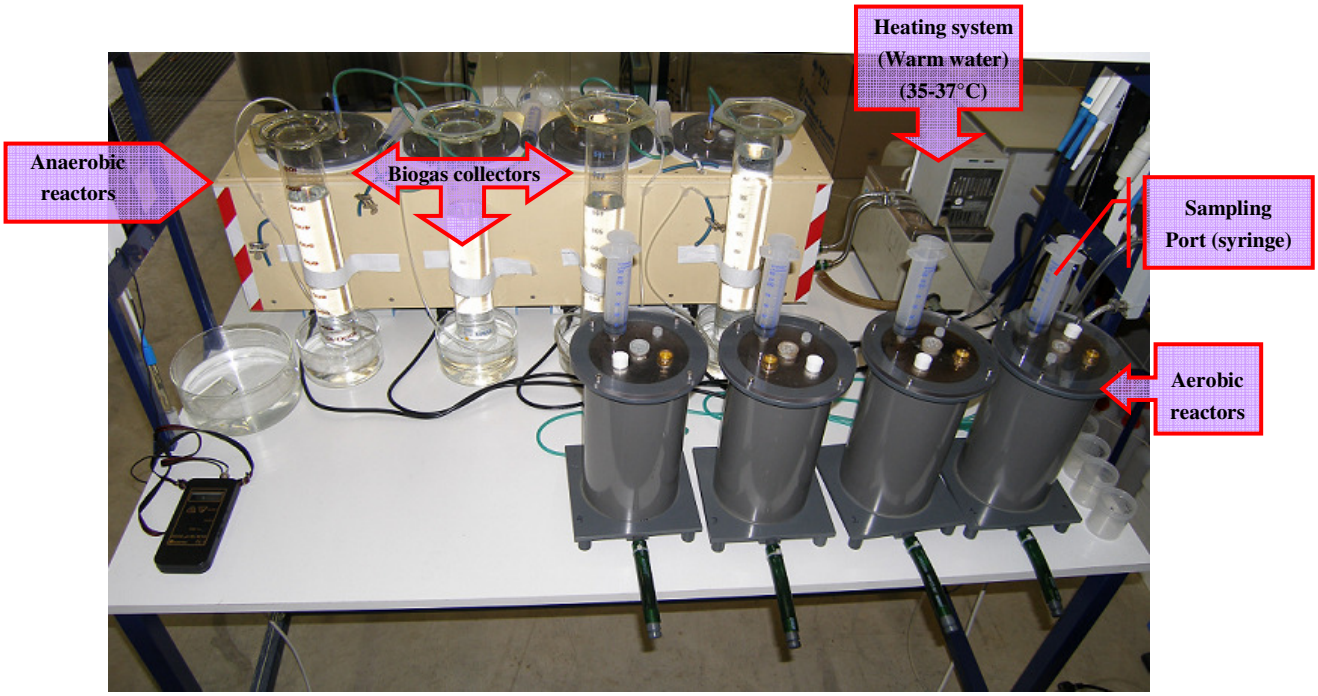

Figure 2-7: Photo of pilot plan with 8 aerobic and anaerobic reactors.

3.4 Calculation of kinetics equations and stoichiometric parameters

In order to evaluate the aerobic and anaerobic digestion performance, both in terms of removal efficiency and energy recovery, an accurate model and reliable kinetic and stoichiometric parameters are required.

3.4.1 Stoichiometric parameters

3.4.1.1 Sludge reduction (Removal rate)

The main parameters used in evaluation of sludge degradation are VSS removal and COD degradation. The suspended solids degree of degradation (digestion) and removal efficiencies (Re) of COD and VSS were evaluated using the following expression:

$$\text{Removal efficiency} = (\text{Re}) = \frac{C_{t_0} - C_{t_f}}{C_{t_0}} \times 100 \qquad \underline{Eq.8}$$

where:

Re = Removal efficiency (%)

C_{t0} = Concentration in influent ($mg.L^{-1}$)

C_{tf} = Concentration in effluent ($mg.L^{-1}$)

3.4.1.2 COD uptake rate and biogas production rate (r)

Instantaneous COD_S uptake rate (r_{COD}) and Instantaneous biogas production rate (r_{Biogas}) were calculated according to equations 9 and 10:

$$\text{COD uptake rate} = r_{COD} = \frac{\Delta COD_{t_1 t_2}}{t_2 - t_1} \quad \text{in mg-}O_2.L^{-1}.d^{-1} \qquad \underline{Eq.9}$$

$$\text{Biogas production rate} = r_{Biogas} = \frac{\Delta V\ biogas_{t_1 t_2}}{t_2 - t_1} \quad \text{in mL BG.}d^{-1} \qquad \underline{Eq.10}$$

3.4.1.3 Specific soluble COD uptake rate and specific biogas production rate (q)

Instantaneous specific soluble COD uptake rate q_{COD} (mg COD_S.g-$VSS^{-1}.d^{-1}$) and instantaneous specific biogas production rate q_{Biogas} (mL BG.g-$VSS^{-1}.d^{-1}$) were calculated according to equations 11 and 12:

Specific soluble COD uptake rate = $q_{COD} = \frac{r_{COD}}{\frac{VSS_{t_1} + VSS_{t_2}}{2}}$ in mg COD_S.g-VSS^{-1}.d^{-1} *Eq.11*

Specific Biogas production rate = $q_{biogas} = \frac{r_{Biogas}}{\frac{VSS_{t_1} + VSS_{t_2}}{2}}$ in mL BG.g-VSS^{-1}.d^{-1} *Eq.12*

3.4.1.4 Removal yield (Y)

Global yield of biogas production Y (mL BG.g-COD_S^{-1}) was calculated according to equation 13 in which volume of biogas represents the total amount of produced biogas between t_0 and t_f :

Yields of biogas = $Y = \frac{V\ Biogas}{(COD_{S\ t_0} - COD_{S\ t_f}) \times V_{reactor}}$ in mL BG.g-COD_S^{-1} *Eq.13*

3.4.1.5 Energetic balance (E)

The consumed energy during solubilization and biological digestion in the pre-treated samples (ultrasonic, ozonation, Bain-Marie and autoclave reactors) and non-pretreated sample (control) were calculated according the following formulas:

a) $E_{Solubilization}$ (E_S)

E_S is the amount of energy consumed during different pretreatment methods in ultrasonic, ozonation, Bain-Marie and autoclave apparatus. E_S is calculated as the product of power of apparatus by the operating time. It is expressed in J or kJ.

$$E_S = p_{(W)} \times t_{(sec)}$$ *Eq.14*

where:

E_S = the rate of energy used for sludge pre-treatment (J or kJ)

P = power of apparatus in terms of (W)

t = operating time of the apparatus during the sludge solubilization step (sec)

The power of apparatus for sonication, ozonation, Bain-marie (40°C, 60°C and 90°C) and autoclave is respectively 50, 180, 400, 600 and 900 and 6000 watt.

b) E_{Total} under aerobic condition (E_T)

For aerobic systems, total energy consumption (E_T) is the sum of applied energy by air compressor during aerobic digestion (E_A) and applied energy for solubilizing samples (E_S). The power of air compressor was 135 watt.

$$E_T = E_S + E_A \qquad \text{Eq.15}$$

where:

E_T = Total energy of aerobic digestion (kJ)
E_S = Energy consumption during solubilization (kJ)
E_A = Energy consumption of air compressor (kJ)

c) E_{Total} under anaerobic condition (E_T)

For anaerobic system, two apparatus are used: agitator and heater. Agitator is used to mix the sludge during the digestion process. Heater is used to maintain the temperature of sludge at 35-37°C. The duty cycle of heater is about 15%. It means that heater works only 15% of the digestion time. The powers of agitator and heater were 40 and 640 watt respectively.

We must also take the energy of methane production into account. Anaerobic digestion results in methane production which may be used to provide a fraction of required energy.

Total energy (E_T) is the sum of solubilization, agitator, and heater energies minus methane energy:

$$E_T = E_S + E_{Ag} + E_H - E_{CH4} \qquad \text{Eq.16}$$

where:

E_T = total energy of anaerobic digestion (kJ)
E_S = energy consumption during solubilization (kJ)
E_{Ag} = energy of agitator (kJ)
E_H = energy of heater (kJ)
E_{CH4} = energy of produced methane (kJ)

4. Analytical methods for wastewater characterization and performance assessment

4.1 Sampling and analyses methods

Required excess sludge was taken from the sludge return line of aeration tank at municipal wastewater treatment plant of Limoges-France (usually at 2 P.M) and was immediately transported to the laboratory where it was thickened and used. In order to thicken the sludge, the sample was poured in jar containers with 3 to 5 liters of capacity. We let the sludge to get totally settled to the bottom of container, and every few hours syringed the extra water on the top of the sludge. Depending on sludge nature, it takes up to 36 hours for the sludge to be thickened. Concentrated sludge was then kept in refrigerator (4°C) in closed one-liter containers to be used in future experiments (pretreatment and digestion).

4.2 Centrifugation and filtration

For the analysis of aqueous phase supernatants, the particulate sludge material was removed by high speed centrifugation and followed by filtration through 1.2 µm pore size cellulose-acetate membrane filters.

To separate the soluble and non soluble fractions, centrifugation was carried out with apparatus centrifuge CR3I multifunction (Thermo Electron Corporation – France). The volumes are approximately centrifuged 50 mL and centrifuge is an acceleration of 6000×g (7800 RPM) for 20 minutes at 4°C. After centrifuge being done, supernatant was separated from solids fraction and was used to perform required tests (soluble and total).

In order to perform soluble measurements it was necessary to filter the supernatant. Thus the supernatant was passed through cellulose-acetate membrane filters with a diameter of 1.2 µm pore size. The supernatant obtained shall be considered as the soluble phase and the bottom nomad particulate phase. Then the desired tests concerning soluble COD, BOD, N, P, carbohydrates, and proteins were done. In order to perform the tests concerning anions and cations, the supernatant was filtered again using 0.22 µm filter paper.

The term "total" refers to the total samples of sludge none centrifuged. Test corresponding to total COD, BOD, N, P, carbohydrates and proteins were done on the rough (not filtered) supernatant. The solid phase substance which was separated from the supernatant was used in the TSS and VSS relative tests. Figure 2-8 shows the above mentioned steps.

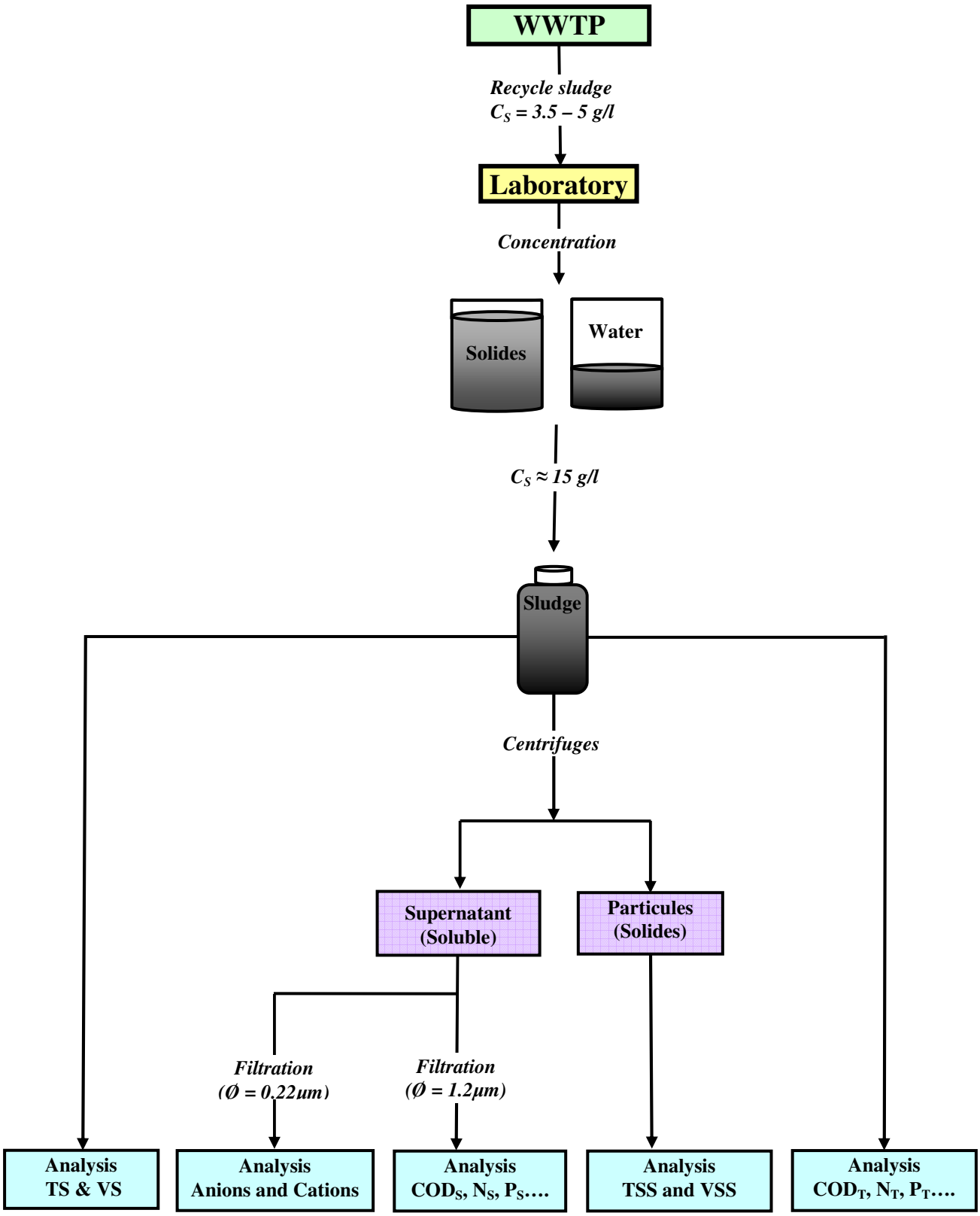

Figure 2-8: The sludge preparing steps containing transport from plant, thickening, centrifuging, filtering, and performing tests.

4.3 Biochemical and chemical analysis

In order to determine sludge composition, several measurements were made on samples. Biochemical oxygen demand (BOD), Chemical oxygen demand (COD), matter (TS, VS, TSS and VSS), nitrogen (N), phosphorus (P), proteins and carbohydrates were measured before and after sonication, ozonation and thermal pre-treatment and along the digestion step. The soluble and particulate fraction was evaluated after centrifugation (centrifuge CR3I multifunction) and filtration through a 1.2 µm membrane and concentration total was determined on total sludge before centrifugation.

For this work, measured on supernatant will be called 'soluble' and the difference between total and soluble will be called 'particulate'. COD, Nitrogen and Phosphorus are measured on the sludge with using of the method HACH, BOD_5 is measured using the Oxi-Top® method, Proteins concentration were determined according to LOWRY method (Lowry *et al.,* 1951), and the technique used for polysaccharides (carbohydrate) are colorimetric method of Dubois *et al.,* (1955). Measures of total and organic solids (TS & VS) were realized on the sludge and on particulate fraction of centrifugation (TSS & VSS) was measured according to the French Standard methods. Ionic species (NH_4^+, NO_3^-, NO_2^- and PO_4^{-3}) are measured using the chromatographic ionic (Dionex DX – 120, USA).

4.3.1 COD and BOD analysis

- **COD analysis**

In environmental chemistry, the chemical oxygen demand (COD) test is commonly used to indirectly measure the amount of organic compounds in water and wastewater. The oxygen is equivalent the organic matter that can be oxidized by using a strong chemical oxidizing agent in an acidic medium. Potassium dichromate has been found to be excellent for this purpose. A catalyst (silver sulfate) is required to aid the oxidation of certain classes of organic compounds.

The COD test is also used to measure the organic matter in industrial and municipal waste that contain compounds that are toxic to biological life. The COD of the waste is, in general, higher than the BOD because more compounds can be chemically oxidized than can be biologically oxidized. For many types of wastes it is possible to correlate COD whit BOD. This can be very useful because the COD can be determined in three hours, compared with five days for the BOD.

COD was measured in duplicates in the total sludge, in supernatant and in the particulate fraction using the colorimetrically analyses at a wavelength of 620 nm. Reagents and equipment were purchased from spectrophotometer DR/2010, HACH, USA. This measurement [COD ampoules HACH in accordance with standard methods, 1992, NF T 90 101, HACK high range plus (0 to 15000 mg $COD.L^{-1}$) and high range (0 to 1500 mg $COD.L^{-1}$)] consists in the oxidation of the organic matter in dichromate de potassium ($K_2Cr_2O_7$), after two hours and heating at 150°C. Chloride ions with a concentration higher than $1.5g.L^{-1}$ interfere with the measure. In this case, the value of the COD may be overestimated and the error of this measurement was around 10 to 15% for COD_S and 15 – 20% for COD_T.

- **BOD_5 analysis**

Biochemical oxygen demand (BOD_5) determination involves the measurement of the dissolved oxygen used by micro-organisms in the biochemical oxidation of organic matter. It is usually performed over a 5-day incubation period at 20° Celsius, but other lengths of time and temperatures can be used. BOD_5 is measured using the Oxi-Top® method (instruction, DIN 38409, part 52). BOD_5 measurement with the Oxi-Top® measuring system is based on pressure measurement (difference measurement). The measuring is made by pressure measurement via piezoresistive electronic pressure sensors. With the following functions, the Oxi-Top® measuring system minimizes the measuring work and is especially suited to the courses of the respirometric BOD_5 measurement: Normally municipal wastewater does not contain toxic or impeding substances. There are enough nutrient salts and suitable micro-organisms. Under these conditions the BOD_5 determination with the Oxi-Top® measuring system is possible in the undiluted sample. The measurement error was about 15 to 20% for this analysis.

4.3.2 Determination of matter composition

Solids concentrations were estimated by heating at 105°C during 24 hr for total solids that water was evaporated off and the total dry matter concentration determined. Then, the samples were heated at 550°C during 2 hr that lead to mineral matter concentrations. Organic matter concentrations were then deduced.

Measures of total and organic solids (TS and VS) were realized on sludge and on solids after centrifugation (total and volatile suspended solids: TSS and VSS) according to standard methods, (1992), NF T 90-105-1. Solids concentration of the supernatant, that is to say the

soluble phase, was then deduced from the difference between total solids and suspended solids concentrations.

In order to determine the volatile solids (VS), the samples were first dried at 103 - 105°C for 24 hr to obtain the concentration of dry solids. Next, the dry solids were incinerated at 550°C for 2 hr. The residues after incineration represent the inorganic dry solids. The difference between the dry solids and the inorganic dry solids represents the volatile solids.

a) TS and VS measurement algorithm

- Crucible is completely dried in an oven (at 103 to 105°C during 12 hr) then it is cooled down in desiccator and its weight is noted as W_1.
- A predefined volume of sample sludge (mL) is poured in the Crucible and is dried in oven at 105°C during 24 hours. It is cooled down in desiccator and its weight is noted as W_2.
- The Crucible is put in furnace (550°C during two hours) and is weighted after being cooled down in desiccator (W_3).

We have:

$$\text{Total solids} = TS = \frac{(W_2 - W_1)\times 1000}{V_{sample}} \quad (\text{g-TS.L}^{-1}) \qquad \underline{Eq.17}$$

$$\text{Volatile solids} = VS = \frac{(W_2 - W_3)\times 1000}{V_{sample}} \quad (\text{g-VS.L}^{-1}) \qquad \underline{Eq18}$$

where:

W_1 = Weight of dish (g)
W_2 = Weight of residue + dish after ignition in oven (g)
W_3 = Weight of residue + dish after ignition in furnace (g)

b) TSS and VSS measurement

The measurement procedure is exactly as above with the only difference that the sludge sample is first centrifuged to separate the soluble fraction (supernatant) from solids (particulate) fraction, and the above mentioned tests are applied on the solids fraction of sludge in order to calculate TSS and VSS.

The error of this measurement was around 5% for TSS and VSS and 5% to 7% for TS and VS analysis.

4.3.3 Proteins and carbohydrates

- **Proteins**

Proteins are large organic compounds made of amino acids arranged in a linear chain and joined together by peptide bonds between the carboxyl and amino groups of adjacent amino acid residues. The sequence of amino acids in a protein is defined by a gene and encoded in the genetic code.

A more sensitive method is measurement of protein with the Folin-Ciocalteau phenol (FCP) reagent (Lowry *et al.,* 1951). The first step is a burnt reaction where peptide bonds in protein react with copper in alkaline solution. The next step is a reduction of the active phosphomolybdic and phosphotungstic acids in the reagent by the copper treated protein. The colour developed is measured spectrophotometrically.

The principal disadvantage of the method of Lowry is the risk of interference from many substances. The Lowry method is slightly variable in sensitivity to various proteins but on average 27 different proteins resemble the colour developed by bovine serum albumin (Davis, 1988).

The choice of method for measuring protein in wastewater is not obvious, because none of the reviewed methods are ideal for this purpose. Considering the requirement for sensitivity and specificity for protein, the choice is between the methods of Lowry *et al.* (1951) and Bradford, (1976). According to variability in extinction between different proteins, the Lowry method seems to be much more accurate than the Bradford method (Kamma *et al.,* 1994).

Proteins were measured using the method proposed by Lowry method using BSA (Bovine Serum Albumin) as a standard protein and modified slightly by Kamma *et al.* (1994). Four reagents were prepared:

- Reagent A: 2% Na_2CO_3 in 0.1N NaOH
- Reagent B_1: 0.5% $CuSO_4 \cdot 5H_2O$
- Reagent B_2: 1% sodium tartrate double Na and K
- Reagent C: 48 mL Reagent A + 1mL Reagent B_1 + 1mL Reagent B_2
- Reagent E: 1N Folin Reagent

To start, 2.5 mL of Reagent C was added to 0.5 mL of sample, immediately mixed, and let stand for exactly 10 min at room temp. Reagent E was added (0.25 mL), the sample mixed, and incubated at room temperature for 30 min. Absorbance was measured at 650 nm, with UV – Visible spectrophotometer; model UV – 1700, Pharma-Spec, (SUIMADZU) and with bovine serum used as the standard. The measurement error is about 5 – 8% for the soluble proteins concentration and 10 to 15% for the total concentration of protein.

- **Carbohydrates**

Carbohydrates (from hydrates of carbon) or saccharides (Greek meaning "sugar") are simple organic compounds that are aldehydes or ketones with many hydroxyl groups added, usually one on each carbon atom that is not part of the aldehyde or ketone functional group.

The dominating carbohydrate sources in wastewater are starch- and dairy products, vegetables, fruit and cellulose having a monomeric composition of glucose, fructose and galactose which are all hexoses (Kamma *et al.,* 1994).

Carbohydrate concentrations were determined using the phenol sulphuric method introduced by Dubois *et al.,* (1956) and modified slightly by Kamma *et al.,* (1994). Carbohydrate concentration was calculated from a calibration curve constructed using a glucose standard. Four reagents were prepared:

- Sulfuric acid, reagent grade 95.5%.
- 5% Phenol solution in water.

To start, 0.5 mL of sugar solution is pipette into a colorimetric tube, and 0.5 mL of 5% phenol is added. Then 2.5 mL of concentrated sulphuric acid is added rapidly, the stream of acid being directed against the liquid surface rather than against the said of the test tube in order to obtain good mixing. The tubes are allowed to stand 5 minutes, and then they are shaken and placed for 5 to 10 minutes in a water bath at 25 to 30°C. Before readings are taken. The colour is stable for several hours and reading may be made later if necessary. The absorbance of the characteristic yellow-orange colour is measured at 490 nm with UV – Visible spectro-photometer; model UV – 1700, Pharma-Spec, (SHIMADZU). The amount of sugar may then be determined by reference standard curve. The measurement error is about 10 - 12% for the concentration of carbohydrates in the soluble phase and around 8 – 10% for total carbohydrates concentration.

4.3.4 Nitrogen and phosphorous

- **Nitrogen**

Nitrogen is recycled in nature almost exclusively by micro-organisms. Total nitrogen is comprised of organic nitrogen, ammonia, nitrite and nitrate. Organic nitrogen is determined by the kjeldahl method. The aqueous sample is first boiled to drive off the ammonia, and then it is digested. During the digestion, the organic nitrogen is converted to ammonia. Total Kjeldahl Nitrogen (TKN) is determined in the same manner as organic nitrogen, except that the ammonia is not driven off before the digestion step. Kjeldahl nitrogen is, therefore, the total of the organic and ammonia nitrogen. Ammonia nitrogen exists in aqueous solution as either the ammonium ion or ammonia, depending on the pH of the solution. Nitrite nitrogen, determined colorimetrically, is relatively unstable and is easily oxidized to the nitrate form. Nitrate nitrogen is the most highly oxidized from of nitrogen found in wastewater (Metcalf and Eddy, 1991).

The concentration of total nitrogen (N_T) was measured using total nitrogen persulfat reagent powder for digestion method and measured 410 nm wavelengths (HACH method 10072). The measurement error is about 10 - 13% for the concentration of nitrogen in the soluble phase and around 20% for total concentration of nitrogen.

- **Phosphorus**

Phosphorus is also essential to the growth of algae and other biological organisms. The usual forms of phosphorus found in aqueous solution include the orthophosphate, polyphosphate, and organic phosphate. Polyphosphates undergo hydrolysis in aqueous solution and revert to the orthophosphate forms; however, this hydrolysis is usually quite slow. The organically bound phosphorus is usually of minor importance in most domestic waste, but it can be important constituent of industrial waste and wastewater sledges.

Orthophosphate can be determined by directly adding a substance, such as ammonium molybdate, that will form a colored complex with the phosphate. The polyphosphates and organic phosphates must be converted to orthophosphates, using an acid digestion step, before they can be determined in a similar manner.

The measuring of total phosphorus (P_T) was carried out molybdovanadate method with acid persulfate digestion and reading at 420 nm wavelength with a DR/2010 spectrophotometer (HACH method 10127, Program No. 451, a total high range Phosphorus test N tube Reagent

set 0 to 100 mg.L^{-1} n$PO4^{3-}$). The measurement error was about 15 to 18% for P_S and P_T analysis.

4.3.5 Anions and cations

Anions and cations concentration (NO_2^-, NO_3^-, PO_4^{-3} and NH_4^+) were measured using an ion chromatograph (DIONEX, DE 120, USA) (arrangement detection threshold of apparatus). The error due to this measure was around 8 - 10%.

4.4 Biogas production

To improve biogas yield and methane content in anaerobic digestion of excess sludge from the wastewater treatment plant, the sludge was disintegrated by using various methods (sonication, ozonation and thermal pre-treatments).Gas form anaerobic digestion contains about 65 – 70 percent CH_4 by volume, 25 – 30 percent CO_2 and small amounts of N_2, H_2, H_2S, water vapour, and other gases. Digester gas has a specific gravity of approximately 0.86 relative to air (Metcalf and Eddy, 1991).

Methanogenic archaea produce biogas in anaerobic digestion of the sludge. Biogas can be utilized to produce heat and electricity or be upgraded to motor vehicle fuel. As the interest in and require of non-fossil fuels increase, ways to produce more biogas from the same amount of sludge become more attractive.

The produced biogas was collected in calibrated glass cylinders were filled with deionised water acidified with HCL (pH is about 2) to avoid the loss of CO_2 due to the fermentation of carbonate (see Figure 2-6).

4.4.1 Biogas composition

At this study, the biogas composition was determined by Acoustic Gas Measurement (AGM). Acoustic techniques for gas measurement are based on the principle that if energy is applied to a gas it will expend. Expansion causes an increase in pressure. The gases of major interest here are hydrocarbons, carbon dioxide and oxygen. Hydrocarbons and carbon dioxide readily absorb infra-red light, so this can be used as the applied energy source to give pressure fluctuations. Oxygen is not affected by infra-red light in the same way, but is highly susceptible to magnetic “energy”, so this is used to give pressure fluctuations. Monitoring system comprising a 1313 fermentation monitor and its associated PC software package BZ 6003 (INNOVA – Denmark).

The produced biogas consists of methane (CH_4) and carbon dioxide (CO_2), together with minor quantities of nitrogen, hydrogen, ammonia and hydrogen supplied (see Table 2-3). The measurement error is about 5%.

Table 2-3: Composition of biogas.

Biogas component	Volume of gas
CH_4	65 – 70 %
CO_2	25 – 30 %
N_2	< 1%
H_2	< 1%
NH_3	< 1%
H_2S	< 1%

5. Experiments Performance

Table 2-4 presents different types of tests carried out on concentrated sludge for each series treatments at bench scale and pilot plant.

Several measurements were made on samples. Biochemical oxygen demand (BOD), Chemical oxygen demand (COD), mineral and organic matter (TS, VS, TSS, VSS), nitrogen (N), phosphorus (P), protein (P), carbohydrate(C) and anions (NO_2^-, NO_3^- PO_4^{-3}) & cations (NH_4^+) were measured before and after sonication, ozonation and thermal pre-treatment (total and soluble).

Table 2-4: Analysis and tests carried out on concentrated sludge.

Scale	Series	Type of pre-treatment	Apparatus used	Range of pre-treatment	Sludge concentration
Bench scale	Series A	Sonication	Ultrasound	1) P= 50 (W) t = 2, 20, 40, 80 (min) SE = 5000, 50000, 100000, 200000 (kj/kg-TSS)	TS = 13.7 (g/l) VS = 10.42 (g/l) TSS = 12.17 (g/l) VSS/TSS = 78.88%
				2) P = 100 (W) t = 1, 10, 20, 40 (min) SE = 5000, 50000, 100000, 200000 (kj/kg-TSS)	
				3) P = 200 (W) t = 0.5, 5, 10, 20 (min) SE = 5000, 50000, 100000, 200000 (kj/kg-TSS)	
	Series B	Thermal	Autoclave	P = 1.5 (atm) T = 121°C, t = 15 (min)	TS = 13 (g/l) VS = 9.19 (g/l) TSS = 12.68 (g/l) VSS/TSS = 71.06%
			Bain-Marie	T =40, 60, 90°C t = 10, 20, 40, 60, 120, 480 (min)	
	Series C	Ozonation	Ozone generator	P = 180 (W) T = 15, 30, 60, 90, 120 (min), M O_3 = 0.101 (g O_3/g-TSS)	TS = 12.36 (g/l) VS = 8.78 (g/l) TSS = 12.23 (g/l) VSS/TSS = 72.12%
Pilot plant Aerobic , Anaerobic	Series D	Pilot Phase (1)	Control (1)	Condition STP	TS = 12 (g/l) VS = 8.62 (g/l) TSS = 11.66 (g/l) VSS/TSS = 80.02%
			Ultrasound	SE = 200000 (kj/kg-TSS), P =50 (Watt)	
			Thermal (90)	T = 90°C, t = 60 (min)	
			Autoclave	T = 121°C, t = 15 (min), P = 1.5 (atm)	
	Series E	Pilot Phase (2)	Control (2)	Condition STP	TS = 21.6 (g/l) VS = 16 (g/l) TSS = 20.00 (g/l) VSS/TSS = 77.50%
			Thermal (40)	T = 40°C, t = 60 (min)	
			Thermal (60)	T = 60°C, t = 60 (min)	
			Ozone	P = 180 (W), t = 60 (min), M O_3 = 0.101 (g O_3/g -TSS)	

Chapter 3

Study of sludge pre-treatment and aerobic/anaerobic biological treatment

Chapter 3: Study of sludge pre-treatment and aerobic/anaerobic biological treatment

Introduction

Municipal wastewater sludge, particularly waste activated sludge (WAS), is difficult to digest due to a rate limiting cell lysis step (hydrolysis). The cell wall and the membrane of prokaryotes are composed of complex organic materials such as peptidoglycan, teichoic acids, and complex polysaccharides, which are not readily biodegradable. Moreover, the bacterial floc is composed by exopolymers such as polysaccharides and proteins, which are also resistant to biodegradation by bacteria. Mechanical (particularly ultrasonic), chemical (particularly ozonation) and physical (particularly thermal) pre-treatments, are emerging as popular method for WAS disintegration. The exposure of the microbial cells to provided energy breaks the cell wall and membrane and releases the extra or/and intracellular organics in the bulk solution, which enhances the overall digestibility. This chapter summarizes the major findings of pre-treatment application in WAS disintegration, and elucidates the impacts of mechanical, chemical and physical pre-treatment on both sludge solubilization.

In this chapter we are going to study the results from three types of sludge treatment aiming to cellular sludge disintegration.

The methods used here for cellular sludge decomposition and disintegration are:

- Sonication
- Ozonation
- Thermal treatment

The objective of this study was to determine optimal treatment conditions for each technique and to understand waste activated sludge modification due to a pre-treatment process.

The feature of this work was to carry out the comparison of the three pre-treatments in the same conditions and on the same kind of sludge (see Table 3-1). Different parameters were used to assess sludge solubilization due the pre-treatment:

- Matter solubilization,
- Global nitrogen solubilization,
- Global phosphorus solubilization,
- Protein and carbohydrate solubilization,
- COD solubilization and disintegration degree.

The optimum parameters will be determined for each treatment technique using bench scale studies. The method consists of performing each treatment using different parameters:

- Input power and specific energy for sonication technique,
- Duration and dosage for ozonation treatment,
- Time and temperature for thermal treatment.

The final objective is to choose the set of parameters which leads to the highest rate of sludge lyse and solubilization which is determined by COD, BOD, N, P, TSS, VSS, glucose, and protein. The selected set of parameters will be used later, in the following chapter, in the aerobic and anaerobic digestion reactors.

Part 1

Solubilization

Determination of optimal pre-treatment for each technique

1. Study of ultrasound pre-treatment on sludge

Since its development sono-chemistry revealed a new and very promising technique for energy introduction. Possible applications of ultrasound have increased both in number and diversity. This technique can be applied in the treatment of industrial and domestic wastewater with encouraging results.

According to the literature, ultrasonic treatment can:

- Reduce the particle size (Kopp *et al.,* 1997)
- Break sludge flocs and break cells (Bougrier *et al.,* 2005)
- Solubilise materials (mineral and organic) (Gonze *et al.,* 2003)
- Release the material intra-cellular and/or extra-cellular (Lehne *et al.,* 2001)
- Improve the degradation of organic matters (Van Lier *et al.,* 2001)
- Reduce retention time in the digester (Nah *et al.,* 2000)
- Increase biogas production (Tiehm *et al.,* 2001-a)

Ultrasounds significantly alter the characteristics of the flocs (size, surface area, shape, density, water content, porosity, charge, etc.), and are therefore liable to modify their settling and filtration properties (Gonze *et al.,* 2003).

Two main parameters affect the process of sonication: provided energy (applied power and exposure duration), and the frequency of ultrasound. The rate of disintegration increases with the amount of applied energy (Müller *et al.,* 1998). At the same time, it has been proved that the degradation of excess sludge is more efficient using low frequencies (Tiehm *et al.,* 2001-b), thus it is preferable to work with low frequencies (Tiehm, 2001 and Bougrier, 2005) to improve degradation of sludge.

The objective of this study is to quantify and understand the changes related to ultrasonic pre-treatment, and to measure its effects on the sludge solubilization and subsequently the potential ability to improve aerobic and anaerobic digestion.

Three power supplied values: (50W, 100W, and 200W) and four specific energies: (5000, 50000, 100000, 200000 kJ.kg-TSS^{-1}) were investigated. Acoustic density of ultrasound in these tests was maintained between 0.5W.mL^{-1} and 2W.mL^{-1}. The main parameters of sonication treatment are reported in Table 3-1.

Sludge samples were collected on the recycle sludge line. Sludge concentration was initially measured between 3.5 and 5g.L^{-1} (Average 4.65g.L^{-1}). After being concentrated in the laboratory, this parameter (TS) increased to 13.7 L.g^{-1} (VS = %76 TS). During the tests, sample temperature was kept below 20°C using ice cubes.

Table 3-1: Different conditions of ultrasound pre-treatment.

Samples	SE (kJ/kg-TSS)	Power (W)	Time (min)	Power density (W/ml)
S_1	5000	50	2	0.5
S_2	50000	50	20	0.5
S_3	100000	50	40	0.5
S_4	200000	50	80	0.5
S_5	5000	100	1	1
S_6	50000	100	10	1
S_7	100000	100	20	1
S_8	200000	100	40	1
S_9	5000	200	0,5	2
S_{10}	50000	200	5	2
S_{11}	100000	200	10	2
S_{12}	200000	200	20	2

1.1 Effect of ultrasound on pH of sludge

Sonicated samples as well as the control sample were analyzed according to Table 3-2. Ultrasonic pre-treatment modified the physicochemical characteristics of sludge. For instance, pH decreases slightly (from 7.62 to 7.22 pH units) during the sonication. In Zhant *et al.* (2007) studies pH of the sludge decreased by less than 0.5 in all sonication experiments and was not adjusted. The cause of pH decrease during the sonication can be considered to be fat destruction and thus production of volatile organic acids.

1.2 Effect of ultrasound on the COD and BOD_5

By applying mechanical disruption, the break-up of flocs and cells occurs in minutes instead of days. The intracellular components are set free and are immediately available to biological degradation, which leads to an acceleration of the process. Facultative, aerobic and anaerobic

micro-organisms are disrupted as well and become degradable, thus resulting in a higher solubilization and degree of degradation. Similar investigations were carried out by several researchers (Tiehm *et al.*, 1997; Dohanyos *et al.*, 1997; Baier *et al.*, 1997; Choi *et al.*, 1997).

Table 3-2: physicochemical properties of the studied sludge.

Samples	SE (kJ/kg-TSS)	pH
S_1	5000	7.38
S_2	50000	7.51
S_3	100000	7.49
S_4	200000	7.22
S_5	5000	7.48
S_6	50000	7.33
S_7	100000	7.35
S_8	200000	7.46
S_9	5000	7.6
S_{10}	50000	7.56
S_{11}	100000	7.45
S_{12}	200000	7.35
Blanc	0.0	7.62

The use of ultrasound leads to a solubilization of the COD (Lehne, *et al.,* 2001), and solubilization rate increases with provided energy. Organic matter solubilization can be evaluated by the measurement of:

- Disintegration degree, (Equation 4, chapter 2)
- COD Solubilization, (Equation 5, chapter 2)
- BOD_5 Solubilization, (Equation 5, chapter 2)

1.2.1 Results of COD and BOD_5 Solubilization

Chemical oxygen demand (COD) measurement allows pollution concentration to be expressed as the amount of oxygen consumed to oxidize matter. For each experiment, while the energy input increased, total COD (COD_T) remained almost constant, but the soluble and particulate COD repartition varied. Soluble COD (CODs) increased with specific energy whereas particulate COD ($COD_P = COD_T - CODs$) decreased (Table 3-3). This phenomenon is observed for intensities of 50W, 100W and 200W. Cells and flocs underwent lysis and organic compounds were released into the liquid phase. The increase in COD_S may result from the

destruction of flocs structure after ultrasonic pre-treatment, promoting the release of colloidal and soluble organics into the solution.

The COD_S/COD_T ratios were measured to evaluate the release of soluble organics from the sludge flocs during ultrasonic pre-treatment. The COD_S/COD_T ratios after ultrasonic pre-treatment were greatly improved (from 1.51% to 18.93%), suggesting that a large amount of insoluble organics of sludge flocs were transferred into soluble organics (see Table 3-3).

Table 3-3: Concentration of COD and BOD in the sludge.

Sampels	SE (kJ/kg-TSS)	COD_T ($mgO_2.L^{-1}$)	COD_S ($mgO_2.L^{-1}$)	BOD_5 ($mgO_2.L^{-1}$)	COD_S/COD_T (%)
S_1	5000	15300 ± 3060	990 ± 210	450 ± 123	6.47
S_2	50000	14990 ± 2998	1780 ± 377	695 ± 191	11.87
S_3	100000	14570 ± 2914	2140 ± 453	710 ± 195	14.58
S_4	200000	13810 ± 2762	2614 ± 554	750 ± 206	18.93
S_5	5000	16350 ± 3270	1010 ± 214	500 ± 137	6.18
S_6	50000	15740 ± 3148	1920 ± 407	885 ± 243	12.2
S_7	100000	15200 ± 3040	2454 ± 520	935 ± 257	16.14
S_8	200000	15000 ± 3000	2712 ± 575	850 ± 233	18.08
S_9	5000	16480 ± 3296	1050 ± 222	600 ± 165	6.37
S_{10}	50000	16440 ± 3288	2100 ± 445	1070 ± 294	12.77
S_{11}	100000	16200 ± 3240	2590 ± 549	1165 ± 320	15.99
S_{12}	200000	15900 ± 3180	2748 ± 582	1170 ± 320	17.28
Control	0	19650 ± 3930	297 ± 63	250 ± 68	1.51

In fact COD_S/COD_T increases with specific energy. This increase is all the same for three intensities (50, 100, and 200 W). It means that the highest COD solubilization occurred at SE = 200000 kJ.kg-TSS^{-1}. This increase is slightly more significant when the applied power is 50 W (18.93, 18.08, and 17.28 for 50, 100, and 200 Watts of power respectively) and energy of 200000 kJ.kg-TSS^{-1}, (according to Table 3-3). The respective impact of input power and specific energy were studied in the following paragraph.

1.2.1.1 Impact of input power

- **COD solubilization**

COD solubilization is a common parameter used to evaluate the release of organic matter due to ultrasonic treatment. In this part, the effect of impact of input power was investigated.

COD solubilization was plotted against specific energy for different power inputs (Figure 3-1). The COD solubilization for intensities of 50, 100, and 200 Watts are nearly the same (11.97%, 12.48%, and 12.66% respectively). Thus for a specific energy of 200000 kJ.kg-TSS^{-1}, the power input does not significantly change the COD solubilization rate.

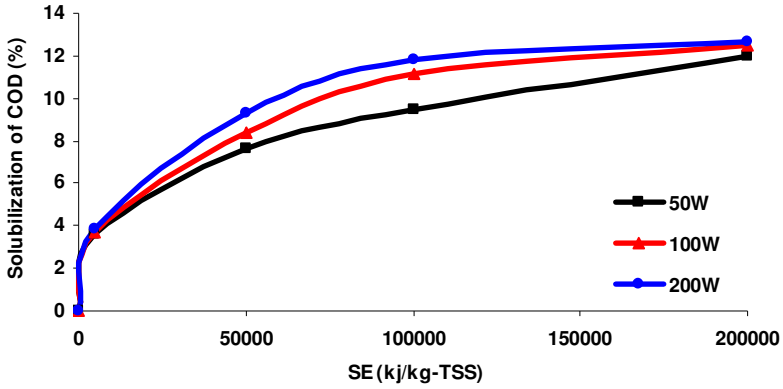

Figure 3-1: Solubilization of COD vs. specific energy.

In fact, the term "solubilization" represents the transfer (of COD or solids) from the particulate fraction of the sludge (solids after centrifugation) to the soluble fraction of the sludge (supernatant after centrifugation). COD solubilization increased linearly with increasing specific energy. The maximal percentage of COD solubilization was less than 15% for a specific energy from 50000 kJ.kg-TSS^{-1} to 200000 kJ.kg-TSS^{-1}. This result was lower than the results of Bougrier et al. (2005) (35 %) for a lower specific energy (14550 kJ.kg-TS^{-1}) obtained in conditions of similar TS concentration and operating frequency but with a more important supplied power (225W). This point could be a decisive parameter of COD solubilization in accordance with the fact that high ultrasound power together with short treatment time was more efficient than low ultrasound power with long treatment time (Grönroos *et al.,* 2005).

If the COD solubilization calculation permits the evaluation of the effectiveness of an ultrasonic treatment (Khanal et al., 2007), the disintegration degree permits to reach the maximum level of sludge solubilization.

- **Disintegration degree**

Kunz and Wagner, (1994) first proposed to use a parameter known as "degree of disintegration (DD)" to quantify the sludge disintegration efficiency (Schmitz *et al.,* 2000). The determination of DD is primarily based on measurement of COD as the comparison between ultrasonic

process and a maximum soluble chemical demand COD_{NaOH} obtained by alkaline hydrolysis. (For DD_{COD} calculation, cf. chapter 2)

Due to the high concentrations of micro-organisms sonication of waste activated sludge results in higher degrees of disintegration as compared to treatment of raw and digested sewage sludge. Therefore the most effective solubilization for a given specific energy input is obtained by treating thickened waste activated sludge.

As it can be seen in Figure 3-2 for high (200000 kJ.kg-TSS^{-1}) and low (5000 kJ.kg-TSS^{-1}) SE, increasing input power intensity does not significantly affect DD_{COD} rate. For instance, at 200000 kJ.kg-TSS^{-1}, increasing power from 50W to 200W leads to a slight 2% increase in DD_{COD} (35.85% for 50W, 37.92% for 200W). For medium SE (50000 and 100000), the DD_{COD} is influenced by the input power: high input power (200W) led to higher DD_{COD}.

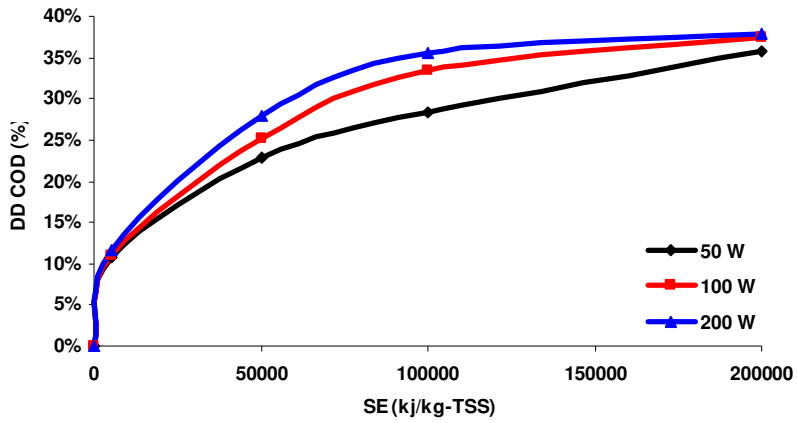

Figure 3-2: Degree of disintegration of COD (DD_{COD}) in terms of the ultrasonic specific energy.

The results at high SE (200000) are in accordance with literature: as a result applying a low power during a long time leads to the same results as applying a high intensity during a short period of time. However according to Neis and Tiehm the former choice has the advantage of decreased growth of filament microorganisms (Dewil *et al.,* 2006).

1.2.1.2 Impact of specific energy

- **COD solubilization**

The impact of specific energy on COD Solubilization was studied (Figure 3-3). COD solubilization was plotted against input power. The highest solubilization rate can be observed at SE of 200000 kJ.kg-TSS^{-1}. It attains from 3-4% for 5000 kJ.kg-$TSS^{-1}$to 12-13% for 200000 kJ.kg-TSS^{-1}. For a given input power, the specific energy seriously affects COD solubilization.

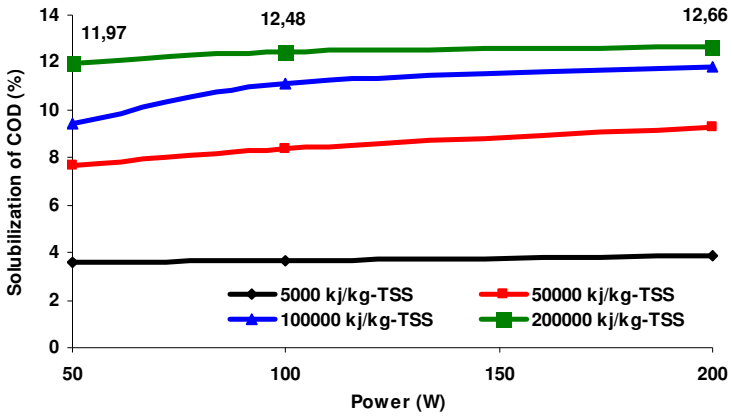

Figure 3-3: Solubilization of COD vs. power.

❁ Disintegration degree

The impact of specific energy on DD_{COD} was also investigated. Figure 3-4 depicts DD_{COD}. As we can see, the highest disintegration rate corresponds to SE of 200000 kJ.kg-TSS^{-1} (36% for 50W, 37% for 100W, and 38% for 200W of power).

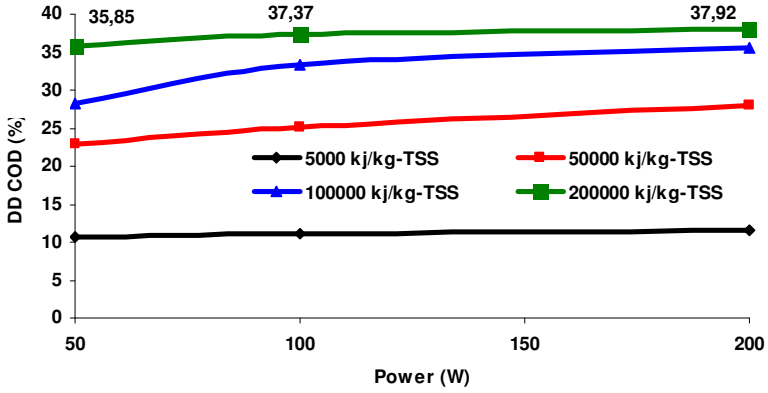

Figure 3-4: Degree of disintegration of COD in terms of power of ultrasound.

In this study for all powers (50, 100 and 200W), prolonging sonication time and consequently increasing specific energy leads to an increase in sludge disintegration efficiency.

Although obtaining the highest DD_{COD}, S_{COD} and COD_S release is the major goal of ultrasonic pre-treatment, the DD_{COD} and S_{COD} must also be correlated with ultrasonic energy input (expressed as ultrasonic density, ultrasonic intensity or specific energy input). Such correlations will help to optimize the energy needs to achieve maximum sludge disintegration.

This study suggests that S_{COD} and DD_{COD} increase linearly with specific energy. It is also revealed that input power intensity has not a significant effect on the solubilization rate and

DD_{COD}. Thus the main parameter for increasing soluble COD, S_{COD} and DD_{COD} in the sonication pretreatment is the applied specific energy.

1.2.1.3 Potential biodegradability of the solubilized COD (BOD_5/COD_s)

The potential biodegradability of solubilized COD was calculated (Table 3-3). For a given input power, BOD_5 increases with specific energy up to a certain limit. However biodegradability (BOD_5/COD_S) does not increase due to specific energy augmentation. On the other hand, by increasing input power for a given specific energy biodegradability increases, and the highest biodegradability occurs at 200W of input power (c.f Table 3-4).

Table 3-4: BOD_5/COD_S ratio and efficiency in terms of power and duration of ultrasonication.

Sampels	Power (w)	Time (min)	SE (kJ/kg-TSS)	BOD_5/COD_s (%)
S_1	50	2	5000	45.45
S_2	50	20	50000	39.04
S_3	50	40	100000	33.43
S_4	50	80	200000	28.69
S_5	100	1	5000	49.50
S_6	100	10	50000	46.09
S_7	100	20	100000	38.10
S_8	100	40	200000	31.34
S_9	200	0.5	5000	57.14
S_{10}	200	5	50000	50.95
S_{11}	200	10	100000	44.98
S_{12}	200	20	200000	42.58

The biodegradability does not increase with specific energy but does increase with power. Figure 3-5 shows the BOD_5 concentration versus specific energy from 0 to 200000 kJ.kg-TSS^{-1} for input powers of 50, 100, and 200W. We can see that the highest BOD_5 concentration corresponds to 200W of input power. We can see that the amount of BOD_5 at 200W does not vary dramatically with specific energy (from 1070 mg.L^{-1} for 5000 kJ.kg-TSS^{-1} to 1170 mg.L^{-1} for 200000 kJ.kg-TSS^{-1}). Input power is the determining factor in the BOD_5 solubilization.

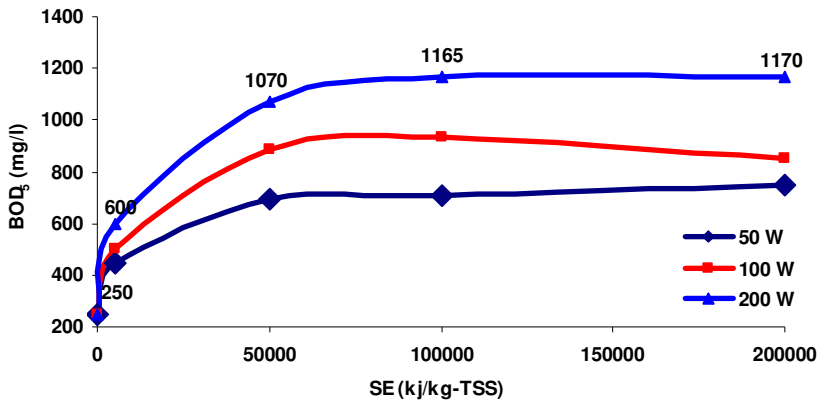

Figure 3-5: Concentration of BOD_5 in terms of the ultrasonic specific energy.

1.2.2 Discussion

A numbers of studies evaluated DD_{COD} and S_{COD} at different specific energy inputs and ultrasonic densities.

All earlier studies examined the degree of disintegration by COD_S release. Schmitz *et al.* (2000) argued that the degree of disintegration in terms of COD_S release (DD_{COD}) is rather slow in the range of a day and is also expensive due to the need of large numbers of COD sample analyses. Other authors therefore proposed protein measurement as an alternative to DD_{COD} determination.

In this study increasing the specific energy led to an increase in COD_S/COD_T, S_{COD}, and DD_{COD}. The highest degree of solubilization and disintegration occurred at the specific energy of 200000 kJ.kg-TSS^{-1} (COD_S/COD_T=18.93%, S_{COD}=11.97% and DD_{COD}=35.85% for 200000 kJ.kg-TSS^{-1} and 50W power). The significant increase of the DD_{COD} was attributed to the breakup of microbial cells. These results comply more or less with studies of Müller (2001, 2000-b), Lehne (2001), Gonze *et al.* (2003), Bougrier (2005), and khanal *et al.* (2007). In all cases, the solubilization rate and degree of disintegration increases with specific energy.

Although the degree of disintegration and solubilization improved with increase in specific energy input, the improvement was not in direct proportion to the energy input. For example, Khanal *et al.* (2006) obtained COD_S/COD_T of 16.2% at an energy input of 66800 kJ.kg-TS^{-1}, whereas Bougrier *et al.* (2005) achieved two times as much at an energy input of only 6951 kJ.kg-TS^{-1}. In another study, DD_{COD} of 40% was obtained at a specific energy input of 60000 kJ.kg-TS^{-1} (Tiehm *et al.,* 2001-b), while Rai *et al.* (2004) reported DD_{COD} of 25% at energy input of 64,000 kJ.kg-TS^{-1}. The DD_{COD} is an important parameter of ultrasonic performances assessment.

Such variations are most likely attributed to energy transfer efficiencies of ultrasonic units. Many of the sludge disintegration were conducted at frequencies of 20 to 40 kHz with 20 kHz being optimal for cavitation. The difference between these studies is that each one uses a different intensity and frequency of ultrasound and sludge concentration.

In this study the sludge concentration (total solids) was 13.7 $g.L^{-1}$, while Gonze *et al.* (2003) used a concentration of 3 $g.L^{-1}$ and Müller (2001, 2000-b) used a concentration of 31 $g.L^{-1}$. It seems that sludge disintegration increases with the increase of the sludge concentration.

The determining parameter for increasing COD solubilization is specific energy and input power has not a significant effect. As a result, we can apply a low power during a long duration to attain desired specific energy. This will lead to a better efficiency because at short ultrasound application times, sludge floc agglomerates are dispersed while no cell destruction occurs. At longer treatment times or higher ultrasound intensities, the microbial cell walls are broken and intracellular material is released to the liquid phase (Tiehm *et al.,* 2001-b).

The intercellular matrix ensuring the cohesion of the flocs comprises a large number of compounds including proteins, carbohydrates, nucleic acids, lipids, and humic products (Frolund *et al*., 1996). During the disruption of the flocs and cells, highly biodegradable organic matter is released and solubilized.

As to the variation of BOD_5, it was concluded that a part of organics released from cell walls was biodegradable. As a result, BOD_5 increases with specific energy and power density. The input power is the determining parameter of BOD_5 solubilization. By increasing sonication time (for a given specific energy), COD_S increased but BOD_5/COD_S decreased (for ES=200000 kJ.kg-TSS^{-1}, 42.58% and 28.69% for 20 and 80 minutes respectively).

1.3 Effect of ultrasound on the matter

1.3.1 Results of matter solubilization

Pre-treatments led to a modification of the repartition of the solids. For all treatments, total solids (TS) concentration is almost constant. Sonication pre-treatment did not lead to a mineralization phenomenon but just to solubilization. According to Bougrier *et al.* (2006) the solubilization is particularly high for organic matter and low for mineral matter.

Organic solids were highly affected by treatment. For ES = 200000 kJ.kg-TSS^{-1}, volatile suspended solids (VSS) concentration in particles decreased from 9.6 $g.L^{-1}$ in raw sludge to

5.21 $g.L^{-1}$, 3.99 $g.L^{-1}$, and 2.03 $g.L^{-1}$ for sludge treated with ultrasounds at 200W, 100W, and 50W respectively.

TSS/TS ratio will decrease during treatments and the more SE augments, the more this ratio will decrease. In our study, as shown in Table 3-5, TSS/TS ratio was 88.83% for untreated sludge. This ratio is strongly reduced in the case of treated sludge (24.16%). In fact, solids content in particulate fraction decreased with increasing supplied specific energy.

Table 3-5: Ratio of TSS/TS and VSS/TSS for different specific energies.

Sampels	SE (kJ/kg-TSS)	TSS (g/l)	VSS (g /l)	S_{TSS} (%)	S_{VSS} (%)	TSS/TS (%)	VSS/TSS (%)
S_1	5000	10.9	8.37	10,44	12,81	79,56	76,79
S_2	50000	8.02	5.87	34,10	38,85	58,54	73,19
S_3	100000	5.82	4.05	42,18	57,81	42,48	69,59
S_4	200000	3.31	2.03	72,80	78,85	24,16	61,33
S_5	5000	11.5	8.86	5,51	7,71	83,94	77,04
S_6	50000	10.32	7.76	15,20	19,17	75,33	75,19
S_7	100000	9.12	6.66	25,06	30,63	66,57	73,03
S_8	200000	5.94	3.99	51,19	58,44	43,36	67,17
S_9	5000	12.96	10.05	0,58	2,29	88,32	77,52
S_{10}	50000	11.2	8.46	7,97	11,88	81,75	75,54
S_{11}	100000	9.73	7.1	20,05	26,04	71,02	72,97
S_{12}	200000	7.49	5.21	38,46	45,73	54,67	69,56
Control	0	12.17	8.37	-	-	88,83	78,88

Also VSS/TSS ratio decreases from 78.88% for raw sludge to 61.33% for sludge sample sonicated with SE = 200000 kJ.kg-TSS^{-1} and intensity of 50W. This shows that the highest matter solubilization rate occurs at specific energy of 200000 kJ.kg-TSS^{-1} and power of 50W. At the same time, organic matter solubilization takes place at higher rates compared to mineral matter solubilization. That is to say, the intensity of ultrasound affects obviously the effect of sludge mass reduction.

1.3.1.1 Impact of input power

At this stage of the research the impact of input power on matter solubilization was investigated. Figure 3-6 shows TSS solubilization versus specific energy for three different power inputs (50, 100 and 200W). As it can be seen in this figure, TSS solubilization rate increases with specific energy. This raise is much more significant for the case of 50 Watts of power and 80 minutes of applying time (achieving 72.80%) than those of 100W (during 40

minutes) and 200W (during 20 minutes). Thus the best results for TSS solubilization happens at SE of 200000 kJ.kg-TSS^{-1} and power of 50W. In other words, to increase matter solubilization for a given energy, power has a significant effect, and it is preferable to increase sonication time and decrease the applied power density (see Figure 3-6).

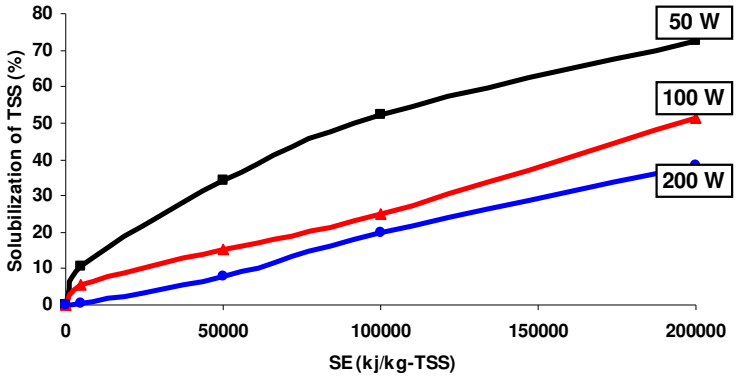

Figure 3-6: Solubilization of TSS in terms of specific energy.

1.3.1.2 Impact of specific energy

The impact of specific energy on TSS solubilization was also investigated. Figure 3-7 depicts TSS solubilization rate in terms of power. It can be observed that the highest solubilization rate corresponds to SE of 200000 kJ.kg-TSS^{-1} and power density of 50W. In other words, the matter solubilization for a given intensity is directly proportional to specific energy input. Considering the fact that a raise in solubilization is equivalent to sludge mass reduction, in this study, sludge mass (as TSS) decreases from 12.17g.L^{-1} for untreated sludge to 3.31g.L^{-1} for pre-treated sludge (72.80% sludge elimination efficiency). For a same input power, specific energy positively influence matter solubilization and thus sludge reduction.

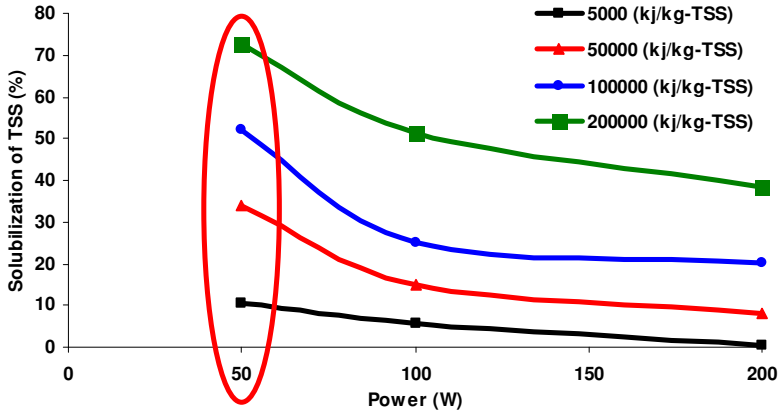

Figure 3-7: TSS Solubilization versus power.

1.3.2 Discussion

Low intensity ultrasounds enhance the sludge disintegration efficiency in terms of organic matter solubilization. The acoustic density, irradiation time, and input energy affect the sludge solubilization and digestion significantly (Ding *et al.,* 2006)

The mechanism of ultrasound treatment is that the ultrasound irradiation can increase the activity of the enzymes, accelerate cell hydrolysis, enhance the microorganism metabolism, accelerate disintegration of sludge floc and intensify liquid solid mass transfer and accelerates organic substance degradation (Chu *et al.,* 2001).

Bougrier reported that ultrasound led to a solubilization phenomenon of organic solids but also of mineral solids. Solubilization of mineral matter was very low (less than 3%) whereas organic solubilization was quite high (29%) for a specific energy of 15,000 kJ.kg-TS^{-1}. In fact, total solid solubilization (S_{TS}) increased with energy input (Bougrier *et al.,* 2005).

This study confirms that using low power intensities (50W) and high specific energies (200000 kJ.kg-TSS^{-1}) leads to higher solubilization rates. Experiments (Table 3-5) showed that the highest TSS and VSS solubilization rates occur at the energy of 200000 kJ.kg-TSS^{-1} and input power of 50W (72.8% and 78.85% respectively). Low intensity ultrasound can not break up the cell walls but accelerates the cell hydrolysis and also accelerates the mass transfer between solid and liquid. However, if the irradiation time is long, it will break up the cell walls (Li Hui, 1994; Chu *et al.,* 2001) and will result in a more efficient disintegration of sludge flocs and thus increases TSS solubilization.

By analysis of test data, it can be deduced that the decrease of TSS was mainly due to the decrease of VSS, because the decreased VSS accounted for main part of the lost TSS, and VSS was a part of TSS. Therefore, the ratio of VSS/TSS reduced with the prolongation of sonication time.

1.4 Effect of ultrasound on the nitrogen and phosphorus

1.4.1 Results of nitrogen and phosphorus solubilization

Sludge sonication increased the contents of nitrogen and phosphorus in the solution phase, and part of the organic nitrogen and phosphorus released from the cells could be disintegrated to inorganic nitrogen and phosphorus.

The total nitrogen comprises of organic and mineral nitrogen. That is to say, that the total nitrogen is equivalent to: $N_T = NO_2^- + NO_3^- + NH_4^+$-N + N-org.

The disintegration as a pre-treatment method for the stabilization or the de-nitrification aims solubility of a high amount of organic components of the sludge solids. The concentrations presented in Table 3-6 illustrate that the dissolved nitrogen and phosphorous are increased noticeably through ultrasonic treatment. The high concentrations of dissolved organic components in the sludge water are important for a cost efficient recycling of these valuable components.

Total nitrogen (N_T) was mostly constant for all specific energies. It means that ultrasound does not lead to nitrogen mineralization. This phenomenon is different in the case of phosphorus.

Sonication leads to nitrogen and phosphorus solubilization. Nitrogen solubilization rate is higher than phosphorus solubilization. For example N_S/N_T varies from 9.94% for untreated sludge to 53.76% for treated sludge while P_S/P_T varies from 31.4% to 48.1% (Table 3-6).

The main kinds of phosphorus existing in wastewater are salts of orthophosphoric acid, poly-phosphates and organic phosphorus. In urban wastewater, in general, all kinds of phosphorus are present, while, after a biological treatment, there are generally only orthophosphates.

Table 3-6: Concentrations of nitrogen and phosphorus in the excess sludge.

Samples	SE (kJ/kg-TSS)	N_T (mg/l)	N_S (mg/l)	P_T (mg/l)	P_S (mg/l)	N_S/N_T (%)	P_S/P_T (%)
S_1	5000	800	110	660	238	13.75	36.06
S_2	50000	810	220	962	422	27.16	43.87
S_3	100000	860	340	984	436	39.53	44.31
S_4	200000	930	500	1052	506	53.76	48.1
S_5	5000	820	120	920	290	14.63	31.52
S_6	50000	880	240	1018	402	27.27	39.49
S_7	100000	920	390	1086	502	42.39	46.2
S_8	200000	950	510	1154	522	53.68	45.23
S_9	5000	890	150	1014	326	16.85	32.15
S_{10}	50000	900	270	1060	404	30	38.11
S_{11}	100000	940	400	1166	498	42.55	42.71
S_{12}	200000	960	550	1184	542	57.29	45.78
Control	0	825	82	691	217	9.94	31.4

1.4.1.1 Impact of input power

❁ Nitrogen

The elements nitrogen and phosphorus are essential to the growth of protista and plants and as such are known as nutrients or bio-stimulants. Nitrogen in untreated wastewater is principally in the form of ammonia or organic nitrogen, both soluble and particulate. Soluble organic nitrogen is mainly in the form of urea and amino acids. Untreated wastewater usually contains little or no nitrite or nitrate.

Cell walls and flocs were broken due to ultrasound. Intracellular compounds were released into the liquid phase and were solubilized. Thus ultrasounds led to a nitrogen release.

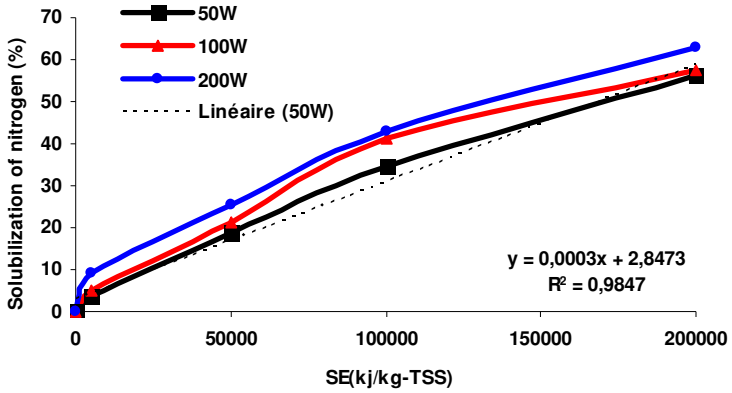

Figure 3-8: Nitrogen solubilization at different ultrasonic intensity and density.

As we can see in Figure 3-8, for a given energy solubilization rate is almost the same for 50, 100 and 200W of input power. Thus nitrogen solubilization is not seriously affected by input power. For example, for the constant specific energy of 200000 kJ.kg-TSS^{-1}, the nitrogen solubilization at 50W of power is 56.26%. This rate attains 62.99% at 200W (only 6.73% increase). However, given a power of 200W, with the specific energy increasing from 5000 to 200000 kJ.kg-TSS^{-1}, the solubilization rate increases from 9.15% to 62.99% showing a 53.84% raise. For all input powers, nitrogen solubilization increased linearly with increasing specific energy.

❁ Phosphorus

Phosphorus exists in different forms, such as dissolved organic phosphate, dissolved inorganic orthophosphate, dissolved inorganic polyphosphate and non-dissolved (particulate) phosphorus. Two types of soluble inorganic phosphates are orthophosphate and polyphosphate. Orthophosphate takes the form of PO_4^{3-}, H PO_4^{2-}, $H_2PO_4^{1-}$ or H_3PO_4, depending on pH value.

Polyphosphates undergo hydrolysis in aqueous solution and revert to the orthophosphate forms; however, this hydrolysis process is usually quite slow. The amount of polyphosphates is obtained by difference as follows (Figure 3-9):

Total inorganic phosphate – orthophosphate = polyphosphate

The amount of organic phosphorus present in industrial wastes or in sludge is sometimes of interest. All forms of phosphorus (total) are measured in an organic phosphorus determination (Sawyer *et al.,* 2002) Therefore, the organic phosphorus is obtained as follows:

Total phosphorus – inorganic phosphorus = organic phosphorus

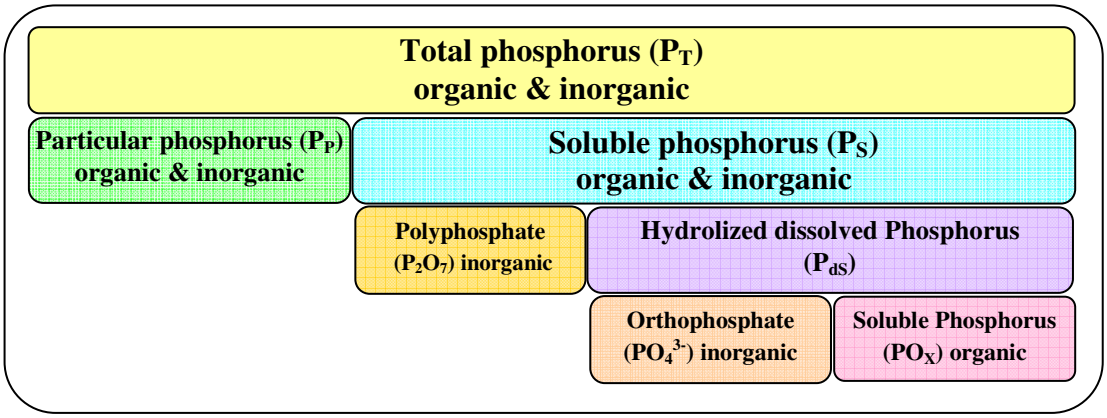

Figure 3-9: Different forms of phosphorus in wastewater

Sonication results in cellular disintegration and thus increases soluble phosphorus concentration (in form of orthophosphates) in supernatants.

Due to the better solubilization of disintegrated WAS, the concentration of phosphorus in the sludge supernatants was higher compared to the control sample. There was no direct correlation of the increased phosphorus concentrations to the volatile solids degradation since the concentration of dissolved phosphorus is strongly affected by precipitation processes like the formation of calcium phosphates.

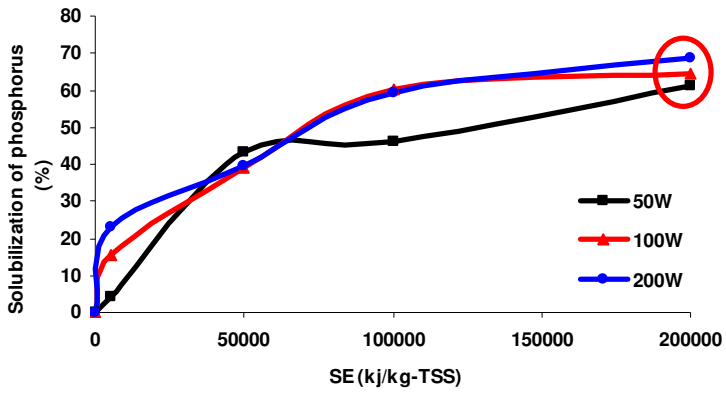

Figure 3-10: Phosphorus Solubilization versus specific energy.

As we can see in Figure 3-10, for a given specific energy there is no significant difference for different power input. For instance for a specific energy of 200000 kJ.kg-TSS^{-1}, increasing power from 50W to 200W, leads to an increase of phosphorus solubilization from 60.99% to 68.57%. Thus input power did not noticeably alter phosphorus solubilization rate. For specific energy lower then 100000 kJ.kg-TSS^{-1}, phosphorus solubilization increased quite linearly with increasing specific energy. For specific energies higher than 100000 kJ.kg-TSS^{-1}, phosphorus solubilization remained constant.

1.4.1.2 Impact of specific energy

- **Nitrogen**

Nitrogen solubilization increases linearly with SE (R^2 = 0.9847). For instance nitrogen solubilization increases from 3-9% for SE = 5000 kJ.kg-TSS^{-1} to 56-63% for SE = 200000 kJ.kg-TSS^{-1} (Figure 3-8 and Table 3-7).

Table 3-7: Rate of nitrogen solubilization.

SE (kJ/kg-TSS)	50 W	100 W	200 W
5000	3.77	5.11	9.15
50000	18.57	21.27	25.3
100000	34.72	41.45	42.8
200000	56.26	57.6	62.99

The results show that by increasing the specific energy, concentrations of organic nitrogen and ammonical nitrogen in soluble phase increase. As a result ultrasound leads to solubilization. In our study solubilization attains its maximum for SE = 200000 kJ.kg-TSS^{-1} (62.99% for 200W).

In other words the main parameter for increasing solubilization is applied specific energy (Figure 3-11).

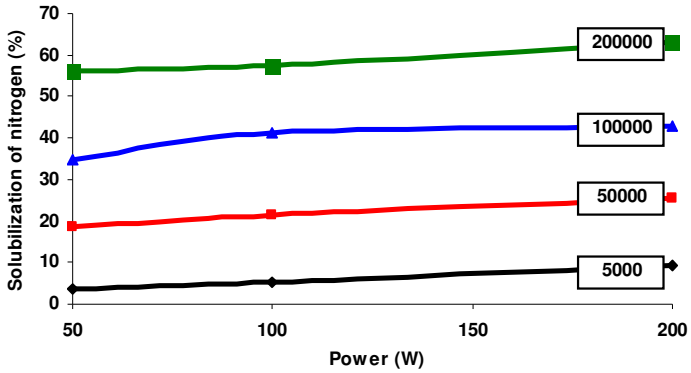

Figure 3-11: Rate of nitrogen solubilization versus power.

Figure 3-12 shows nitrogen distribution as particulate nitrogen and soluble nitrogen (organic and ammonical). For a given intensity, by increasing specific energy, the quantity of organic nitrogen in particulate phase decreases while organic and ammonical nitrogen concentrations in soluble phase increase. Thus particulate organic nitrogen is transformed into soluble form but is not degraded. For instance organic nitrogen solubilization rate increases from 11-15% for SE of 5000 kJ.kg-TSS^{-1} to 51-55% for 200000 kJ.kg-TSS^{-1} and a slight portion (less than 3%) of ammonical nitrogen can be found in the soluble phase. In our study, the highest solubilization rate for nitrogen happens at energy of 200000 kJ.kg-TSS^{-1}, regardless of the input power.

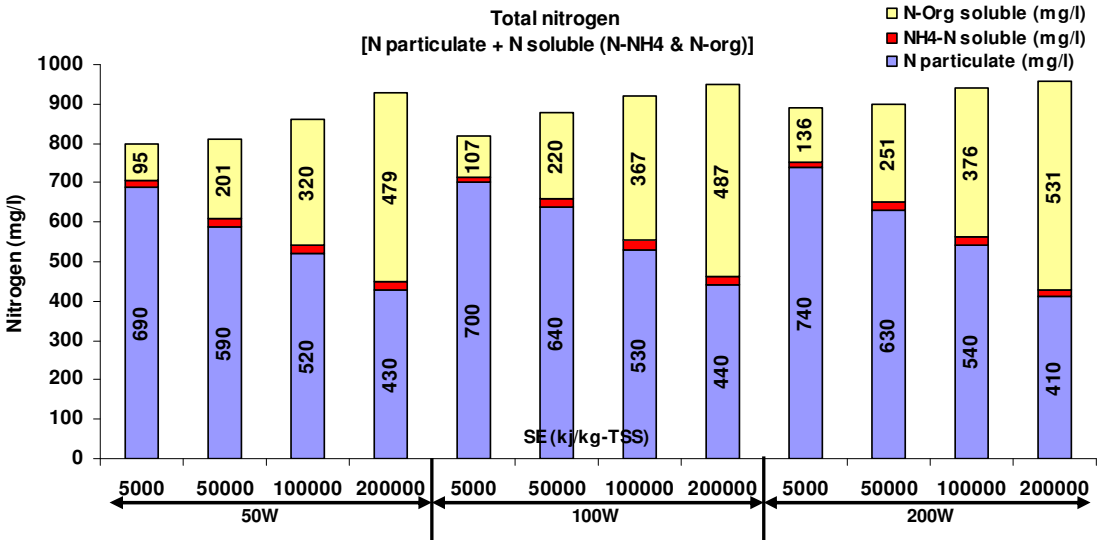

Figure 3-12: Nitrogen distribution as function of specific supplied energy.

❁ Phosphorus

Figure 3-13 illustrates the impact of specific energy on the rate of phosphorus solubilization for different input powers. Phosphorus solubilization rate increases dramatically with specific energy. For example, for a given input power intensity of 200W, phosphorus solubilization rate increases from 23% for SE=5000 kJ.kg-TSS^{-1} to its maximum value of 68.57% for 200000 kJ.kg-TSS^{-1} (see Figure 3-10). Figure 3-13 clearly showed that input power had no significant effect on phosphorus solubilization for a given specific energy. Therefore applied specific energy is the main parameter in phosphorus solubilization.

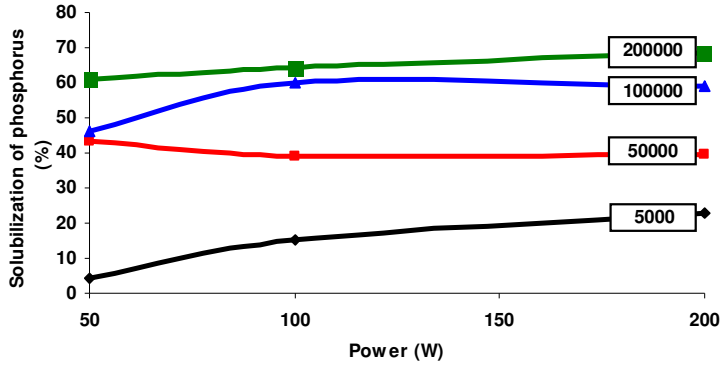

Figure 3-13: Solubilization of phosphorus vs. power.

Figure 3-14 shows that the amount of particulate phosphorus decreases and soluble phosphorus increase with the increase of specific energy for all powers of 50, 100 and 200 watts. Soluble phosphorus includes organic (P-org) and inorganic (P-PO_4) parts. For soluble phosphorus, during sonication and solubilization, the ratio of inorganic phosphorus (phosphate) and organic phosphorus (P-org) to soluble phosphorus (P_S) is about 35 and 65 %, respectively. The maximum amount of phosphate is obtained in 50000 and 100000 specific energy, and the maximum amount of organic phosphorus is occurred in 200000 kJ.kg-TSS^{-1} specific energy. This means that the amount of soluble phosphorus contained in soluble part increases with the increase of specific energy.

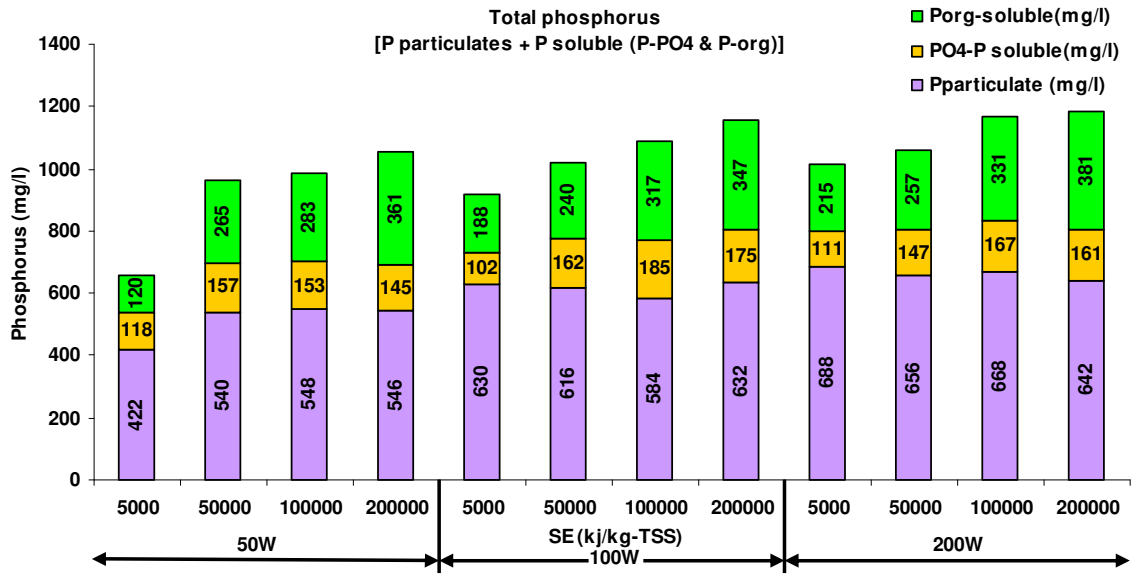

Figure 3-14: phosphorus distribution as function of specific supplied energy.

1.4.2 Discussion

During sonication, bacterial flocs and cells are disintegrated releasing intracellular organic nitrogen and total phosphorus into the aqueous phase, which is subsequently hydrolyzed to ammonia and orthophosphate. This results in an increase in ammonia nitrogen and orthophosphate in the aqueous phase.

This work aims to investigate new potential uses of ultrasound in sludge treatment for the depletion level of nitrogen and phosphorus. Short sonication times results in sludge floc de-agglomeration without the destruction of bacterial cells. Longer sonication brought about the break-up of cell walls, the sludge solids were disintegrated and dissolved organic compounds were released.

Ultrasound has been used for biological cell disruption for the recovery of intracellular materials for decades (Harrison, 1991), and it is finding increasing application in municipal sludge disintegration on full-scale (Hogan *et al.,* 2004). Ultrasound disintegration is essentially a physical process and therefore it neither generates secondary toxic compounds nor contributes additional chemical compounds. In addition to physical sludge disintegration, many toxic and recalcitrant organic pollutants, such as aromatic compounds, chlorinated aliphatic compounds, surfactants, organic dyes, etc., are also broken down into simpler forms. This is due to generation of the highly oxidative reactive radicals-hydroxyl ($OH^{\bullet}$), hydrogen ($H^{\bullet}$), and hydroperoxyl ($HO^{\bullet}_2$) and hydrogen peroxide (H_2O_2) during ultrasound pre-treatment, which leads to the oxidative breakdown of these recalcitrant compounds (Adewuyi, 2001).

Our study also confirms that ultrasound does not lead to nitrogen and phosphorus mineralization, but increases solubilization. The highest solubilization for both parameters occurred at 200000 kJ.kg-TSS^{-1} and 50W of power. Also our study revealed that specific energy was the dominant parameter for increasing solubilization and input power had less effect.

Bougrier *et al.* (2005) monitored nitrogen release (soluble organic and ammonia nitrogen) during sonication of thickened WAS at different specific energy inputs. The maximum nitrogen solubilization was achieved at a specific energy input of 10000 kJ.kg-TS^{-1}. Also for this study at specific supplied energy of 15000 kJ.kg-TS^{-1}, organic nitrogen solubilization was about 40% and very little organic nitrogen was transformed into ammonium. Proteins were made soluble but were not completely degraded.

Proteins and polysaccharides are two of the most predominant organic matters in extra-cellular and intracellular polymeric substances and make up a large proportion of COD in sludge. Therefore, the measurement of proteins and polysaccharides after ultrasonic pre-treatment can provide a more thorough understanding of the influences of ultrasonic pre-treatment on digestion processes (Liu and Fang, 2003; Yu *et al.,* 2008).

1.5 Conclusion on effect of ultrasonic pre-treatment on the sludge

In this study, 12 samples of concentrated sludge were sonicated using specific energies of 5000, 50000, 100000, and 200000 kJ.kg-TSS^{-1}. For each value of specific energies we have used ultrasound powers of 50, 100, and 200 Watts applied during a period of time. Application time varies between 0.5 min and 80 min (c.f Table 3-1). Power densities of our study were 500, 1000, and 2000 W/L.

Table 3-8 summarizes results obtained from the solubilization of different parameters during this study. The aim of the ultrasonic treatment is to increase the availability of organic matter by disrupting the flocs and/or lysing the bacterial cells leading to the significant decrease of excess sludge.

In fact ultrasound leads to an increase in sludge solubilization. COD, nitrogen, phosphorus and matters solubilization increases with supplied specific energy. This solubilization is more concentrated on organic substances and transfer of particulate phase to soluble phase. In

general, solubilization increases with SE. This phenomenon starts initially with a high speed which will degrade later.

Table 3-8: Results in terms of solubilization by ultrasound.

Sampels	SE (kJ/kg-TSS)	DD_{COD} (%)	S_{COD} (%)	S_{BOD} (%)	S_{TSS} (%)	S_{VSS} (%)	S_N (%)	S_P (%)
S_1	5000	10.72	3.58	1.90	10.44	12.81	3.77	4.43
S_2	50000	22.95	7.66	4.22	34.10	38.85	18.57	43.25
S_3	100000	28.27	9.44	4.36	42.18	57.81	34.72	46.20
S_4	200000	35.85	11.97	4.74	72.80	78.85	56.26	60.97
S_5	5000	11.03	3.68	2.37	5.51	7.71	5.11	15.40
S_6	50000	25.11	8.39	6.02	15.20	19.17	21.27	39.03
S_7	100000	33.37	11.15	6.49	25.06	30.63	41.45	60.13
S_8	200000	37.37	12.48	5.69	51.19	58.44	57.60	64.35
S_9	5000	11.65	3.89	3.32	0.58	2.29	9.15	23.00
S_{10}	50000	27.90	9.32	7.77	7.97	11.88	25.30	39.45
S_{11}	100000	35.48	11.85	8.67	20.05	26.04	42.60	69.28
S_{12}	200000	37.92	12.66	8.72	38.46	45.73	62.99	68.57

Seeing Table 3-8, we observe that the maximum DD_{COD} and solubilization of the measured parameters occur at SE = 200000 kJ.kg-TSS^{-1}. For most of measured parameters, the results obtained from 50, 100 or 200 Watts are nearly the same, but TSS and VSS solubilization rates were better for an input power of 50W.

As we have stated in the previous sections, the optimum sonication specific energy for the sludge solubilization is 200000 kJ.kg-TSS^{-1}. Also the best configuration leading to this specific energy is applying a power of 50W.

In fact ultrasound helps to transfer organic matters from particular phase to soluble phase. This transfer takes place more quickly and more efficiently at higher specific energies. As a result solubilization percentage and degree of disintegration will also increases.

The above explications suggest that in the process of sludge digestion, biodegradation occurs more quickly in a sonicated sludge compared to control sample.

Thus in order to study pre-treated sludge fermentation and digestion in digesters, we will use ultrasonic pre-treatment with SE = 200000 kJ.kg-TSS^{-1}, P = 50 W. In the next stages we will investigate thoroughly biodegradability of sonicated sludge, under aerobic and anaerobic conditions.

2. Study of ozone pre-treatment on sludge

Two of the strongest oxidizing agents in wastewater and sludge treatment are ozone and hydroxyl radicals. Müller, (2000) reported that ozonation of sludge was the most cost effective among several developing disintegration methods and reached the highest degree of disintegration.

Ozone is an unstable gas, which can be produced at the point of use, acting as a strong oxidizing agent.

According to the bibliographic results ozone treatment allows:

- Releasing of the material intra and / or extra-cellular in the liquid phase (Egemen *et al.,* 2001)
- Solubilizing mineral matter and organic (Salhi, 2003)
- Improving the degradation of organic matter (Weemaes *et al.,* 2000)
- Increasing the production of biogas (Goel *et al.,* 2003)
- Improving the sedimentation ability of sludge (Battimelli *et al.,* 2003)

Because of its strong oxidizing ability, ozone reacts with particulate matter, and also soluble (Cesbron *et al.,* 2003), and only 5% of the material is resistant to ozone (Déléris *et al.,* 2000). However, it is necessary to limit transferred ozone dose thus mineralization in this area is limited (Yeom *et al.,* 2002).

The objective of this study is to quantify and understand the changes related to treatment by ozonation and evaluate their effects on the solubilization to determine the optimum operating conditions of treatment.

Table 3-9: Different conditions in ozonation pre-treatment.

No, Sample	Power (W)	Time (min)	Con. of ozone (gO_3/g-TSS)
1	180	15	0.011
2	180	30	0.034
3	180	60	0.101
4	180	90	0.139
5	180	120	0.150

Considering prior bibliographical studies and in order to determine the optimum ozone dosage allowing to attain maximum solubilization rate, high sludge elimination efficiency and high biodegradability with minimum ozone consumption, the concentrated sludge was ozonated using different dosages (from 0.01 to 0.15 gO_3.g-TSS^{-1}). We will use the conditions leading to the highest solubilization rate for digestion and biodegradation in pilot plant during the next stages. The power of ozonation apparatus was set on 180 W (Table 3-9).

2.1 Effect of ozonation on physicochemical characteristic of sludge

The ozonation was done on the sludge originating from the same source as the sludge used for sonication. The sludge was concentrated to attain a concentration of 12.36 $g.L^{-1}$ (TS = 12.36, VS = 71.07% TS). Then the samples were ozonated by different dosages, the range of ozone treatment varied from 0 to 0.15gO_3.g-TSS^{-1}. Different parameters of the resulting sludge (total and soluble) were measured. Same parameters were measured for a control sample in order to compare with the results obtained from the test samples. In these series of studies total BOD_5 was 4950 $mg.L^{-1}$ before ozonation.

Table 3-10: Characteristics of studied sludge.

Sample	M O_3 (gO_3/g-TSS)	pH	COD_T (mg/l)	COD_S (mg/l)	BOD_S (mg/l)	TSS (g/l)	VSS (g/l)
1	0.011	6.53	13070 ± 2548	410 ± 86	160 ± 44	11.63	8.34
2	0.034	6.41	12560 ± 2449	490 ± 103	260 ± 71.5	10.63	7.58
3	0.101	6.08	13390 ± 2611	1280 ± 269	560 ± 154	10.54	7.41
4	0.139	5.52	12210 ± 2381	1100 ± 231	520 ± 143	10.18	7.28
5	0.150	5.17	11700 ± 2281	1050 ± 220	300 ± 82.5	10.49	7.54
Blanc	0.00	6.89	11590 ± 2260	85 ± 17	35 ± 9	12.23	8.82

Ozonation pre-treatments lead to modification of the physicochemical characteristics of sludge. For instance, ozonation decreases pH: pH of the sample before and after ozonation was 6.89 and 5.17 respectively (see Table 3-10). This can be explained by formation of acidic compounds (Bougrier *et al.,* 2006; Chu *et al.,* 2008). In fact during ozone pre-treatment, fats degrade and volatile organic acids are formed which will cause pH to decrease. It is clear that ozonation can reduce pH more efficiently than sonication. The temperature of the sample did not change. Another advantage of sludge ozonation is a significant improvement of settleability and dewaterability (Park *et al.,* 2003).

2.2 Effect of ozonation on COD and BOD_5

2.2.1 Results of COD and BOD_5 solubilization

Ozone is the strongest oxidizing agent in sludge treatment. Ozone oxidation with the direct and indirect reaction enables the destruction of flocs or cell walls of micro-organisms in waste activated sludge and elutes cytoplasm into bulk solution (Scheminski *et al*., 2000).

The ozonation of sludge leads to solubilization of particulate solids, and increases their biodegradability. Organic substances released from activated sludge flocs can then be degraded in the subsequent activated sludge treatment, ultimately leading to a reduced overall biomass production.

In this step, one series of batch studies were carried out to get an understanding of the effect of ozonation on sludge properties. It was found that the cryptic condition caused by sludge ozonation could amplify microbial cell lysis, for ozone could disrupt the cell walls and cause the release of plasma from the cells. The amounts of soluble organics matter in the supernatant increases with ozonation time. In this work, Soluble COD, COD solubilization (S_{COD}), Disintegration degree (DD_{COD}) and subsequent biodegradability were studied.

2.2.1.1 COD solubilization and disintegration degree

To obtain a better understanding of the action of ozone, solubilization has been described using different parameters. COD was used for the quantification of ozone's effect on organic and mineral matter. The impact of the ozone dose on COD distribution is shown in Table 3-11, Figure 3-15 and Figure 3-16.

According to Table 3-11, by increasing ozone dose from 0.01 to 0.15 $gO_3.g\text{-}TSS^{-1}$, COD_S/COD_T increases from 0.73% for not ozonated sample to 9.56%. But by using higher ozone doses than 0.1g, this ratio tends to decrease slightly.

Table 3-11: COD solubilization and DD_{COD} due to sludge ozonation.

Sample	Ozone Dose (gO_3/g-TSS)	S_{COD} (%)	COD_S/COD_T (%)	DD_{COD} (%)
1	0.011	2.82	3.14	6.68
2	0.034	3.52	3.90	8.32
3	0.101	10.39	9.56	24.56
4	0.139	8.82	9.01	20.86
5	0.150	8.39	8.97	19.84
Control	0.00	-	0.73	-

By increasing ozone, DD_{COD}, like COD solubilization, increases and attains its maximum after 60 minutes of ozonation (0.1g). This ratio decreases by prolonging ozonation duration (i.e. increasing ozone dose). The reason is that ozone results in oxidation of organic matter in sludge, and increases the percentage of soluble organic matter in supernatant. But after 60 minutes of ozonation, formation of soluble organic matter slows down. The decrease of the concentration of soluble organic matter in sample can be explained by raise of mineralization of soluble organic matter.

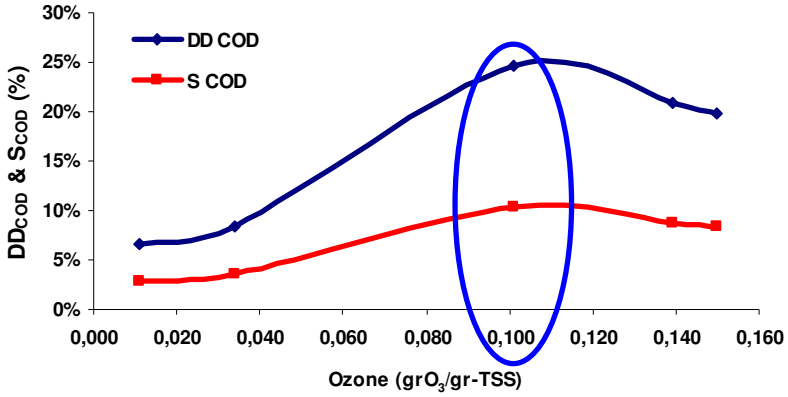

Figure 3-15: Comparison of degree of disintegration (DD_{COD}) and solubilization of COD (S_{COD}) in ozonation process.

As we can see in Figure 3-15, the highest COD solubilization (S_{COD}) and degree of disintegration (DD_{COD}) occurs at 60 minutes (concentration $0.1gO_3.g\text{-}TSS^{-1}$). If we continue ozonation further more, these parameters will decrease.

Figure 3-16 shows that during 15, 30, and 60 minutes of ozonation (i.e. from 0.01 to 0.15 $gO_3.g\text{-}TSS^{-1}$ ozone dose), COD_T (COD_S + COD_P) remains nearly constant (12420 $mg.L^{-1}$, standard deviation: ±622.62) while COD_S increases. By continuing ozonation, both soluble COD rate (COD_S) and particulate COD (COD_P) decrease meaning that total COD decreases slightly. In other words, a limited mineralization has occurred, however the mineralization in this study has been very slow and insignificant due to poor ozone dosage (0 to 0.15 gO_3).

Ozonation increases the rate of soluble COD from 85 $mg.L^{-1}$ for control sample to 1280 $mg.L^{-1}$ for a treatment with an ozone dose of 0.1g. This increase in the soluble COD and S_{COD} may be due to deflocculation, cell lysis and release of intercellular organic matter. By continuing ozonation, the rate of soluble COD decreases. In other words the highest COD solubilization rate (10.39%) is attained after 60 minutes of ozonation and subsequently $0.1gO_3.g\text{-}TSS^{-1}$.

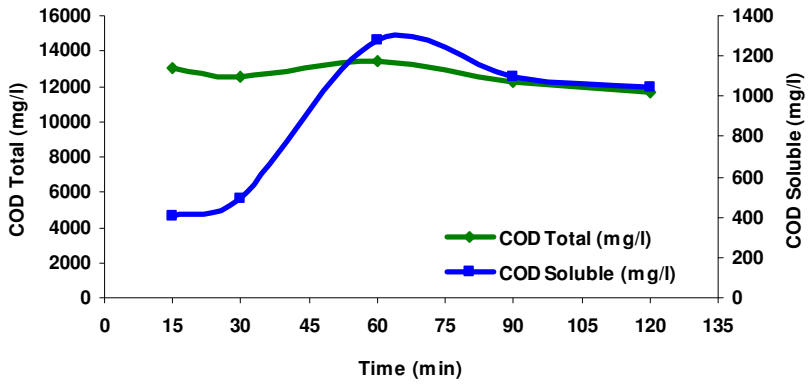

Figure 3-16: Comparison of soluble and particular COD in terms of O_3 dosage and duration.

2.2.1.2 Biodegradability of ozonated sludge

BOD_5 solubilization and BOD_5/COD_S ratio were calculated. BOD_5 behaves much like COD. In other word for ozone doses less than $0.1gO_3.g\text{-}TSS^{-1}$, BOD_5 solubilization rate augments with ozone dose and the highest BOD_5 solubilization rate (7.02%) occur at $0.1gO_3.g\text{-}TSS^{-1}$. By increasing ozone concentration to more than $0.1gO_3.g\text{-}TSS^{-1}$, BOD_5 solubilization rate will decrease (see Table 3-12).

Table 3-12: BOD_5, BOD solubilization and BOD_5/COD_T for different ozonation times.

Sample	Ozone Dose (gO_3/g-TSS)	BOD_5 (mg/l)	Solubilization of BOD (%)	BOD_5/COD_T (%)
Control	0.0	35	-	0.3
1	0.011	160	2.54	1.22
2	0.034	180	2.95	1.43
3	0.101	380	7.02	2.84
4	0.139	310	5.60	2.54
5	0.150	300	5.39	2.56

One of the concerns regarding the use of ozone is its tendency to increase the level of biodegradability of sludge. Biodegradability is defined by the BOD/COD ratio. As we can see in Table 3-12, BOD_5/COD_T ratio was strongly increased (2.84% for ozonated sample for 60 minute and concentration of $0.1gO_3.g\text{-}TSS^{-1}$compared to 0.3% for control sample). It means that oxidant radicals in ozone have been able to oxidize biodegradable organic matters. Increasing ozone dose led to less biodegradable soluble organic matter.

2.2.2 Discussion

Former results (Kamiya and Hirotsugi, 1998) indicate that ozonation not only solubilizes the sludge, but also mineralizes it. This is because ozone oxidizes some organic substances into H_2O and CO_2. At the same time, in some experiments, ozonation did not mineralize sludge (Bougrier, 2005) or did it very little (Yasui and bata, 1994). The authors explained this phenomenon by injected ozone dose or sludge characteristics.

In fact, soluble COD generated due to ozonation was biodegradable form at the early stage of ozonation, while the remaining soluble organic matter was refractory and increases along the ozonation. Therefore, increasing ozone consumption did not definitely lead to an increase of the biodegradability of solubilized sludge. This finding agrees with Nishijima *et al.* (2003) who suggested that the long-term ozonation was not effective to produce biodegradable form because ozone was also utilized to oxidize biodegradable products produced in the beginning and consequently ozone was not consumed for the transforming of the remaining refractory organic matter in biodegradable substance. Other works also state that around 60% of soluble COD generated due to ozonation was biodegradable form at the early stage of ozonation, while the remaining soluble organic matter is refractory and does not biodegrade along the ozonation. Therefore, increasing ozone consumption does not definitely lead to an increase of the biodegradability of solubilized sludge.

In this study the highest COD and BOD solubilization and COD degree of disintegration occurred for the ozone concentration of $0.1 gO_3.g\text{-}TSS^{-1}$ (i.e. ozonation during 60 minutes). By increasing ozone dosage further more, solubilization did not improve and even decreased slightly.

2.3 Effect of ozonation on the matter

2.3.1 Results of matter solubilization

During ozonation of sludge, biomass (flocs, cells and organic matters) degradation could be described as two main mechanisms: one is disintegration due to cell destruction of suspended solids in waste sludge and the other is mineralization due to subsequent oxidation of soluble organic matter to carbon dioxide. Sludge reduction could be accomplished by these two ways, disintegrated solids and mineralized material.

During ozonation foam formation was observed in the reactors. More foam is generated if a more concentrated sludge is used.

The TSS and VSS-profiles demonstrate the attack of ozone on the sludge particles. During the course of the experiments, the disintegration of the sludge cells was also reflected in decreasing TSS and VSS contents of the sludge.

Solids content was also determined for all ozone doses. Total suspended solids concentration remained almost constant at an average value of 10.69 $g.L^{-1}$ (standard deviation, sd: ± 0.49). According to Table 3-10, TSS rate shows no significant decrease compared to control sample (TSS = 12.23 $g.L^{-1}$). At the same time, we can see in Table 3-13 that VSS/TSS ratio reaches from 72.12% for control sample to 63.28% after one hour of ozonation with 0.1 $gO_3.g\text{-}TSS^{-1}$ concentration (12.26% decrease).

By analysis of test data, it can be deduced that the decrease of TSS (from 12.23 $g.L^{-1}$ for the control sample to 10.18 $g.L^{-1}$ for the ozonated sample) was mainly due to the decrease of VSS, because the decreased VSS accounted for main part of the lost TSS, and VSS was a part of TSS. Therefore, the ratio of VSS/TSS reduced with the prolongation of ozonation time. Also, considering Figure 3-17, we can say that ozonation during 60 minutes, results in the highest volume reduction (VSS reduction).

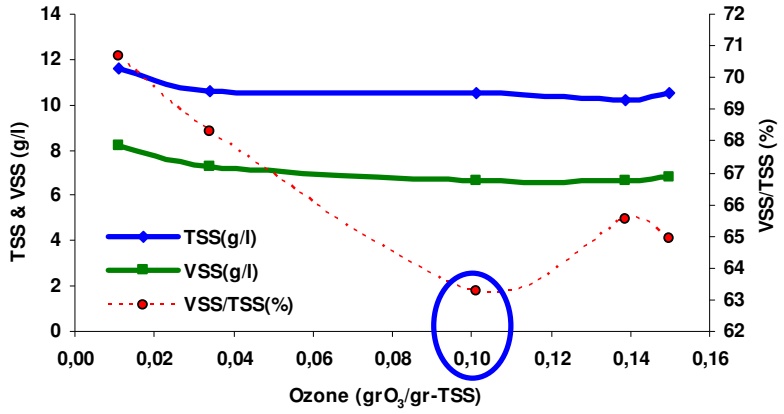

Figure 3-17: Variation of TSS and VSS and VSS/TSS with ozonation concentration.

Table 3-13 shows the solubilization rates of TSS and VSS and by increasing ozone dose more than 0.14 $gO_3.g\text{-}TSS^{-1}$, TSS solubilization rate has decreased. The reason may be the mineralization phenomenon. Regarding VSS solubilization, 60 minutes can be chosen as the optimum ozonation time.

In our study solubilization rates were not very high and probably in order to achieve higher solubilization rates ozonation must take place at lower doses during a longer time.

Table 3-13: Rate of solubilization of TSS and VSS.

Sample	Ozone Dose (gO_3/g-TSS)	S_{TSS} (%)	S_{VSS} (%)	TSS/TS (%)	VSS/TSS (%)
1	0.011	4.91	6.80	94.09	70.68
2	0.034	13.08	17.69	86.00	68.3
3	0.101	13.82	24.38	85.28	63.28
4	0.139	16.67	24.38	82.36	65.52
5	0.150	14.23	22.79	84.87	64.92
Control	0.00	-	-	98.95	72.12

As shown in Table 3-13, solubilization is represented by the S_{TSS}, S_{VSS} and TSS/TS ratios for each ozone dose. The maximum TSS solubilization is obtained with an ozone dosage of 0.14 gO_3 (16.67%), and TSS solubilization decreases with further increase in the ozone concentration. At the same time, the VSS solubilization is observed at the ozone dosage of 0.1 gO_3 (24.38%), and VSS solubilization is not affected by further increases in ozone concentration.

A significant decrease in suspended solids concentrations was observed: the initial TSS/TS ratio was 98.95% (for untreated sludge) and the minimal TSS/TS ratio, obtained for an ozone dose of 0.139gO_3.g-TSS^{-1}, was 82.36%. A logarithmic relationship was established between the TSS/TS ratio and the ozone dose (see Figure 3-18). For the studied ozone doses this formula was: TSS/TS = -3.6 Ln (ozone dose) +76.3

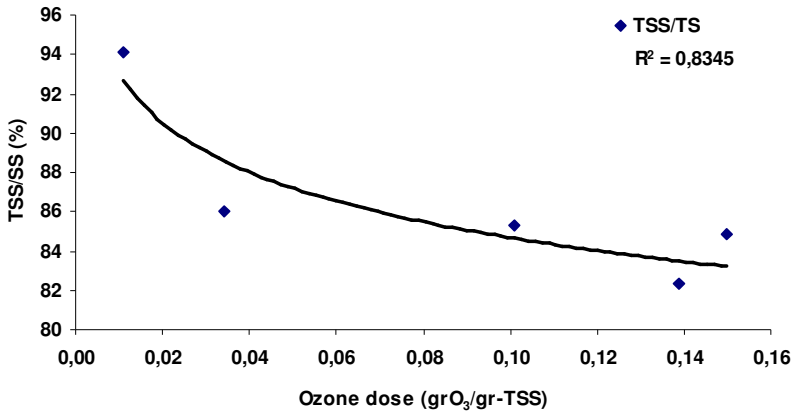

Figure 3-18: Effect of ozone dose on suspended solids solubilization.

2.3.2 Discussion

The disintegration of sludge cell can be reflected directly in the decrease of TSS and VSS. There is no disagreement in the literature that ozone treatment reduces excess sludge production.

Ahn *et al*.(2002) claim that the excess sludge reduction is explained by a series of subsequent reactions, starting with disintegration of cells, solubilization of cell content, which is then mineralized, causing a large sludge mass reduction. This seems to be in agreement with conclusion of Salhi *et al*. (2003).

The highest TSS and VSS solubilization rates occurred at 0.1g to 0.14g of ozone concentration (Figure 3-17 and Table 3-13). Thus concerning that VSS is solubilized more than TSS (organic matters are solubilized better than mineral matters) and concerning that VSS solubilization rate was 24.38% at ozone concentration of 0.1g and VSS solubilization rate does not vary by further increasing of ozone dose, $0.1gO_3$ is considered as the optimum ozone concentration for solids solubilization.

The organic matters content (VSS/TSS) was decreased after 60 minutes of ozonation with 0.1 $gO_3.g\text{-}TSS^{-1}$ concentration and then increased (Table 3-13). It can be concluded that there existed a threshold beyond which the sludge flocs could be sufficiently disintegrated. In fact increasing ozone dose (prolonging ozonation time) does not lead to an increase in the sludge solubilization.

Consequently, many works indicated that sludge ozonation caused both solubilization and mineralization of the sludge. In this work the sludge mineralization caused by ozonation was observed for ozone doses above $0.1gO_3.g\text{-}TSS^{-1}$. This difference in the results concerning sludge mineralization suggests that the influence of ozonation on activated sludge depended on the properties of the sludge and especially on the radical reaction on organic matter.

2.4 Effect of ozonation on the Protein and carbohydrate

2.4.1 Results of Proteins and carbohydrates solubilization

According to other works, protein and carbohydrate were easy-to-be-oxidized fractions in sludge (Nishimura *et al.,* 2001). Table 3-14 and Figure 3-19 show that total carbohydrate and protein are nearly constant. As a result in this series of tests solubilization of proteins and carbohydrates increase strongly while mineralization of these parameters were negligibly small.

Proteins and carbohydrates solubilizations were also investigated. Looking at Table 3-14 we can see that by increasing ozonation time and dosage, the amount of soluble protein and carbohydrate increase in sludge. It means that solubilization increases strongly (from 3.65% to 15.91% for protein and from 1.8% to 15.5% for carbohydrate). It is important to note that protein solubilization will slightly decrease after 60 minutes of ozonation whereas carbohydrate solubilization will slightly decrease after 90 minutes of ozonation. In other words, a better solubilization of carbohydrates requires more ozonation time and dosage compared to protein solubilization.

Proteins solubilization is comparable to carbohydrate solubilization. Figure 3-19 (a & b) shows that by increasing ozone dosage, soluble protein and carbohydrates concentration in supernatant will increase. This concentration attains its maximum at 0.1 to 0.14 $gO_3.g\text{-}TSS^{-1}$ ozone dose, and decreases afterwards.

Table 3-14: Characteristics of protein and carbohydrate after ozonation.

Ozone dose (gO_3/g-TSS)	Time (min)	Protien $_T$ (mg eq-BSA/l)	Protien $_S$ (mg eq-BSA/l)	$S_{protein}$ (%)	Carbohydrate $_T$ (mg/l)	Carbohydrate $_S$ (mg/l)	$S_{Carbohydrate}$ (%)
0.0	0	3660	25	-	1212	9	-
0.011	15	3872	154	3.65	1278	30	1.80
0.034	30	3622	264	6.73	1166	68	4.93
0.101	60	3815	589	15.91	1084	153	12.01
0.139	90	3584	579	15.65	1085	195	15.50
0.150	120	3933	518	13.92	1198	194	15.41

This result indicates that the organic particulates in sludge were liquidized to soluble carbohydrates and proteins or converted into lower molecular weight compounds by ozonation pre-treatment.

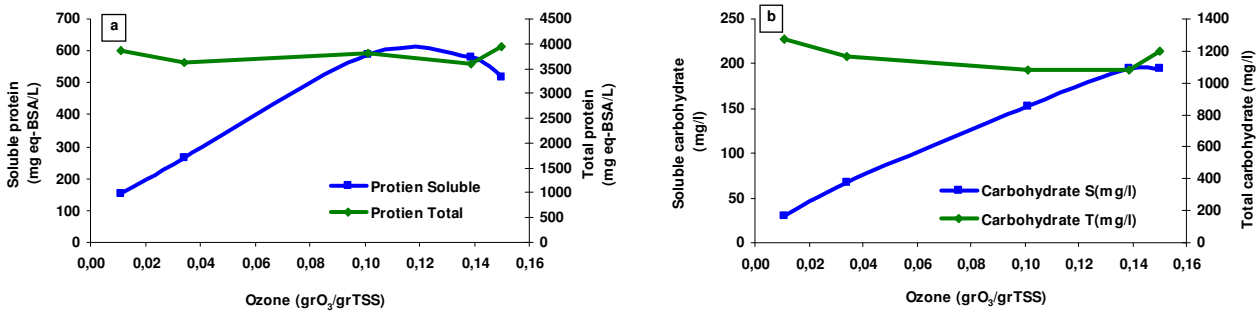

Figure 3-19: Effect of ozone pre-treatment on proteins (a) and carbohydrates (b).

2.4.2 Discussion

Proteins are principle constituents of organisms and they contain carbon which is a common organic substance like hydrogen, oxygen and nitrogen. For this reason, it was considered that as the level of soluble protein increased, the efficiency of aerobic and anaerobic digestion would be improved.

Figure 3-19 and Table 3-14 indicate that optimum ozone concentration is $0.1gO_3.g\text{-}TSS^{-1}$ for proteins solubilization and $0.14gO_3.g\text{-}TSS^{-1}$ for carbohydrates solubilization. In other words proteins require less ozone injection compared to carbohydrates in order to attain the optimum solubilization rate.

The appearance of soluble protein and carbohydrate in the supernatant at a low ozone dose ($0.011\ gO_3.g\text{-}TSS^{-1}$) verified the fact that the breakup of sludge flocs began from the surface of sludge. Then the highly porous sludge was broken into microflocs and some extracellular polymer released. By increasing ozone dose, the microbia wrapped in sludge flocs were exposed to ozone directly and the wall of cell was broken, which led to the leaking of the intracellular materials (proteins and carbohydrates). Therefore, some indissoluble macro-molecules were oxidized into soluble micromolecules which accounted for remarkable increase of the organic matters in the supernatant (Zhao *et al.,* 2007).

Concerning the rise of solubilization, both Scheminski *et al*. (2000) and Yasui *et al.* (1994) refer to earlier articles that show how microorganism cell walls are destroyed by reactions with ozone. The destruction proceeds from the bacterial exterior to the interior by degradation of slime layers, cell walls, and outer membranes. Thereby, intracellular proteins are released, that may temporarily subside in the sludge liquor. Yasui *et al*. (1994) are of the opinion that these proteins won´t linger, as they should be degraded by bacterial enzymes rather quickly. Scheminski *et al*. (2000) performed a gel chromatography, but could not measure any noticeable protein concentrations, which seemingly supports Yasui *et al´*s predictions. However, the conclusion drawn from this was that the protein had not been degraded enzymatically, but by subsequent reactions with ozone. Up to 60% of the solid organic components of the sludge were transformed to soluble substances in the Scheminski *et al*. (2000) experiments. About 63% of the intra and extracellular polysackarides were dissolved, which was also attributed to subsequent reactions with ozone. Protein content in the sludge decreased with about 90% during the ozonation. Decomposition of the polysaccharides occurred at a much lower rate than the protein, leading to an increased polysaccaride

concentration in the sludge liquor, though at the same time, the total polysaccaride concentration in the sludge seemed to decrease linearly with the ozone consumption.

It can thus be concluded that ozone reacted with proteins, but protein hydrolysis was not noticeable. The ozone effect seemed to be limited to solubilization of organic solids as described elsewhere (Salhi, 2003).

2.5 Effect of ozonation on nitrogen and phosphorus

2.5.1 Results of nitrogen and phosphorus solubilization

Due to non stabilization of flocs and release of organic compounds in liquid phase, ozonation leads to nitrogen and phosphorus solubilization.

During ozonation, total nitrogen (N_T) does not change significantly and remains mostly constant. At the same time, organic nitrogen in particulate phase (N_P) reduces. As a result the concentration of organic nitrogen in soluble phase (N_S) increases and nitrogen solubilization (S_N) increases considerably (from 0.64% for ozonation dose of 0.01g to 17.31% for ozonation dose of 0.15g). Due to ozonation, organic nitrogen in supernatant increases and released organic nitrogen oxides directly to nitrate (NO_3–N) resulting in a rise in nitrate concentration of solution (see Table 3-15).

Solubilization is also represented by the Ns/N_T ratio as shown in Table 3-15. Since proteins are the main compounds in excess activated sludge (Stuckey and McCarty, 1979; Li and Noike, 1992), nitrogen fraction analysis can be used as an indicator for the quantification of the ozone effect on proteins. Due to cell solubilization, particulate nitrogen was converted into a soluble fraction; the initial ratio was 8.24% whereas high ozone doses led to a maximal ratio of about 29% (At 0.139 gO_3.g-TSS^{-1} and 90°C).

Table 3-15: Survival rate of nitrogen vs. ozonation time.

Ozone dose (gO_3/g-TSS)	Nitrogen $_T$ (mg/l)	Nitrogen $_S$ (mg/l)	$S_{Nitrogen}$ (%)	N_S/N_T (%)	NH_4^+-N (ppm)	NO_2^--N (ppm)	NO_3^--N (ppm)
0.0	850	70	-	8.24	8.87	n.a	0.15
0.011	800	75	0.64	9.38	13.98	n.a	1.23
0.034	710	80	1.28	11.27	13.20	n.a	1.45
0.101	770	115	5.77	14.94	12.33	7.44	35.69
0.139	690	200	16.67	28.99	8.19	1.72	96.96
0.150	810	205	17.31	25.31	11.92	0.15	162.99

Figure 3-20 shows that ozonation with $0.1gO_3.g\text{-}TSS^{-1}$ during one hour cannot induce an extended solubilization in nitrogen and phosphorus. In other words ozonation has a limited effect on solubilizing these two parameters. In our study, to increase nitrogen and phosphorus solubilization, ozonation must take place during 90 minutes and with a dosage of 0.14 - 0.15 $gO_3.g\text{-}TSS^{-1}$.

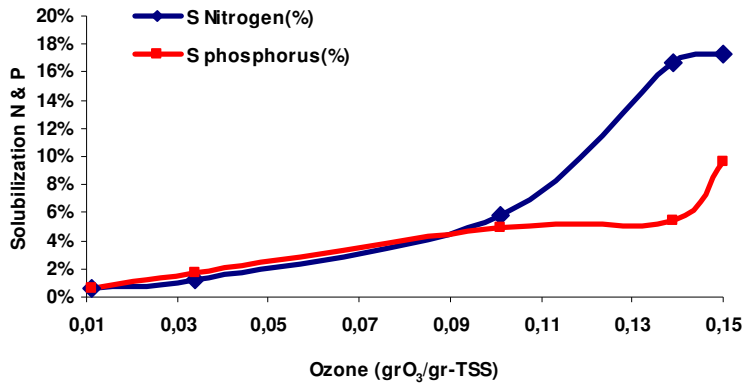

Figure 3-20: Nitrogen and phosphorus solubilizations versus dose of ozone pre-treatment.

The NH_4^+-N, NO_2^--N, NO_3^--N, Total N and soluble N were also measured, and the results are reported in Table 3-15 and Figure 3-21. During the course of ozonation, variations of NH_4^+-N and especially NO_2^--N were very limited, whereas there was a significant rise in NO_3^--N and N_S (after 120 minute of ozonation, NO_3^--N increased from 0.15 $mg.L^{-1}$ to 162.99 $mg.L^{-1}$, and N_S increased from 70 $mg.L^{-1}$ to 205 $mg.L^{-1}$).

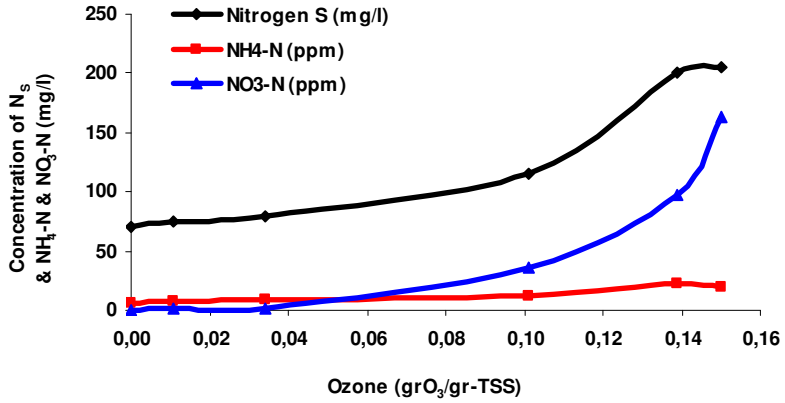

Figure 3-21: Variation of $NH4^+$-N, NO_3^--N and N_S with ozonation time.

Therefore, the organic nitrogen in the solution had a remarkable rise due to sludge ozonation, and 20.5% of released organic nitrogen was directly oxidized to NO_3^--N.

Considering phosphorus, by increasing ozone dose, total phosphorus does not considerably decrease whereas soluble phosphorus increases slightly. Consequent soluble organic phosphorus changes to phosphate (PO_4^{3-}-P) resulting in an increase in the phosphate concentration in supernatant (Table 3-16).

Table 3-16: Survival rate of phosphorus vs. ozonation time.

Ozone dose (gO_3/g-TSS)	$phosphorus_T$ (mg/l)	$phosphorus_S$ (mg/l)	$S_{phosphorus}$ (%)	P_S/P_T (%)	PO_4^{3-}-P (ppm)
0.0	980	120	-	12.24	59.78
0.011	1005	125	0.58	12.44	57.99
0.034	945	135	1.47	14.29	62.95
0.101	910	163	5	17.91	66.28
0.139	995	167	5.47	16.78	72.56
0.150	865	203	9.65	23.47	84.38

The variation of PO_4^{3-}-P and P_S in sludge mixed liquid with ozonation time is shown in Figure 3-22. Orthophosphates and P_S increased with the ozonation, and increased PO_4^{3-}-P accounted for 58.43% of the increased P_S in 120 min of ozonation time, which indicated that a part of organic phosphorus was oxidized to phosphate (Table 3-16 and Figure 3-22).

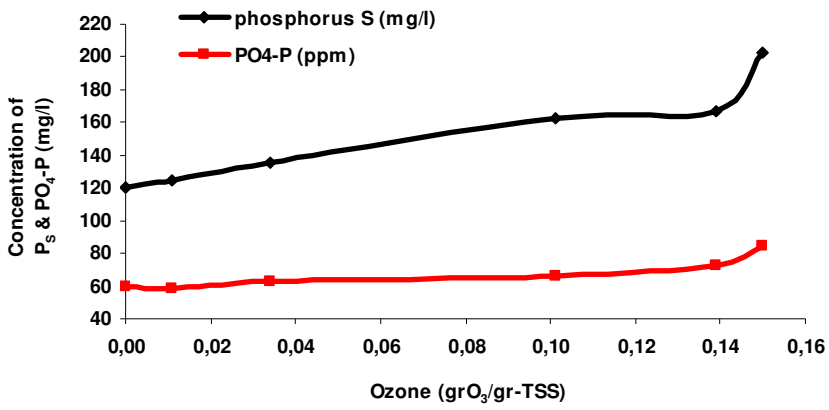

Figure 3-22: Variation of PO_4^{3-}-P and P_S with ozonation time.

2.5.2 Discussion

With the breakup of the cell wall and the release of proteins and carbohydrates, nitrogen and phosphorus compounds, as the major components of microorganisms, were released into the liquid phase (Scheminske *et al.,* 2000; Cui and Jahng, 2004; Saktaywin *et al.,* 2005).

In this study highest nitrogen and phosphorus solubilization rates were observed at ozone dosages of 0.14 and 0.15gO_3.g-TSS^{-1}. We can expect that phosphorus solubilization rate would increase with further increasing of ozone concentration (see Figure 3-22).

Results have shown that, the soluble nitrogen, NO_3^- and soluble phosphorus, PO_4^{---} both increased with increasing ozone dose. But there was no significant increase in the concentration of NH_4^+-N, NO_2^--N and PO_4^{3-}-P. Therefore, it can be concluded that organic nitrogen and organic phosphorus occupied the most part of soluble nitrogen and soluble phosphorus. These results comply with the results obtained by Zhao *et al.* (2007).

2.6 Conclusion on sludge solubilization due to ozonation

Ozone attacks on sludge particles and leads to the destruction of cell wall of micro-organisms and increases organic matter in soluble phase, resulting in TSS reduction and generation of soluble COD, protein, carbohydrate, nitrogen and phosphorus.

For ozone pre-treatment we have selected five samples of sludge with a predefined concentration (TSS = 12.23 g.L^{-1}). Each of these samples was subject to ozonation with 180W of power, 0.7 bar of pressure, 600 NL/h of debit, during 15, 30, 60, 90, and 120 minutes. The ozone concentration in terms of gO_3.g-TSS^{-1} was computed (Table 3-9).

Table 3-17 resumes the optimum solubilization results of different parameters caused by ozonation process. This table indicates clearly that ozonation leads to solubilization phenomenon. Ozonation causes a considerable organic matter solubilization and a limited solubilization of mineral matters.

Ozone is a strong oxidizing agent in sludge treatment and can solubilize and limitedly mineralize (less than 10% in this study) sludge. Table 3-10,Table 3-14,Table 3-15 and Table 3-16 indicate that the fraction of soluble COD, protein, carbohydrates, nitrogen, phosphorus, TSS, and VSS which are solubilized due to ozonation can be up to 93.36%, 95.68%, 95.58%, 65.85%, 40.89%, 16.76%, and 17.46% respectively. It means that ozonation plays an important role in transferring organic matter from particulate phase to soluble phase, and by increasing ozonation dosage and time solubilization rate increases, however, for the majority of parameters, the maximum solubilization rate occurs at 60 minutes (concentration from 0.101 to 0.139 gO_3.g-TSS^{-1}) and remains constant or even decreases afterwards.

Considering Figure 3-15 and Table 3-12, the highest degree of disintegration, solubilization, and BOD_5/COD_T ratio is attained after 60 minutes of ozonation (DD_{COD} = 24.56%, S_{COD} = 10.39% and BOD_5/COD_T = 2.84%).

We can see that by increasing ozonation dose up to $0.101 gO_3.g\text{-}TSS^{-1}$ (60 minutes) solubilization increases, and by prolongation of ozonation time (increasing ozonation dose) this growth will saturate or even decreases slightly except for nitrogen and phosphorus for which solubilization increases continuously.

Table 3-17: Optimum solubilization results in terms of ozone dose

Sample	Ozone dose (gO/g-TSS)	S_{COD} (%)	S_{BOD5} (%)	$S_{Protein}$ (%)	$S_{Carbohydrate}$ (%)	$S_{Nitrogen}$ (%)	$S_{phosphorus}$ (%)	S_{TSS} (%)	S_{VSS} (%)
3	0.101	10.39	7.02	15.91	12.01	5.77	5.00	13.82	24.38
4	0.139	8.82	5.60	15.65	15.50	16.67	5.47	16.76	24.38
5	0.150	8.39	5.39	13.92	15.41	17.31	9.65	14.23	22.79

According to Table 3-17, the highest solubilization rate for BOD, COD, VSS, and protein are attained for 0.101 $gO_3.g\text{-}TSS^{-1}$ of ozone dose. Although for carbohydrate and TSS the highest solubilization rate corresponds to 0.139 $gO_3.g\text{-}TSS^{-1}$ of ozonation, but there is no considerable difference between the results obtained for ozone doses of 0.1 and 0.14 $gO_3.g\text{-}TSS^{-1}$. The only parameters, for which the solubilization rate increases continuously with ozonation time, are nitrogen and phosphorus.

Figure 3-20 indicates that in order to attain highest solubilization rates we need an ozonation time longer than 60 minutes. With 0.1 g of ozone concentration, solubilization rate for both nitrogen and phosphorus is about 5-6%. However, by prolonging ozonation time to 120 minutes (i.e ozone dose of $0.15 gO_3.g\text{-}TSS^{-1}$), solubilization rate increases remarkably (especially for nitrogen for which solubilization rate attains 17.31%).

It is important to note that according to some other works (Nishijima *et al.,* 2003), ozone usage during a long time does not necessarily lead to biological lysis of remaining refractory organic matter. Thus it seems that it is not economic to increase ozonation time and dosage.

Contrary to ultrasonic pre-treatment, Ozonation does not lead to considerable sludge elimination. For instance, VSS decreases from 8.82 $g.L^{-1}$ to 7.41 $g.L^{-1}$ at 0.1 g of ozone dose and to 7.28 $g.L^{-1}$ at 0.14 g of concentration. In other words removal yield is 15.99% after 60 minutes and 17.46% after 90 minutes. After 60 minutes of ozonation ($0.101 gO_3.g\text{-}TSS^{-1}$), VSS

solubilization rate and VSS/TSS ratios attain 24.38% and 63.28% respectively (Table 3-10, Table 3-13 and Figure 3-17).

Finally considering the fact that the majority of most important parameters attain their maximum of solubilization after 60 minutes and the solubilization rates of some other parameters do not increase considerably after 60 minutes, ozonation during 60 minutes with a concentration of 0.1 $gO_3.g\text{-}TSS^{-1}$ is selected as the optimum configuration. Thus in order to study pre-treated sludge digestion in digesters, we will use sludge ozonated during 60 minutes and with ozone dosage of 0.1 $gO_3.g\text{-}TSS^{-1}$. In the next stages we will investigate thoroughly biodegradability of ozonated sludge, under aerobic and anaerobic conditions.

3. Study of thermal pre-treatment on sludge

Thermal treatment followed by a biological treatment results in a significant reduction in excess produced sludge. In general, thermal treatment is described as a sludge disintegration technique (Paul *et al.,* 2006).

According to the literature thermal pretreatment allows:

- Increasing material solubilization, biodegradability, dewater-ability and hygienization (Haug *et al.,* 1978)
- Improving the degradation of organic matter (Li and Noike, 1992)
- Increasing biogas production (Tanaka *et al.,* 1997)
- Sanitizing sludge and reducing pathogen micro-organisms (Odegaard *et al.,* 2002)
- Modifying sludge characteristics (increasing filterability and reducing viscosity) (Bougrier *et al.,* 2007)

Thermal lysis process is affected by two main parameters as follows:

The objective of this study is to quantify and understand the changes induced by thermal treatment and to evaluate their effects on the sludge solubilization and biodegradability in order to determine the optimum operating conditions of treatment.

In this study, selected samples were thermally pretreated using Bain-Marie method with different temperatures and times (40°C, 60°C and 90°C during 10 to 480 minutes). One other sample was treated by autoclave treatment (121°C during 15 minutes under 1.5 bar of pressure). Required tests were done on these samples as well as one untreated sample (Blank or

control sample). The results obtained from analyzing these samples are indicated in Table 3-18. The aim of this study was to compare high and low temperatures as well as different times, and choose the condition leading to highest solubilization and biodegradability rate to be used in pilot during next stages.

Thermal treatment was done on the sludge originating from the same source as the sludge used for sonication and ozonation. The sludge was concentrated up to 12.68 $g.L^{-1}$ then the samples were heated by different temperatures during different times. Then different parameters of the resulting sludge (total and soluble) were measured.

In order to analyze different configurations, tests were done in two different schemes:

- Fixed temperature, different durations (Bain-Marie) plus autoclave.
- Different temperatures, different durations.

3.1 Effect of thermal treatment on sludge characteristics

Thermal treatment leads to the modification of sludge composition: organic compounds are directly affected by treatment, pH decreases with thermal treatment. In fact, it seems that lipids are degraded in order to form volatile fatty acids, which decreases the pH (Bougrier, 2003).This can be explained by the formation of acidic compounds. In this study pH does not decrease remarkably (Table 3-18), this can be explained by low treatment temperature. According to the works of Bougrier *et al.* in 2006, using high temperatures (more than 100°C), can lead to a more significant pH decrease.

Sludge concentration (TS) in laboratory reached 13$g.L^{-1}$ (VS/TS = 70.70%). The BOD_5 of sample for untreated sludge was measured to be 5600 $mg.L^{-1}$.

Table 3-18: Characteristics of studied sludge.

Samples	T°C	Time (min)	pH	COD_T (mg/l)	COD_S (mg/l)	BOD_5 (mg/l)	TSS (g/l)	VSS (g/l)
1	40	10	7.14	11140	70	44	10.05	7.25
2	40	20	6.88	11840	78	48	10.21	7.41
3	40	40	6.59	11670	98	60	10.2	7.39
4	40	60	7.15	11960	130	80	10.87	7.78
5	40	120	7.06	12990	220	135	10.84	7.73
6	40	480	6.89	12820	230	140	10.95	7.82
7	60	10	7.53	14920	302	200	10.48	7.50
8	60	20	7.41	14570	604	390	10.82	7.63
9	60	40	7.21	12880	1045	640	10.49	7.34
10	60	60	6.69	14910	1470	850	9.74	6.81
11	60	120	6.87	15050	1920	1050	10.71	7.41
12	60	480	6.55	14850	1870	1000	10.85	7.60
13	90	10	7.13	14300	1410	900	8.91	6.25
14	90	20	7.15	11740	1570	950	8.13	5.71
15	90	40	6.98	11950	2020	1150	8.06	5.59
16	90	60	7.03	13490	2320	1150	7.85	5.33
17	90	120	6.53	15720	2620	1300	9.15	6.32
18	90	480	6.41	14960	2600	1350	9.18	6.32
Autoclave	121	15	6.75	12210	2393	1300	9.43	6.38
Control	0	0	7.08	13410	69	30	12.68	9.01

3.2 Effect of thermal pre-treatment on COD and BOD_5

3.2.1 Results of COD and BOD_5 solubilization

Thermal treatment results in the breakdown of the gel structure of the sludge and the release of intracellular bound water (Weemaes *et al.,* 1998). This treatment allows a solubilization of sludge, an improvement in biogas production, modification in sludge characteristics (increase in filterability and viscosity reduction) and reduction of pathogen micro-organisms (Bougrier *et al.,* 2007).

Thermal pre-treatment is used to solubilize sludge. Generally, we can use high or low temperatures to attain this objective. Using low temperatures (less than 100°C) necessitates a longer contact time compared to high temperatures (more than 100°C) in order to reach a high level of solubilization and sludge elimination. In this study 40°C, 60°C, 90°C and autoclave (121°C) were uses.

❁ COD solubilization

In experiments concerning solubilization of thermal treatment, by increasing temperature from 40°C to 90°C and by increasing contact time from 10 minutes to 480 minutes, we can see that in most cases solubilization rate and sludge elimination rate reach to their maximum values for 90°C of temperature from 40 to 480 minutes of contact time. There is no significant difference between sludge solubilization for 90°C of temperature at 40, 60, 120, or 480 minutes. Thus higher contact times were not considered because of the significant increase in the energy requirements that these values imply (Table 3-19).

This table and Figure 3-24 reveal that for tests at 40°C, COD solubilization and degree of disintegration are not remarkably affected by prolonging treatment duration from 10 minutes to 480 minutes. At the same time, by increasing temperature from 40°C to 60°C, these ratios evolve dramatically for the first 60 minutes of treatment (S_{COD} augments from 1.75 to 10.5 and DD_{COD} increases from 2.85 to 17.13). This increase will slow down for durations longer than one hour.

Table 3-19: DD_{COD} and solubilization rate of COD and BOD.

Series 2	T°C	Time (min)	S_{COD} (%)	S_{BOD} (%)	DD_{COD} (%)	COD_S/COD_T (%)
1	40	10	0.01	0.25	0.01	0.63
2	40	20	0.07	0.32	0.11	0.66
3	40	40	0.22	0.54	0.35	0.84
4	40	60	0.46	0.9	0.75	1.09
5	40	120	1.13	1.89	1.85	1.69
6	40	480	1.21	1.97	1.97	1.79
7	60	10	1.75	3.05	2.85	2.02
8	60	20	4.01	6.46	6.45	4.15
9	60	40	7.32	10.95	11.93	8.11
10	60	60	10.5	14.72	17.13	9.86
11	60	120	13.87	18.31	22.63	12.76
12	60	480	13.5	17.41	22.01	12.59
13	90	10	10.05	15.62	16.39	9.86
14	90	20	11.25	16.52	18.35	13.37
15	90	40	14.62	20.11	23.85	16.9
16	90	60	16.87	20.11	27.51	17.2
17	90	120	19.12	22.8	31.18	16.67
18	90	480	18.97	23.7	30.94	17.38
Autoclave	121	15	20.69	20.38	33.15	19.6
Blanc	0	0	-	-	-	0.51

Furthermore, increasing the temperature from 60°C to 90°C causes a great increase in DD_{COD} and S_{COD} during first 40 minutes of heating. These parameters will stop evolving or even decrease for long durations.

Between Bain-Marie (90°C) and autoclave, thermal treatment at 90°C during 60 minutes is the most cost effective configuration of thermal treatment. The choice is justified because there is no significant difference between 90°C Bain-Marie and autoclave, and considering high energy requirements of autoclave method, it seems more reasonable to choose Bain-Marie method with a temperature of 90°C during 60 minutes (see Table 3-19 and Figure 3-23).

Thermal treatment results in COD and BOD solubilizations. According to Figure 3-23 highest BOD and COD solubilization rates and degree of disintegration (COD) corresponds to autoclave and Bain-Marie treatment with 90°C during 60 minutes (16.87% and 20.11% for S_{COD} and S_{BOD} respectively in Bain-Marie 60 min while 20.69% and 20.38% for S_{COD} and S_{BOD} respectively in autoclave 15 min).

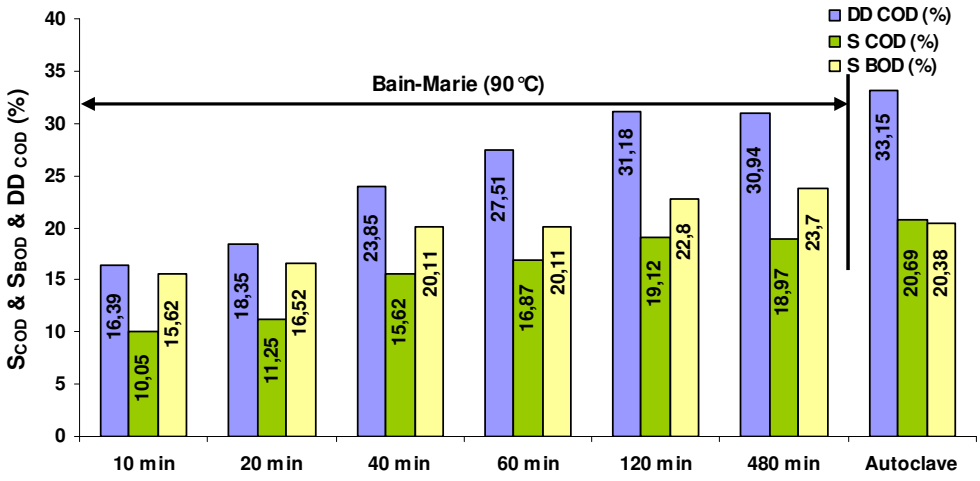

Figure 3-23: BOD & COD solubilizations and DD_{COD} for thermal treatment with Bain-Marie and Autoclave.

According to Figure 3-24 and Table 3-19 (corresponding COD_S/COD_T) we can see that:

- At 40°C, whatever duration may be solubilization is negligible (from 0.63 to 1.79%).
- At 60°C, solubilization increases very quickly until 120 minutes and decreases afterwards (9.86, 12.76 and 12.59 for 60, 120 and 480 min respectively).
- At 90°C solubilization rate is higher than solubilization rate attained at 60°C. For example, after 10 minutes of heating at 90°C, solubilization rate equals roughly that of 60

minutes of heating at 60°C (see Table 3-20). At the same time solubilization rate increases rather quickly during the first 60 minutes of heating and does not increase dramatically afterwards.

Table 3-20: Comparison of solubilization of COD & BOD at 60°C and 90°C.

T°C	Time (min)	S_{COD} (%)	DD_{COD} (%)	S_{BOD5} (%)
60	60'	10.5	17.13	14.72
90	10'	10.05	16.39	15.62

Using higher temperatures were not considered, because for higher temperature, (more than 200°C) biodegradability of sludge is no more improved and can decrease. This can be due to the formation of refractory compounds linked to Maillard reactions (Pinnekamp, 1989; Haug *et al.,* 1978)**.**

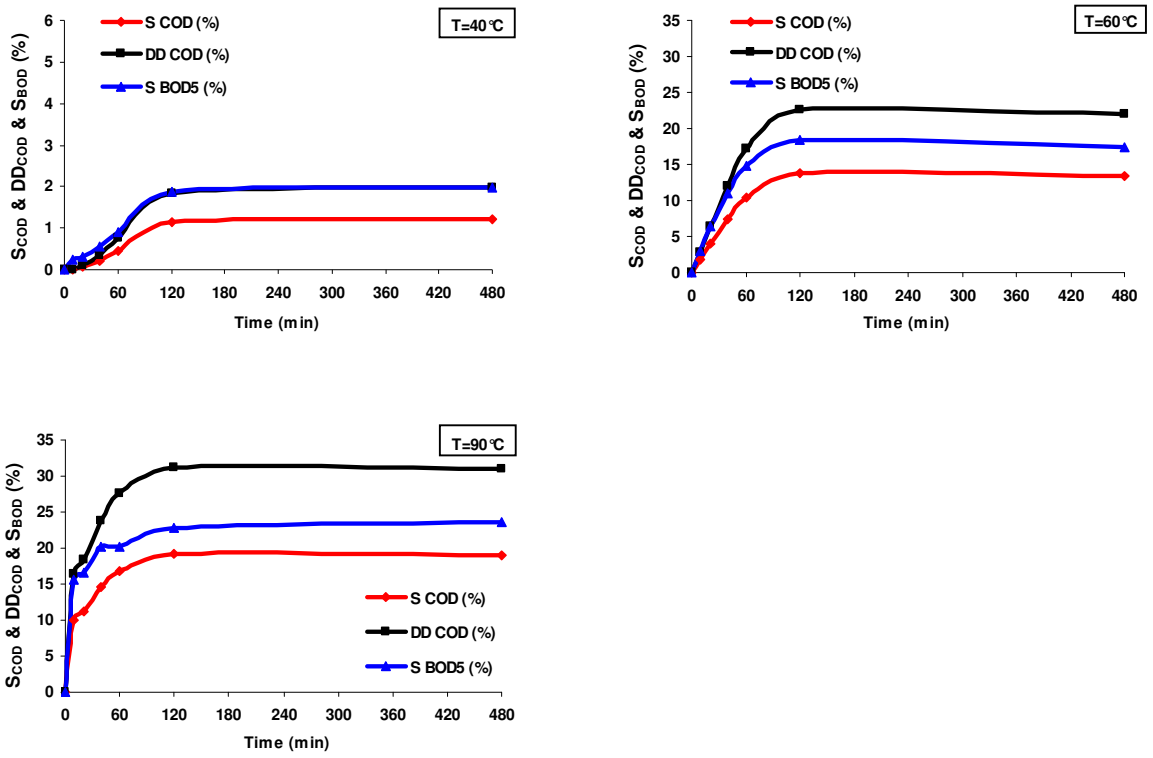

Figure 3-24: BOD & COD solubilizations and DD_{COD} for thermal treatment with Bain-Marie (series 2).

We can conclude that for low temperature treatments (lower than 100°C), temperature is a more determining parameter to increase solubilization rate and degree of disintegration compared to treatment time.

- BOD solubilization

The aim of thermal pre-treatments is to solubilize (i.e. to make a transfer from the particulate phase to the liquid fraction) organic compounds and especially refractory compounds, in order to make them more biodegradable (Bougrier *et al.,* 2006).

Concerning BOD also, the highest solubilization is observed with Bain-Marie at 90°C and autoclave (Table 3-19 and Figure 3-23). We can see that at 90°C of temperature, BOD solubilization rate is 20.11% after 60 minutes and 23.7% after 480 minutes of process (only 3.59% increase in solubilization). This complies with the findings of Barlindhaug and Odegaard, (1996) reporting that the processing time has little influence compared to the temperature.

- **Biodegradability of COD**

Table 3-21 shows the sludge biodegradability (BOD_5/COD_T). For both series, the highest biodegradability is attained for 90°C and autoclave. For the autoclave tests at 121°C, biodegradability was 8.55%. But for the Bain-Marie, at 40°C any increase in biodegradability can be observed (between 0.39% and 1.09%). At 60°C, biodegradability increases by heating duration and evolves from 1.34% (for 10 minutes of heating) to 6.98% (for 120 minutes of heating). At 90°C, biodegradability is high. For this temperature, biodegradability reaches to its maximum value (9.62%) after 40 minutes of heating. By prolonging heating process beyond 40 minutes, this ratio will remain constant or even decreases. We can conclude that in our study heating at 90°C during 40 minutes suffices to attain the maximum of biodegradability.

Table 3-21 indicates that the highest biodegradability (BOD_5/COD_T) ratio corresponds to autoclave treatment (10.65%) and 90°C of Bain-Marie during 60 minutes (8.52%). For Bain-Marie, highest rate occurs after 40 minutes of heating at 90°C (9.62%). Further prolonging the process duration has no effect on sludge biodegradability.

Table 3-21: Biodegradability of sludge.

BOD_5/COD_T (%)	10 min	20 min	40 min	60 min	120 min	480 min
40°C	0.39	0.41	0.51	0.67	1.04	1.09
60°C	1.34	2.68	4.97	5.70	6.98	6.73
90°C	6.29	8.09	9.62	8.52	8.27	9.02

In all cases, biodegradability (BOD_5/COD) increases with temperature. On the other hand, however increasing treatment duration initially increases biodegradability; this rate will cease increasing after a certain duration. As a result for increasing biodegradability temperature is the main parameter while duration has less effect.

3.2.2 Discussion

Thermal treatment also leads to the release of more water by breaking the sludge structure. The temperature can have an effect on hydrogen bonds which give structure to sludge. By modifying this structure, it is possible to release a part of the initial bound water. Moreover, thermal treatment was initially used as a dewatering pre-treatment (Haug *et al.,* 1978).

At low temperatures (below 100°C), for a given temperature (e.g. 90°C), by prolonging the treatment further than its optimum duration (60 min for this study), no significant improvement can be observed in BOD and COD biodegradability and solubilization. The optimum treatment in terms of COD and BOD solubilization was 19.12% and 22.8% for S_{COD} and S_{BOD} respectively at 90°C of Bain-Marie during 120 minutes and the highest solubilization ratio (COD_S/COD_T) happened at 90°C of temperature and 60 minutes of heating time (17.2%) (see Figure 3-23).

Considering the above facts, increasing temperature is more effective than prolonging contact time and the main parameter for increasing solubilization and biodegradability is temperature. These results comply with the researches of Li and Noike (1992) and Haug *et al.* (1978).

3.3 Effect of thermal treatment on the matter solubilization

3.3.1 Results of matter solubilization

TSS and VSS concentrations meet their minimum values at 90°C and 60 minutes (Table 3-18). For example TSS decreases from 12.68 $g.L^{-1}$ to 7.85 $g.L^{-1}$ (38.09% reduction) for Bain-Marie at 90°C and 60 minutes and from 12.68 $g.L^{-1}$ to 9.43 $g.L^{-1}$ (26.63 % reduction) for autoclave treatment.

Looking at Figure 3-25, we can see that for the Bain-Marie (from 10°C to 480°C) and autoclave (121°C) experiments, the highest TSS and VSS solubilization rates occur at 60 minutes (even more than autoclave treatment).

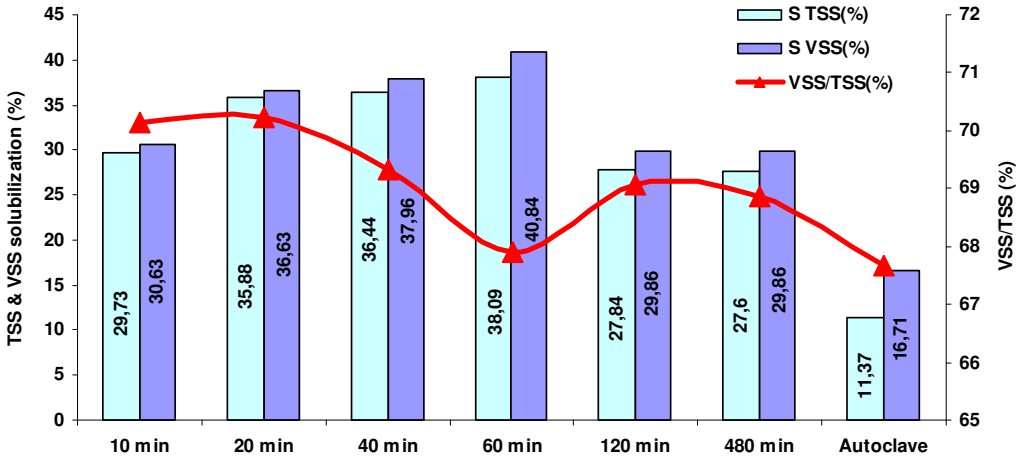

Figure 3-25: Compare of solubilization of TSS, VSS & VSS/TSS for Bain-Marie and Autoclave.

The results of thermal treatment experiment are given in Table 3-22. TSS/TS ratio confirms that highest solubilization rate happens at 90°C of temperature and 60 minutes of heating time. According to this table, TSS/TS decreases from 97.54% for control sample to 60.38% for 90°C and 60 minutes of contact time, and to 78.45% for autoclave (solubilization rate increased 38.1% and 19.57% for Bain-Marie and autoclave respectively).

Table 3-22: TSS and VSS solubilization Rates.

Samples	T°C	Time (min)	S_{TSS} (%)	S_{VSS} (%)	VSS/TSS (%)	TSS/TS (%)
1	40	10'	20.74	19.53	72.14	77.31
2	40	20'	19.48	17.76	72.58	78.54
3	40	40'	19.56	17.98	72.45	78.46
4	40	60'	14.27	13.65	71.57	83.62
5	40	120'	14.51	14.21	71.31	83.38
6	40	480'	13.64	13.21	71.42	84.23
7	60	10'	17.35	16.76	71.56	80.62
8	60	20'	14.67	15.32	70.52	83.23
9	60	40'	17.27	18.53	69.97	80.69
10	60	60'	23.19	24.42	96.92	74.92
11	60	120'	15.54	17.76	69.19	82.38
12	60	480'	14.43	15.65	70.05	83.46
13	90	10'	29.73	30.63	70.15	68.54
14	90	20'	35.88	36.63	70.23	62.54
15	90	40'	36.44	37.96	69.35	62.00
16	90	60'	38.09	40.84	67.9	60.38
17	90	120'	27.84	29.86	69.07	70.38
18	90	480'	27.60	29.86	68.85	70.62
Autoclave	121	15'	11.36	16.71	67.66	78.45
Blanc	0	0	-	-	71.06	97.54

At the same time VSS/TSS ratio indicates organic matters solubilization and sludge reduction. Mineralization efficiency is 4.45% for Bain-Marie and 4.78% for autoclave which is less than 5% for both cases. Finally, the highest TSS and VSS solubilization rates takes place for a temperature of 90°C applied during 60 minutes.

3.3.2 Discussion

Heating treatment is an interesting treatment to reduce the excess sludge production (ESP) when associated with a conventional biological process, an activated sludge or a digestion process. Data concerning the effect of heating at temperatures lower than 100°C on sludge are scarce. Hence, our objective is to bring more information into this point.

Graja *et al.* (2005) showed that contrary to the results obtained by Bougrier *et al.* (2007), only a slight fraction of the total sludge COD is eliminated (3.2%). Considering that temperature and heating duration is the same for both studies, this difference may be explained by the difference in nature of used sludge. Anyway, our study indicated that thermal treatment leads to a slight solubilization, but not to a mineralization of organic matter.

Thermal treatment led to a solubilization of organic solids and mineral solids. Solubilization of mineral matter was very low, whereas organic matter solubilization was quite high. In fact total solids solubilization (S_{TSS} + S_{TVS}) increased with raise of temperature. In this study, for all sludge samples, TSS/TS ratio as well as VSS/TSS ratio decreased with the increase of treatment temperature. Therefore, solid concentration in particles fraction decreased. For all tested samples, the solubilization level increased regularly with temperature.

For temperatures lower than 100°C, only a fraction of sludge is disintegrated. Paul *et al,* (2006) reported that flocs were not destroyed by heating at 100°C. On the contrary, the flocs appeared greater at 95°C with a fluffy structure. He concluded that the effect of the thermal treatment could have been simply to improve the availability of the already biodegradable matter.

3.4 Effect of thermal treatment on protein and carbohydrate

3.4.1 Results of proteins and carbohydrates solubilization

By action on chemical bounds, thermal treatment can modify protein and carbohydrates structures and transfers them from particulate phase to soluble phase. This transfer rate augments by increasing temperature.

Table 3-23: Concentration of protein and carbohydrate (total & soluble).

Sample	T°C	Time (min)	$Protien_T$ (mg eq-BSA/l)	$Protien_S$ (mg eq-BSA/l)	$Carbohydrate_T$ (mg/l)	$Carbohydrate_S$ (mg/l)
1	40	10'	3655.07	18.84	1620.03	10.79
2	40	20'	3918.84	23.55	1775.35	16.18
3	40	40'	3852.9	28.26	1656.7	26.96
4	40	60'	3537.32	47.1	1673.96	43.14
5	40	120'	3862.32	108.33	1712.79	53.93
6	40	480'	3680.25	122.46	1751.62	59.32
7	60	10'	4333.33	164.86	1749.46	10.79
8	60	20'	4606.52	268.48	1490.6	26.96
9	60	40'	4517.03	386.23	1783.98	124.04
10	60	60'	4540.58	536.96	1753.78	199.54
11	60	120'	4757.25	664.13	1632.97	334.36
12	60	480'	4663.04	673.55	1691.24	339.75
13	90	10'	4422.83	497.57	1637.29	127.57
14	90	20'	3951.81	645.29	1630.82	188.75
15	90	40'	4521.74	852.54	1753.78	307.4
16	90	60'	4135.51	1092.75	1699.85	382.9
17	90	120'	4140.22	1281.16	1889.68	501.45
18	90	480'	4286.23	1290.58	1911.25	512.33
Autoclave	121	15'	3969	1125	1910	563
Control	0.0	0.0	4611	14	1740	8

Table 3-23 shows protein and carbohydrate concentrations for the Bain-Marie and autoclave of experiments. Total proteins and carbohydrates concentrations were almost identical in all samples. For the same time, in Bain-Marie method, soluble carbohydrate and protein concentration increases with contact time. Total carbohydrate and protein concentrations remain almost constant. Thus, proteins and carbohydrates were not degraded during thermal treatments, they were only solubilized.

Soluble protein concentration increases from 14 $mg.L^{-1}$ for the control (untreated) sample to 1093 $mg.L^{-1}$ for a sample treated using Bain-Marie method at 90°C during 60 minutes. This concentration attains 1125 $mg.L^{-1}$ for a sample treated by autoclave method (121°C, 15 min, and 1.5 bar). At the same time, soluble carbohydrate concentration increases from 8 $mg.L^{-1}$ for the control sample to 383 $mg.L^{-1}$ for a sample treated using Bain-Marie method at 90°C during 60 minutes. This concentration attains 563 $mg.L^{-1}$ for the sample treated by autoclave method.

For the Bain-Marie series of thermal treatment experiments, as reported in Figure 3-26, the solubilization rate for both parameters reaches to its maximum for temperature of 90°C during

120 minutes and does not increase furthermore. However the maximum solubilization rate occurs at 90°C and 120 minutes (27.56% and 28.45% for protein and carbohydrate solubilization respectively), considering that there is not a noticeable difference between solubilization rates for 60 minutes and 120 minutes, and considering the fact that in thermal treatment the main parameter is temperature and the duration has less effect than temperature (Bougrier *et al.,* 2007), we have selected 90°C and 60 minutes as the optimal configuration.

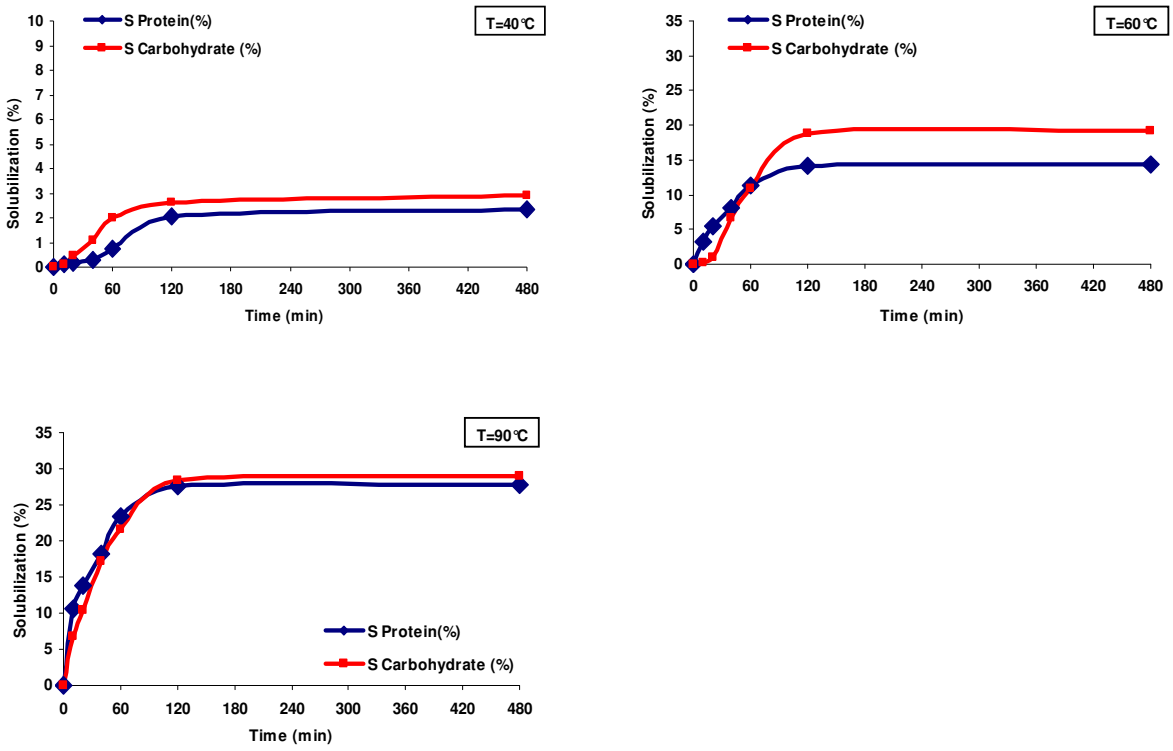

Figure 3-26: protein and carbohydrate solubilization.

3.4.2 Discussion

To provide a more thorough understanding of the effect of thermal treatment, solids and soluble fractions of proteins and carbohydrates concentrations were measured.

Thermal hydrolysis results in breaking the flocs and cell wall and releasing the proteins that are protected from enzymatic hydrolysis for biodegradation. Thermal treatment led to an improvement in degradation of carbohydrates. Proteins were not degraded remarkably during thermal treatment, they were only solubilized. Neyens and Baeyes, (2003) observed that, while the carbohydrates of the sludge were easily degradable, the proteins were well protected from the enzymatic hydrolysis by the cell wall. The authors concluded that carbohydrates would be more easily hydrolyzed but proteins would be easier to solubilize. For instance for the Bain-

Marie tests, the highest protein solubilization rate (25% approximately) happens after 60 minutes of heating at 90°C. For the same conditions, carbohydrates solubilization rate is less than 22%.

Thus, this could suggest a hypothesis on the location of these compounds. It seemed that carbohydrates were mainly located in the exopolymers of sludge structure whereas proteins were mainly located inside the cells. So, for low temperatures, only exopolymers were affected by thermal treatment: carbohydrates were degraded and also few proteins.

3.5 Effect of thermal treatment on the nitrogen and phosphorus

3.5.1 Results of nitrogen and phosphorus solubilization

Nitrogen and phosphorus solubilization were assessed for the different temperature and the different contact times. Figure 3-27 shows the results of experiments concerning thermal treatment.

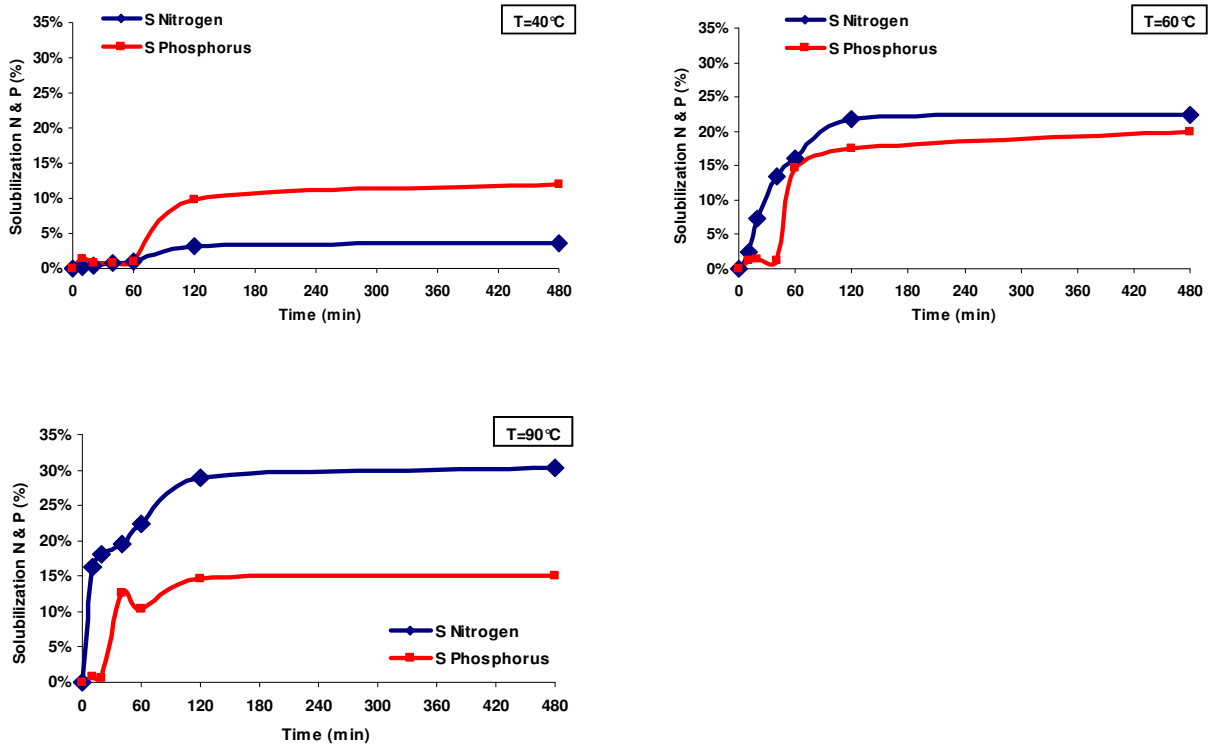

Figure 3-27: Nitrogen and phosphorus solubilization rates.

As we can see, for a temperature of 90°C, nitrogen solubilization rate augments by prolonging contact time. It means that we need a long duration of heating in order to gain a high nitrogen

solubilization rate (e.g. treatment during 120 minutes led to and 28.82% solubilization rate). The reason is that in low temperature thermal treatment, the concentration of organic nitrogen in particulate phase decreases (the concentrations of organic nitrogen and ammonical nitrogen in soluble phase increase) when longer contact times are used.

Phosphorus solubilization does not follow a well-behaved curve. The highest phosphorus solubilization rate corresponds to a temperature of 60°C and a contact time of 480 minutes (15.06%), however the solubilization rates after 120 and 480 minutes are very close (about 15%). Also, the usage of autoclave (121°C, 1.5 bars) method has not led to a high solubilization rate (16.67% and 17.14% for nitrogen and phosphorus respectively).

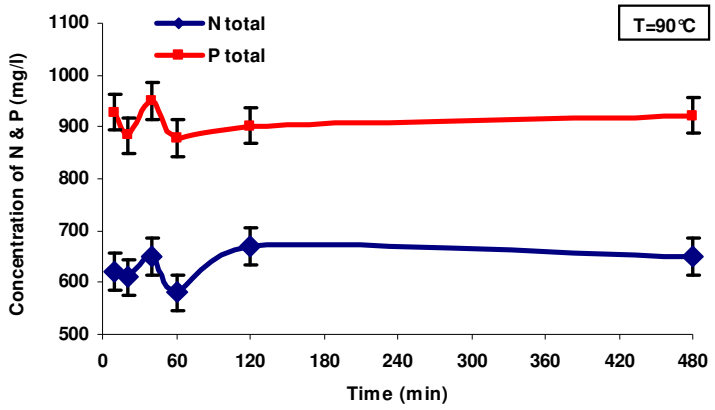

Figure 3-28: Concentration of total nitrogen and total phosphorus at 90°C.

Thermal treatment does not induce a mineralization of nitrogen and phosphorus (see Figure 3-28). The highest transfer rate from solid organic phase to soluble organic phase (solubilization) occurs at 90°C for nitrogen and at 60°C for phosphorus. This maximum, for both cases, takes place after 120 minutes or later.

Figure 3-27 shows that N and P solubilization rates for thermal treatment experiments. It can be easily verified that solubilization rate increases with treatment time and temperature (from 0.3% to 30.24% for nitrogen and 1.33% to 19.88% for phosphorus). Figure 3-29 depict the rates of N_S, P_S, ammonium ions (NH_4^+-N), and phosphate (PO_4^{3-}-P). For both series of test, soluble nitrogen and phosphorus concentrations increase with treatment time and temperature (because due to cell solubilization, particulate nitrogen in converted into the soluble fraction), but phosphate do not change significantly (very little organic nitrogen was transformed into ammonium). Ammonium concentration increases slightly with increasing contact time.

This is because during the thermal treatment, the applied energy is not enough important to convert organic phosphorus to orthophosphate. By prolonging treatment (e.g. from 60 to 120 minutes and further) ammoniacal nitrogen increases (Figure 3-29-a) while phosphate stays unchanged (Figure 3-29-b).

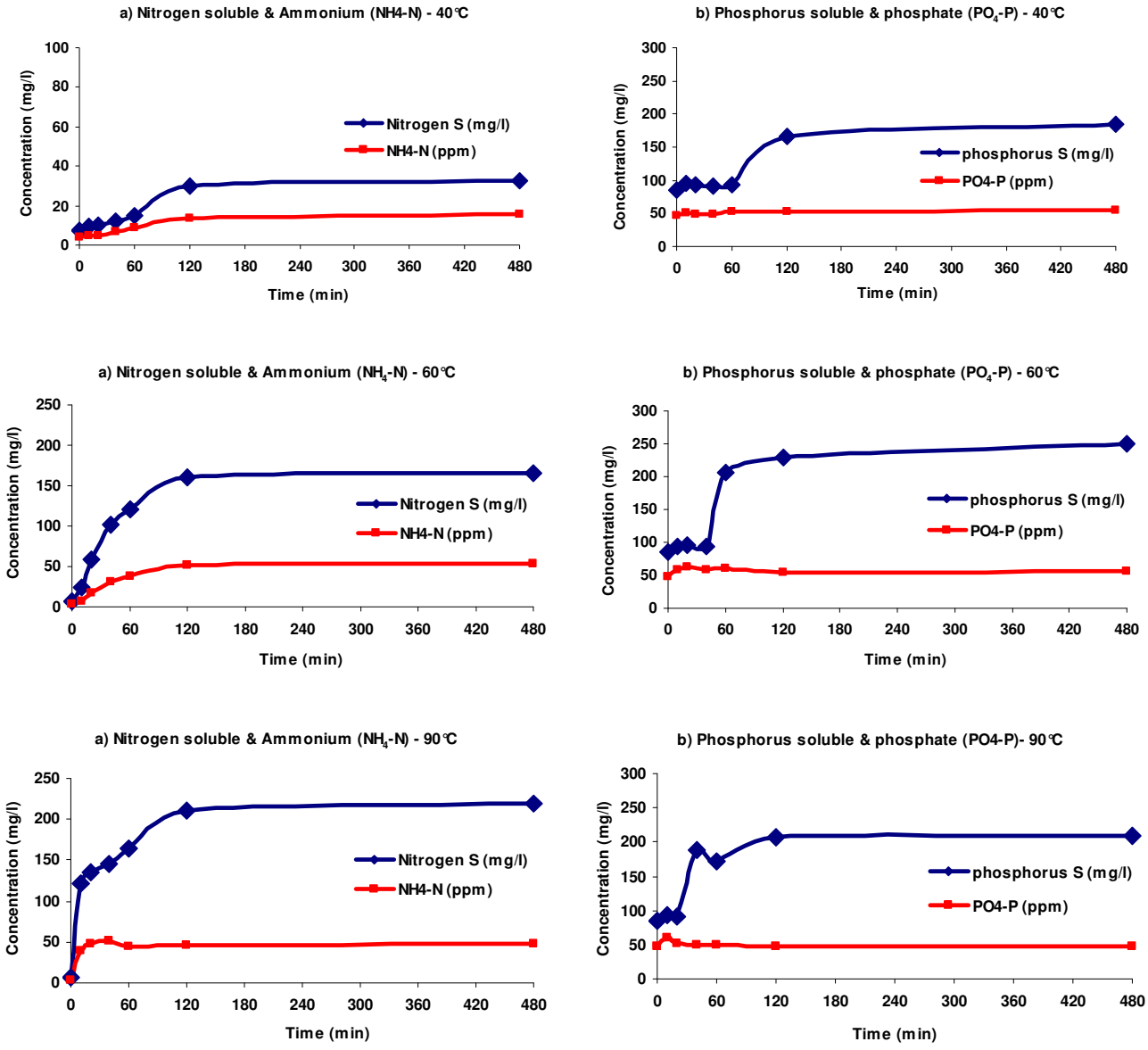

Figure 3-29: (a) Soluble nitrogen and NH_4^+-N concentrations and (b) soluble phosphorus and PO_4^{3-}-P concentrations.

More thermal energy is required to increase phosphate in soluble fraction. As a result, during low temperature thermal treatments, the most of organic nitrogen and phosphorus released to supernatant stays in organic form.

In this study nitrate and nitrite values were always below the detection limit (< 0.5 ppm), and therefore these values are not reported.

Finally we can conclude that in this study, solubilization rate of phosphorus is less than that of nitrogen (about half as much). It seems also that low temperature thermal treatment leads to a limited solubilization of nitrogen and phosphorus. However using high temperatures (e.g. autoclave) a higher solubilization rate is achieved.

3.5.2 Discussion

With the break-up of the cell wall and the release of proteins and carbohydrates, nitrogen and phosphorus compounds, as the major components of microorganisms, were released into the liquid phase (Scheminske *et al.,* 2000; Cui and Jahng, 2004; Saktaywin *et al.,* 2005).

By performing nitrogen and phosphorus balance, the fractions of organic nitrogen in (N_T and N_S) and of organic phosphorus in (P_T and P_S) were determined.

In sludge, nitrogen is mainly found in proteins. As the intracellular materials were released out of cells and solubilized, the soluble protein and phosphorus concentrations increased.

In general among the nitrogen compounds, the nitrate and nitrite concentration were low, whereas the concentrations of ammonium increased slightly, as the treatment proceeded. The slight increase of ammonium concentration resulted from the transformation of organic nitrogen.

In this study, the highest solubilization rate for nitrogen and phosphorus is observed with Bain-Marie treatment with 90°C during 120 minutes (28.82% and 14.70% respectively) and for NH_4^+ and PO_4^{3-} it is observed after 60 minutes of heating at 90°C (236.70% for ammonium and 23.78% for phosphate).

3.6 Conclusion on the effect of thermal treatment on solubilization

Thermal treatment can solubilize COD, TSS, nitrogen, and etc. These solubilizations are concentrated on organic matters and in a limited extent on mineral matters. Heating also leads to a transfer of matters from particulate phase to soluble phase without a total molecular degradation.

Thermal pre-treatments can be used in order to enhance the efficiency of digestion of waste activated sludge (WAS) in aerobic and anaerobic conditions.

In this study 18 concentrated samples (TS = 13 $g.L^{-1}$) were heated using Bain-Marie method at three different temperatures (40°C, 60°C, and 90°C) during different contact times (10, 20, 40, 60, 120, and 480 minutes). Both series of samples as well as control sample were subject to different tests and measurements for total and soluble states. Then for each parameter, solubilization rates, degree of disintegration, and soluble to total ratios were calculated. Another sample was pre-treated using autoclave method at 121°C during 15 minutes under 1.5 bar of pressure.

Thermal treatment leads to organic matter transfer from particulate phase to soluble phase and this transfer takes place more effectively and more quickly in higher temperatures. As a result solubilization rate, degree of disintegration, and soluble to total ratio, increase as well.

In this experiment, for all parameters excepting phosphorus, the highest solubilization rate occurs at 90°C of temperature and 60 or 120 minutes of contact time.

TSS and VSS solubilization rates attain their maximum values after 60 minutes of heating at 90°C. By prolonging the contact time further more these rates begin to decrease. However, highest solubilization rates for all other parameters takes place after 120 minutes of heating at 90°C (Table 3-22).

By analyzing results, we can observe that BOD, COD, protein, carbohydrate, nitrogen and somehow phosphorus rates increase in soluble phase. This phenomenon takes place more strongly by increasing temperature or contact time (Table 3-18 andTable 3-22)

The highest solubilization rate for COD and BOD, DD_{COD} occurred at 90°C temperature and after 60 to 120 minutes of contact time (16-19 percent for S_{COD}, 20-22% for S_{BOD} and from 17% to 31% for DD_{COD}), and autoclave (20.69%, 20.38%, and 33.15% respectively) method. For TSS and VSS solubilization rates, TSS/TS and VSS/TSS ratios indicate that highest solubilization rate and elimination efficiency correspond to 90°C of temperature and 60 minutes of contact time (38.09%, 40.84%, 60.38%, and 67.90% respectively) while autoclave led to minimum rates (11.36% for S_{TSS} and 16.71% for S_{VSS}). For protein, carbohydrate, nitrogen, and phosphorus, the highest solubilization rate occurs in Bain-Marie after 120 minutes of treatment at 90°C (27.56%, 28.45%, 28.82%, and 14.70% respectively) and

autoclave after 15 minutes of treatment at 121°C (32.55%, 33.49%, 16.67%, and 17.14% respectively).

In this experiment, the soluble nitrogen and soluble phosphorus both increased with the thermal treatment. But there was no significant increase in the concentrations of NO_2^--N, NO_3^--N and PO_4^{3-}-P. Therefore, it can be concluded that organic nitrogen and organic phosphorus occupied the most part of total nitrogen and total phosphorus and remained in soluble fraction.

Considering that for most parameters the results obtained after 60 and 120 minutes of heating are really close, and considering the fact that the main parameter for thermal treatment is temperature and time of treatment has less influence (Haug *et al.,* 1978; Li and Noike, 1992; Barlindhaug and Odegaard, 1996; Bougrier *et al.,* 2007).

Thus, it can be concluded that using Bain-Marie at 90°C is the most cost-effective choice. Considering that for the most parameters solubilization rate do not differ that much after 60 and 120 minutes, and taking economic limitations of long-term heating into account, we recommend 90°C of temperature and 60 minutes of contact time as the optimum pre-treatment configuration.

4. Comparison of results in terms of solubilization

Novel pre-treatment processes have been developed in order to improve sludge handling and disposal. This work focuses on pre-treatment processes, which will disintegrate the sludge into the aqueous phase. This treatment will change the floc structure and enhance the solubility of sludge solids. The dissolved components can either be used to improve the efficiency of a subsequent biological degradation process or for the recycling of useful components like nitrogen and phosphorus. Other applications are the improvement of sludge dewatering, the reduction of pathogens or the suppression of foaming. Processes representing independent ways of sewage sludge disposal such as pyrolysis, Krepro, Vertech and various high-temperature oxidation processes will not be considered in this study.

Several disintegration methods have been applied so far:

- heat treatment, in the temperature range from 40° to 180°C (Kepp *et al*., 2000, Barjenbruch *et al*., 1999).
- chemical treatment using ozone, acids or alkali (Tanaka *et al*., 1997; Sakai *et al*., 1997)
- mechanical disintegration using ultrasounds, mills, homogenizers and others (Müller *et*

al., 1998).

- freezing and thawing (Chu *et al*., 1999)
- biological hydrolysis with or without enzyme addition.(Kristensen *et al*., 1992; Kayser *et al*., 1992).

Some investigations have covered a combined chemical and thermal treatment, a combination of alkaline addition and ultrasound or others (Chiu *et al*., 1997, Weemaes and Verstraete 1998).

In order to improve hydrolysis and aerobic and anaerobic digestion performance, one possibility is to use cell lyse pre-treatments. Several pre-treatments were considered: mechanical, thermal or chemical treatments. The aim of these treatments is to solubilize and/or to reduce the size of organic compounds, and especially refractory compounds, in order to make them more easily biodegradable. Final quantity of residual sludge and time of digestion can thus be reduced and biogas production can be increased.

Table 3-24: Comparison of applied energy rate for different pre-treatments.

Pre-treatment	Power (W)	Time (Sec)	Volume (ml)	TSS (g/l)	SE (kJ/kg-TSS)
Ultrasonic	50	4800	100	12.17	197206
Ozonation	180	3600	700	12.23	75692
Autoclave	6000	900	700	12.68	608382
Thermal (40°C)	400	3600	500	12.68	227129
Thermal (60°C)	600	3600	500	12.68	340694
Thermal (90°C)	900	3600	500	12.68	511041

In this study for each treatment, the best set up in respect of solubilization was considered. Table 3-24 shows different pre-treatments and the characteristics of each method. In this table, corresponding specific energy of each method is calculated using the applied power of apparatus, treatment duration, volume of treated sludge, and sludge concentration. As we can see in this table, the highest specific energy corresponds to autoclave (608000 kJ.kg-TSS^{-1}) and the lowest SE corresponds to ozonation method (75000 kJ.kg-TSS^{-1}). The different solubilization Parameters, for different pre-treatment are compared later.

4.1 Degree of disintegration and solubilization of COD and BOD_5

a) Degree of Disintegration of COD

If the disintegration is used to improve the sludge digestion, a high degree of disintegration is necessary in order to realize a noticeable acceleration and enhancement of the degradation.

The maximum degree of disintegration was taken as being released by a thermal extraction method, which gives similar results with other methods used in literature for the same purpose (Lehne *et al.,* 2001; Müller, 2000-b; Tiehm *et al.,* 2001-b).

Comparing our results from three sludge pre-treatment methods (sonication, ozonation, and thermal treatment), we find out that the highest DD_{COD} corresponds to ultrasonic treatment. Figure 3-30 indicates that among thermal treatments, DD_{COD} for autoclave is higher than Bain-Marie (40, 60, and 90°C). This suggests that in thermal treatment, increasing temperature and/or pressure can lead to an increase in DD_{COD}. Figure 3-30 also shows that DD_{COD} for autoclave and ultrasonic method are nearly the same (33.15% for autoclave and 35.85% for ultrasonic).

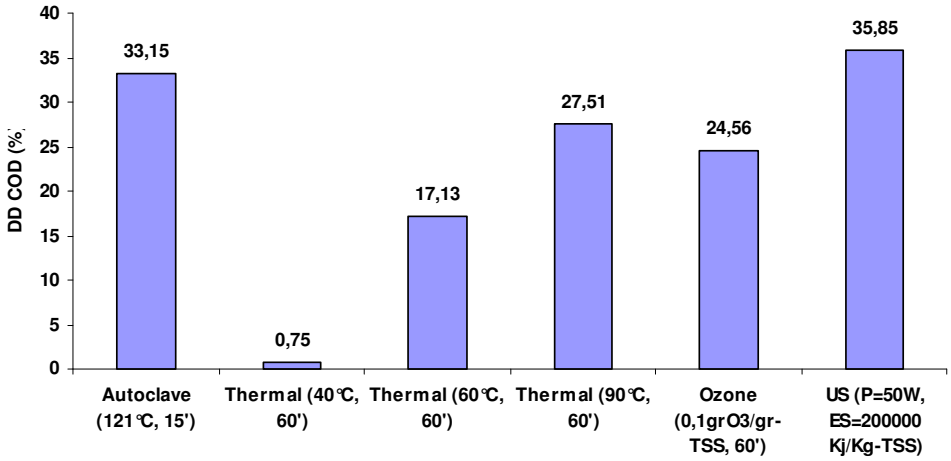

Figure 3-30: Degree of disintegration of COD for different disintegration methods.

Comparison of these three methods reveals that ultrasonic and autoclave treatments are more successful in sludge disintegration than ozonation (about 35% in contrast with 25%). This can be because of higher specific energy of autoclave and ultrasonic treatments compared to ozonation (see Table 3-24). We conclude that:

$$\text{ultrasonic} \geq \text{autoclave} > \text{thermal}\,(90°C) \geq \text{ozonation}$$

b) Solubilization of COD

During these comparative tests, pre-treatments led to flocs breakage, the rupture of the cell walls and membranes of the WAS bacteria, and resulted in release of their cellular components. The cellular components, mainly proteins and carbohydrates, could then be easily hydrolyzed to unit molecules by the extra-cellular enzymes.

Pre-treatment leads in increasing sludge solubilization rate. The solubilization rate of pre-treatment is among others function of pre-treatment method and applied specific energy. Figure 3-31 shows the COD solubilization rate for different techniques of pre-treatment.

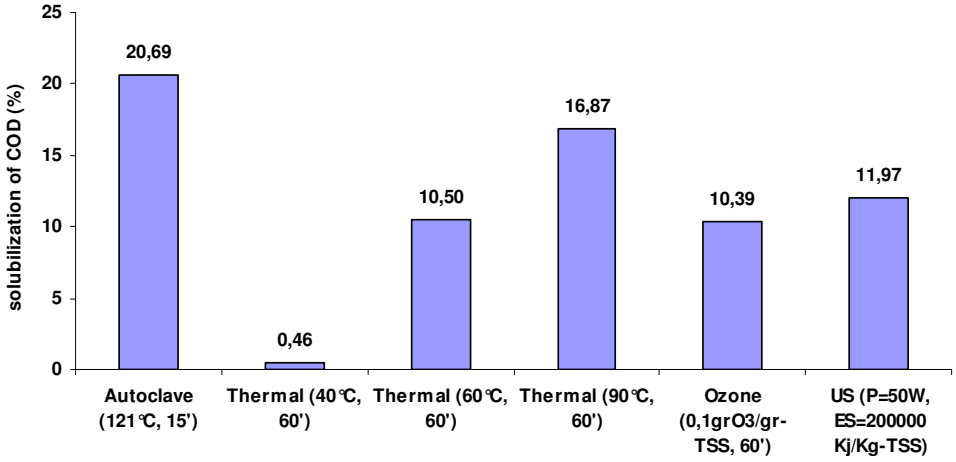

Figure 3-31: Comparison of S_{COD} for different pre-treatment styles.

The highest COD solubilization corresponds to thermal treatment (16.87 for heating at 90°C and 20.69 for autoclave). Also we can see that solubilization rate increases with heating temperature.

Concerning ozonation and sonication, we can say that solubilization rate in this study is nearly the same for both methods (11.97 for US and 10.39 for O_3). Thus we can conclude that thermal treatment has had a better effect on COD solubilization. Bougrier *et al*, (2006) in their studies have also concluded that solubilization was much higher with thermal treatment than with sonication and ozonation.

$$\text{autoclave} > \text{thermal}\,(90°\text{C}) > \text{ultrasonic} \geq \text{thermal}\,(60°\text{C}) \approx \text{ozonation}$$

c) Solubilization of BOD_5

BOD_5 solubilization is subject to the same series of evolutions as COD solubilization; with the only difference that the solubilization rate for thermal treatment is higher than that of ozonation, and the solubilization rate of ozonation is higher than that of sonication (20.11% for thermal treatment, 7.02% for ozonation, and 4.74% for ultrasonic methods).

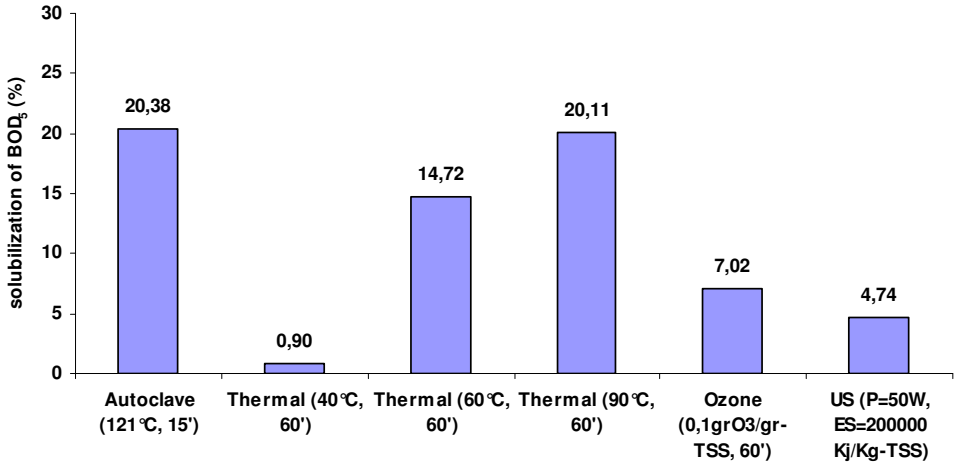

Figure 3-32: BOD_5 solubilization for different pre-treatment methods.

The low percentage of ultrasonic solubilization and ozonation in contrast with thermal treatment shows that heating treatment effectively leads to the solubilization of degrading bacteria; conversely, ozonation and ultrasonic are unable to solubilize these bacteria. The reason may be the high amount of energy applied by heating treatment comparing to ozonation and ultrasonic (see Table 3-24).

autoclave ≈ thermal (90°C) > thermal (60°C) > ozonation > ultrasonic

4.2 Solubilization of proteins and carbohydrates

a) Protein

The solubilization rate in protein for each pre-treatment was compared in Figure 3-33. As we can see, thermal treatment leads to an improvement in solubilization of protein. Moreover, increasing temperature leads to an increase in solubilization rate.

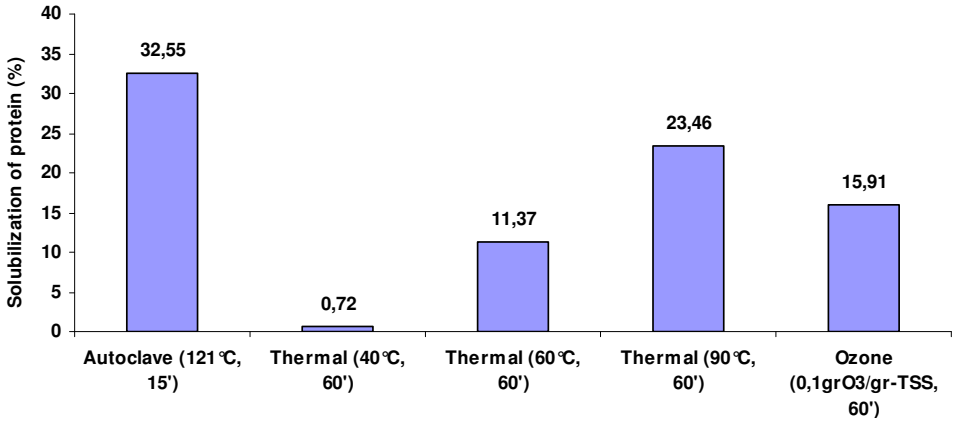

Figure 3-33: Comparison of protein solubilization for different pre-treatment methods.

In this study protein solubilization rates of autoclave and thermal treatment at 90°C were respectively about three times and two times more than ozonation. Autoclave pretreatment led to the best result in terms of protein solubilization. This parameter was not measured for ultrasonic pre-treatment.

autoclave > thermal (90°C) > ozonation > thermal (60°C)

b) Carbohydrate

Carbohydrates solubilization obtained with the different pretreatments is represented in Figure 3-34. The highest solubilization rate is obtained using an autoclave pre-treatment. This rate is roughly 1.6 times more than the one obtained after heating at 90°C and 2.8 times more than that of ozonation. Indeed, autoclave treatment by action on chemical bound could modify carbohydrate structure and increased solubilization.

In our study, carbohydrate solubilization rate for ozonation pre-treatment is less than thermal pre-treatment (90°C) and autoclave (12.01% for ozone contrary to 21.62% and 33.49% for thermal treatment at 90°C and autoclave respectively). Solubilization of this parameter was not measured for ultrasonic method.

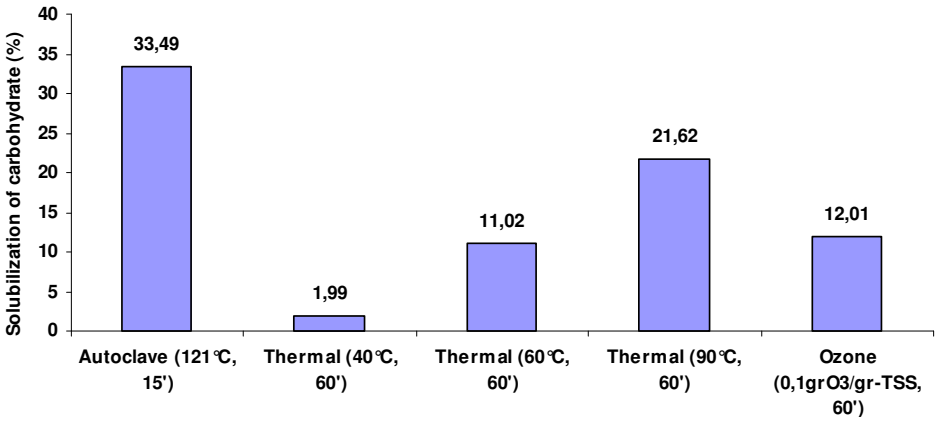

Figure 3-34: Comparison of carbohydrate solubilization of different pre-treatment methods.

For thermal treatment, Barlindhaug and Odegaard (1996) emitted the hypothesis that carbohydrates were more easily degraded than proteins, but proteins were better solubilized. Our study confirms the latter by revealing that protein is solubilized about 10% more than carbohydrates for 90°C thermal pre-treatment, almost 25% more for ozonation and approximately 35% more for 60°C thermal pre-treatment (see Figure 3-33 and Figure 3-34).

autoclave > thermal (90°C) > ozonation ≥ thermal (60°C)

4.3 Solubilization of nitrogen and phosphorus

a) Nitrogen and ammonium

The primary nitrogen sources are proteins that are hydrolyzed to yield ammonia in the digester and disintegration of the sludge may increase free ammonia. Nitrogen in the excess activated sludge was constituted mainly of organic compounds (soluble or particulate) and ammonium ions.

As we can see in Figure 3-35, the highest nitrogen solubilization occurred during the ultrasonic process (56.26%). On the other hand ozonation did not lead to a significant nitrogen solubilization (5.77%). We conclude that comparing to thermal and ozonation pre-treatments, ultrasound can better solubilize nitrogen.

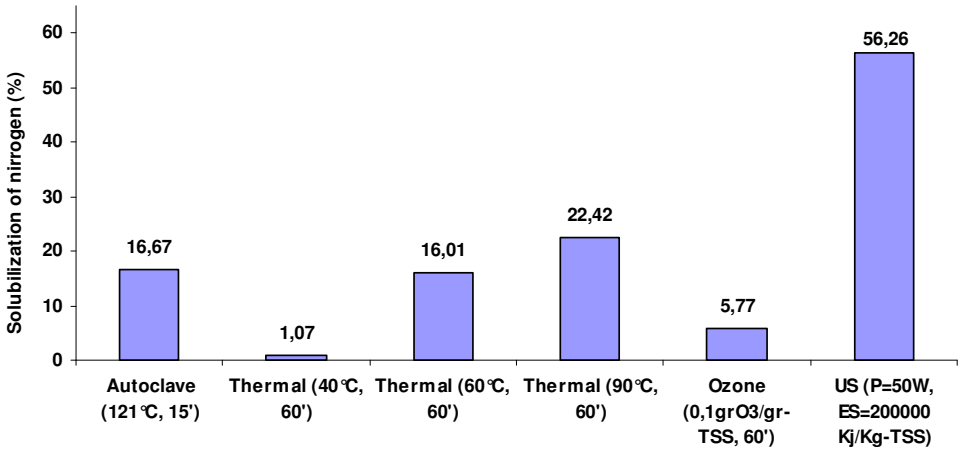

Figure 3-35: Comparison of nitrogen solubilization for different pre-treatment methods.

During the ultrasound process, the quantity of organic nitrogen in particles phase decreased and organic nitrogen concentration in soluble phase and ammonia concentration increased (very little organic nitrogen was transformed into ammonium). Thus organic nitrogen was made soluble. This effect has not been produced in an effective manner during ozonation and thermal pre-treatments.

ultrasonic >> thermal (90°C) > autoclave ≈ hermal (60°C) > ozonation

Figure 3-36 shows that ammonium solubilization rate for ultrasound and ozonation pre-treatments is very low compared to thermal process (95% and 40% against 237%).

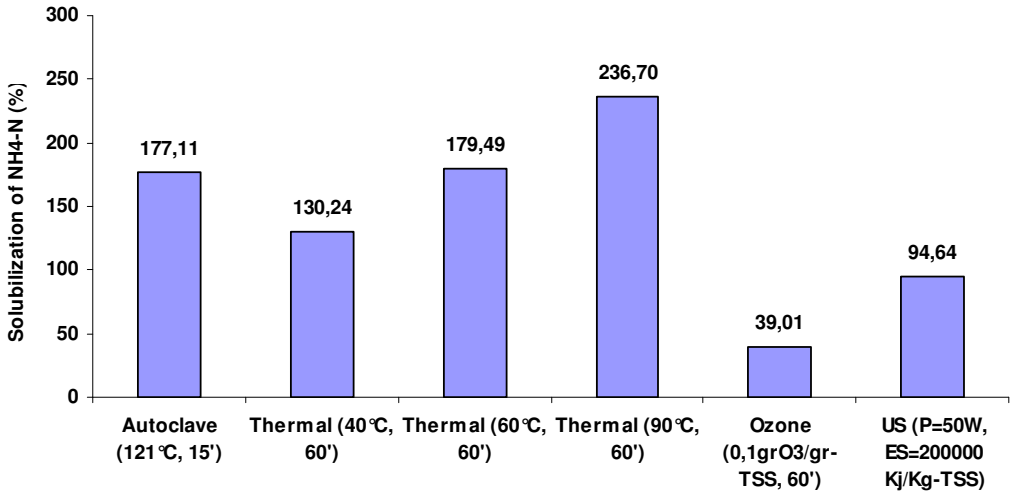

Figure 3-36: Variations of ammonium solubilization in terms of different pre-treatments.

In other words during ultrasonic pre-treatment, nitrogen solubilization (N_S/N_T) increases strongly while NH_4-N solubilization rate increases very slowly. These results comply with the results obtained by Bougrier *et al,* (2005). Thus ultrasonic, contrary to thermal treatment, transfers a great amount of nitrogen from solid phase into soluble phase. This treatment is not successful in transferring organic nitrogen into ammonical nitrogen. Figure 3-36 also shows that in thermal treatment nitrogen and ammonium solubilization rates increase with temperature.

thermal > ultrasonic > ozonation

b) Phosphorus and phosphate

In wastewater, phosphorus exists as orthophosphate (PO_4^{3-}), polyphosphate (p_2O_7) and organically bound phosphorus. Polyphosphate and organic phosphate may be as much as 70% of the incoming phosphorus load.

The solubilization rate in phosphorus for each pre-treatment was compared. As we can see, Figure 3-37 shows that ultrasonic compared to ozonation and thermal treatments, leads to higher phosphorus solubilization (60.97%). It means that ultrasonic pre-treatment transfers phosphorus from solid phase to soluble phase.

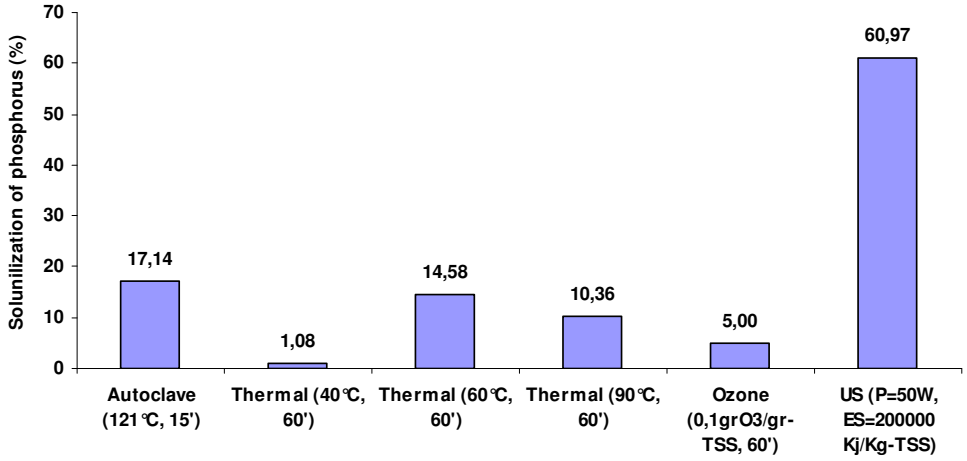

Figure 3-37: Comparison of phosphorus solubilization for different pre-treatment methods.

ultrasonic ≥ autoclave > thermal (60°C) > thermal (90°C) > ozonation

Treatment process can transform all types of sludge phosphorus into orthophosphates. The ability of the different treatment to generate PO_4^{3-} was assessed (Figure 3-38). During ultrasonic pretreatment a great portion of organic phosphorus in soluble phase is transformed

into inorganic phosphorus (e.g. phosphate). On the other hand, ozonation and thermal treatments (except for autoclave) can not effectively transform organic phosphorus into phosphate.

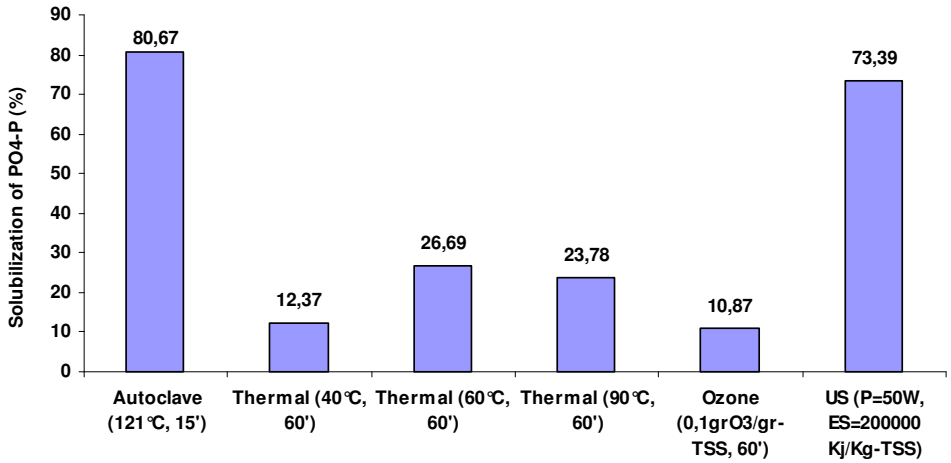

Figure 3-38: Variations of phosphate solubilization in terms of different pre-treatments.

Autoclave (heating plus pressure) is not successful in phosphorus solubilization (17.14%), but can effectively transform organic phosphorus into mineral phosphate (orthophosphate). We can see that ozonation has the lowest particulate phosphorus to organic phosphorus transfer rate.

autoclave > ultrasonic ≥ thermal (60°C) ≥ thermal (90°C) > ozonation

4.4 Solubilization of TSS and VSS

a) TSS and VSS solubilization

In all cases, solubilization of matter was focused on organic solids: mineral solids solubilization was lower than organic solids solubilization.

TSS solubilization results varied significantly from one technique to another. Figure 3-39 shows that in this study the highest TSS solubilization corresponds to ultrasonic pre-treatment (72.80%) and the lowest rates correspond to ozonation (13.82%) and autoclave (11.37%).

In thermal process TSS solubilization rate increases with the treatment temperature which complies with other researches.

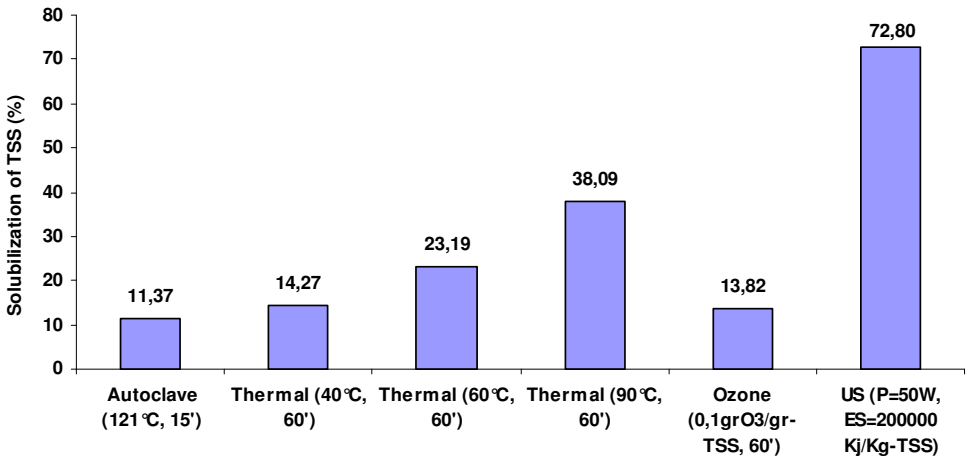

Figure 3-39: Total suspended solids (TSS) solubilization under different pre-treatment conditions.

In our study thermal treatment is less successful than ultrasonic treatment in TSS solubilization; this is not in concordance with other researches. For instance, in Bougrier *et al,* (2006) TSS solubilization for thermal treatment was much more than that of sonication and ozonation (40-45% for thermal against 15% for sonication and 25% for ozonation). This can be due to different pre-treatment conditions (e.g. temperature) or different sludge types and different sludge concentration rates.

ultrasonic ≥ thermal (90°C) > thermal (60°C) > ozonation ≥ autoclave

The same results are obtained for VSS solubilization (see Figure 3-40). In this study the highest VSS solubilization corresponds to ultrasonic pre-treatment (78.85%) and the lowest rates correspond to autoclave (16.71%) and ozonation pretreatment (15.99%), except thermal treatment at 40°C (13.65%).

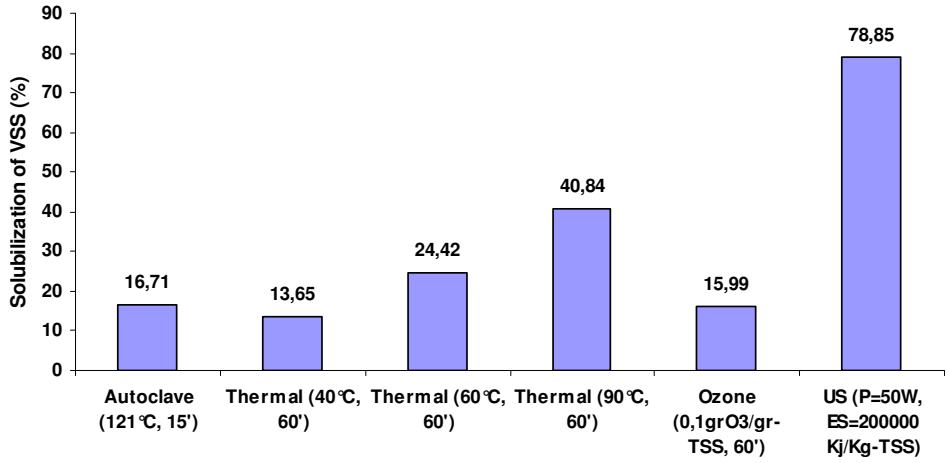

Figure 3-40: VSS solubilized during different pre-treatment methods.

In our study we can see that:

ultrasonic ≥ thermal (90°C) > thermal (60°C) > autoclave ≥ ozonation

b) The TSS/TS ratio

In this literature, TSS solubilization was assessed for the six tested sludge samples. For thermal treatment samples, TSS/TS ratio decreased with increasing treatment temperature and the best result is obtained at 90°C (60.38%). Studying other pre-treatment methods, we can observe that this ratio is the highest for ozonation (85.28%) and ultrasound has the lowest TSS/TS ratio (24.16%). Thus the highest TSS solubilization corresponds to ultrasonic pre-treatment (Figure 3-41).

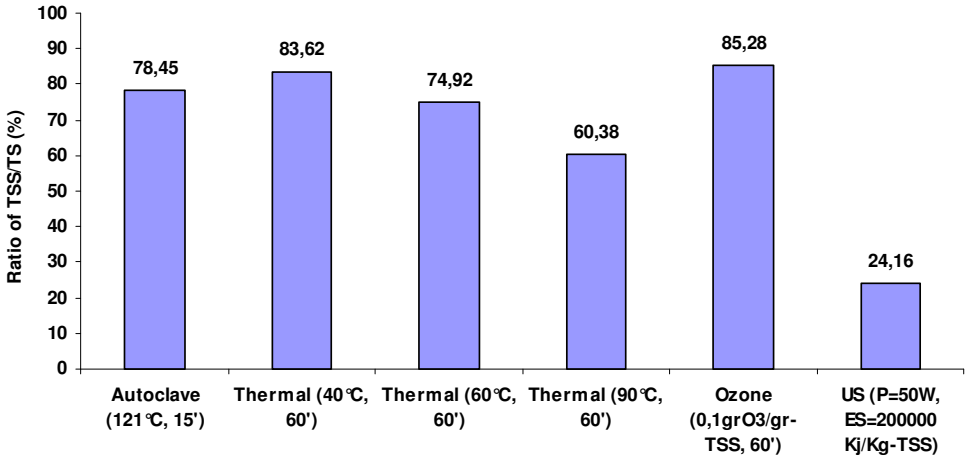

Figure 3-41: Ratio of TSS/TS with respect to different pre-treatments.

ultrasonic ≤ thermal treatment < ozonation

c) The ratio of VSS/TSS

Due to pre-treatment, solids, especially organic solids, were solubilized. Figure 3-42 shows that VSS/TSS ratio is nearly the same for ozonation and sonication pre-treatment, and both lead to a lower VSS/TSS rate compared to thermal process. It means that ultrasound and ozonation treatments yield 10 to 15 percent higher solubilization level than thermal treatment.

Figure 3-42 also shows that in thermal treatment, by increasing temperature a slight decrease in VSS/TSS is observed. We can see that only 4.3% of organic solids are solubilized due to thermal treatment. This is not in accordance with the findings of Bougrier *et al,* (2008). In Bougrier researches, for the temperatures higher than 150°C, organic solids solubilization was more than 43%, while in our studies we observe a much less rate. We can justify this difference

by the fact that Bougrier has used high temperatures (130°C to 190°C), and we have a low temperature range (40°C to 90°C). It can be concluded that using high temperatures can lead to a more effective organic solids solubilization.

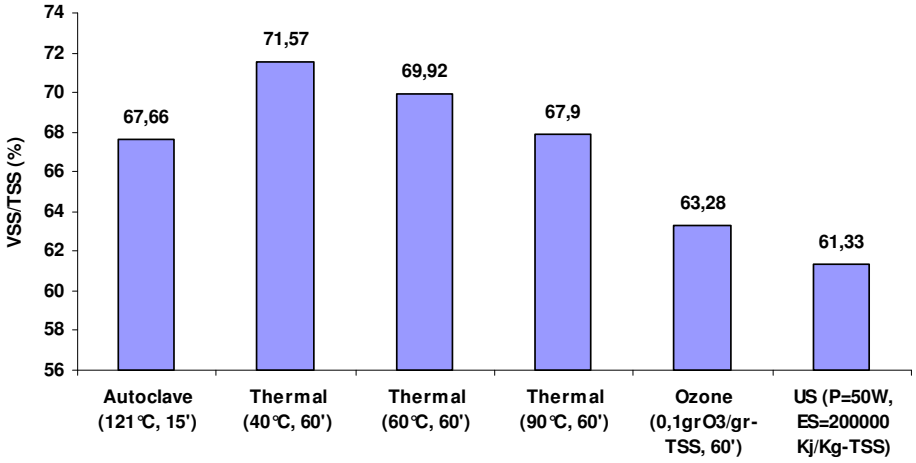

Figure 3-42: VSS/TSS vs. Various pre-treatment methods.

Ozonation has solubilized a more significant portion of organic solids compared to thermal treatment (Figure 3-42). We can conclude that although TSS and VSS solubilization rates are very low (13-16%), a great portion of TSS solubilization is due to organic solids solubilization (see Figure 3-39 and Figure 3-42).

Therefore, for all pretreatments, solid concentration in particles decreased and particles became more mineral. But the mineralization level is different for different pretreatment types. In our study, the following relation in organic matter (VSS) solubilization:

ultrasonic < ozonation < thermal treatment

4.5 Final balance of solubilization obtained with three disintegrating methods

The aim of these treatments is to solubilize and/or to reduce the size of organic compounds, and especially refractory compounds, in order to make them more soluble and easily biodegradable (Bougrier *et al.,* 2006).

In this study, the three pre-treatments (ultrasonic, ozonation and thermal treatment) lead to an increase in sludge solubilization. In all cases, solubilization was focused on organic solids: mineral solids solubilization was lower than organic solids solubilization.

Prior studies have shown that pre-treatment helped to obtain a better sludge digestion and increased sludge solubilization in waste water treatment plants (Salsabil *et al.,* in press).

We have considered three types of pre-treatment and compared them in order to determine the optimum pre-treatment. These pre-treatments are:

1. Ultrasonic (SE = 5000 to 200000 kJ.kg-TSS^{-1}, P = 50, 100, 200 W).
2. Ozonation (C = 0.011 to 0.15 gO_3.g-TSS^{-1}, t = 15 to 120 minutes).
3. Thermal treatment (1^{st} series: Bain-Marie T = 40, 60, 90°C, t = 10 to 480 minutes and 2^{nd} series: autoclave T = 121°C, t = 15 min, P = 1.5 atm).

Table 3-25 summarizes best COD and TSS solubilization rates for each of these treatments.

Table 3-25: Comparison of the results obtained for each technique.

	Ultrasonic (200000 kJ/kg-TSS)			Ozonation (gO_3/g-TSS)		Thermal treatment				
	50 (W)	100 (W)	200 (W)	T=60 min, C=0,101 gO_3	T=90 min, C=0,139 gO_3	Bain-marie (40°C, 60 min)	Bain-marie (60°C, 60 min)	Bain-marie (90°C, 60 min)	Bain-marie (90°C, 120 min)	Autoclave (121°C, 15 min)
S_{COD} (%)	11.97	12.48	12.66	10.39	8.82	0.46	10.50	16.87	19.12	20.69
COD_S/COD_T (%)	18.93	18.08	17.28	9.56	9.01	1.09	9.86	17.20	16.67	19.60
DD_{COD} (%)	35.85	37.37	37.92	24.56	20.86	0.75	17.13	27.51	31.18	33.15
S_{TSS} (%)	72.80	51.19	38.46	13.82	16.76	14.27	23.19	38.09	27.84	11.37
TSS/TS (%)	24.16	43.36	54.67	85.28	82.36	83.62	74.92	60.38	70.38	78.45
VSS/TSS (%)	61.33	67.17	69.56	63.28	65.52	71.57	69.92	67.9	69.07	67.66

As it can be seen in Table 3-25, for the ultrasonic pre-treatment, the sludge solubilization rates (S_{TSS}) are in most cases much higher for 50W than 100 and 200W. For S_{COD} and DD_{COD} the value is higher for the case of 200W, however the differences are negligible (S_{COD} = 11.97%, 12.48% and 12.66% for 50W, 100W and 200W respectively). Thus specific energy of 200000 kJ.kg-TSS^{-1} and power of 50W were selected. The determining parameter for increasing COD solubilization is specific energy and input power has not a significant effect. As a result, we can apply a low power during a long duration to attain desired specific energy. This will lead to a better efficiency because at short ultrasound application times, sludge floc agglomerates are dispersed while no cell destruction occurs. At longer treatment times or higher ultrasound

intensities, the microbial cell walls are broken and intracellular material is released to the liquid phase (Tiehm *et al.,* 2001-b).

Concerning ozonation, for most parameters sludge solubilization (S_{COD}, COD_S/COD_T, DD_{COD}, and VSS/TSS) after ozonation during 60 minutes with a dosage of 0.101 g O_3 is higher than 90 minutes of ozonation with 0.14 g ozone. The exception is TSS/TS for which the results are however close enough to be considered equal (82.36% against 85.28%). Therefore, ozonation during 60 minutes with a dosage of 0.101gO3.g-TSS^{-1} were selected Because of ozonation with dosage higher than 0.1g O_3 led to decreased of removal yield. Thus, lower pretreatment time, typically about 1 hour has been recommended for cost effective treatment approach.

For thermal treatment, solubilization rates for autoclave are higher than Bain-Marie for all parameters but S_{TSS}. For second series of thermal treatment, TSS solubilization rate of Bain-Marie (90°C, 60min) is 26.91% higher than that of Bain-Marie (90°C, 120 min). But COD solubilization rate for Bain-Marie (90°C, 120 min) is 12.24% higher than the same parameter for Bain-Marie (90°C, 60min). In other words the difference is more considerable for TSS (38.09% against 27.84%) than for COD (19.12% against 16.78%). It means that using Bain-Marie at 90°C of temperature during 60 minutes is more cost effective. Between Bain-Marie and autoclave pre-treatments, considering that TSS solubilization is too poor for autoclave pre-treatment (11.3% against 38.09%) Bain-Marie is preferred to autoclave.

In thermal treatment to compare low thermal treatment with high thermal treatment and to determine the rate of their biodegradability, thermal treatment at 40°C and 60°C and autoclave (121°C and 15 min) with thermal treatment (90°C and 60 min) were selected and they were investigated under aerobic and anaerobic conditions. The highest rate of solubilization of thermal treatment (40°C and 60°C) occurred in 60 minutes like the thermal (90°C) and this is why thermal treatment at 40°C, 60°C and 90°C during 60 minutes and autoclave for biological digestion were used in the next step.

As we can see in Table 3-26, highest solubilization rate, degree of disintegration, and sludge elimination ratio, for all items but COD (11.97% for ultrasonic against 16.87% for thermal treatment) and BOD (20.11% for thermal against 4.74% for ultrasonic treatment), correspond to ultrasonic pre-treatment.

Table 3-26: Comparison of three pre-treatment types.

	Sonication (50W & 200000 kJ/kg-TSS)	Ozonation (60 min & 0.101 gO_3/ g-TSS)	Thermal (90°C & 60 min)
S_{COD} (%)	11.97	10.39	16.87
S_{BOD} (%)	4.74	7.02	20.11
DD_{COD} (%)	35.85	24.56	27.51
S_{TSS} (%)	72.80	13.82	38.09
S_{VSS} (%)	78.85	24.38	40.84
TSS/TS (%)	24.16	85.28	60.38
VSS/TSS (%)	61.33	63.28	67.90
BOD_5/COD	28.69	29.69	49.57
$S_{Protein}$ (%)	-	15.91	23.46
$S_{Carbohydrate}$ (%)	-	12.01	21.62
$S_{nitrogen}$ (%)	56.26	5.77	22.42
$S_{phosphorus}$ (%)	60.97	5.00	10.36

Table 3-26 shows that DD_{COD} and S_{COD} results for the three pre-treatments. Ultrasound pre-treatment led to a higher DD_{COD} compared to ozonation and thermal treatment (23-31% higher rate). At the same time, Thermal treatment led to a higher S_{COD} value than ultrasound (about 30% more) and ozonation (38% more) however this rate does not considerably vary for different pre-treatment types. The COD solubilization rates for ozonation and ultrasound treatment are relatively close (10.39% against 11.97%).

The treatment allowing the highest TSS solubilization rate is by far ultrasound (Table 3-26). This table also shows that the highest biodegradability rate (BOD_5/COD) is obtained using thermal treatment and least VSS/TSS ratios is obtained using ultrasonic and ozonation treatments suggesting a high matter elimination rate after sonication or ozonation compared to other methods. On the other hand, thermal treatment which is not successful in TSS solubilization is more effective in increasing sludge biodegradability compared to ozonation and sonication.

As a result, considering that S_{COD} in thermal treatment is higher than other methods, and considering than thermal treatment is more economic than sonication or ozonation and thermal energy is often cheaper than electrical energy, we can say that thermal treatment is more successful in solubilization of COD, BOD and biodegradability of BOD compared to ultrasonic and ozonation treatment and in contrast, ultrasonic pre-treatment is more successful in solubilization of TSS, VSS and degree of disintegration compared to ozonation and thermal pre-treatment.

In this manuscripts, to investigate the rate of sludge biodegradability, the rate of sludge solubilization pre-treated in ultrasonic, ozonation and thermal treatment methods were measured with a sample control (unpre-treated) and were chosen to perform a biological digestion in batch reactors under aerobic and anaerobic conditions (in sequence step).

In ultrasonic method, between 12 solubilized samples (with different specifics energy), the sample with ES = 200000 kJ.kg-TSS^{-1} and power of 50 W during 80 minutes that had the highest COD solubilization and the most TSS reduction was chosen (see Table 3-8).

In ozonation method, between 5 analyzed samples in different dosages, the sample with a dose 0.101gO_3.g-TSS^{-1} at 60 minutes that had the highest solubilization and highest removal yield of TSS was chosen (see and Table 3-13).

In thermal treatment method, between 18 analyzed samples (with different temperatures and times), the samples in temperatures at 40°C, 60°C and 90°C and duration of 60 minutes that had the highest TSS elimination and COD solubilization were selected. An autoclave sample in temperature = 121°C, Pressure = 1.5 bar and duration of 15 minutes was also chosen (under standard condition = STP) and the results of its solubilization was investigated (see Table 3-19 and Table 3-22).

Table 3-27: The rate of solubilization (%) in terms of specific energy and type of treatments.

	SE (kJ/kg-TSS)	DD_{COD} (%)	S_{COD} (%)	S_{BOD} (%)	S_{TSS} (%)	S_{VSS} (%)	$S_{nitrogen}$ (%)	$S_{phosphorus}$ (%)	S_{PO4-P} (%)	S_{NH4-N} (%)	$S_{Protein}$ %	$S_{Glucose}$ (%)
Ultrasonic	197206	35.85	11.97	4.74	72.80	78.85	56.26	60.97	73.39	94.64	-	-
Autoclave	608382	33.15	20.69	20.38	11.37	16.71	16.67	17.14	80.67	177.11	32.55	33.49
Ozonation	75692	25.56	10.39	7.02	13.82	6.80	0.64	0.58	2.99	57.61	3.65	1.80
Thermal (40°C)	227129	0.75	0.46	0.9	14.27	19.53	0.3	1.33	5.49	18.80	0.1	0.12
Thermal (60°C)	340694	17.13	10.5	14.72	23.19	24.42	16.01	14.58	26.69	865.49	11.37	11.02
Thermal (90°C)	511041	27.51	16.87	20.11	38.09	40.84	22.42	10.36	3.77	1052.75	23.46	21.61

All samples in the next step (chapter 3–part 2) under aerobic and anaerobic will be biologically digested and the rate of biodegradability and volume of biogas production will be studied. Table 3-27 shows the rate of solubilization of different parameters in terms of specific energy and type of pre-treatment.

4.6 Comparison of energy consumption

The performance of various disintegration methods can be compared on the basis of the specific energy applied per mass of solids treated (ATV, 2000). Specific energy is defined as the amount of mechanical energy that stresses a certain amount of sludge.

The success of a disintegration method depends strongly on the amount of organic matter that is solubilized: it is quantified by the degree of disintegration. This parameter is determined by released or solubilized COD compared to the total initial COD or TSS (Müller, 1996).

Solubilization level in terms of specific energy is presented in Figure 3-43 for different disintegration methods. As we can see in Figure 3-43-a, thermal treatment (90°C during 60 minutes) and autoclave disintegration led to high COD solubilization (18.97% for thermal (90°C) and 20.69% for autoclave), whereas considerably less COD was released with thermal disintegration at 40°C (1.21%). For all thermal pre-treatment, with increased specific energy the rate of COD solubilization was rising and there was a logarithmic relation with a correlation factor of 0.85. Ultrasonic and ozone treatment yield medium degrees of disintegration with relatively low energy input. In fact, the degradability of the solubilized COD depends on the disintegration method. In this study, with increased SE, the rate of S_{COD} for ozonation increased too and its maximum occurred at SE = 75600 kJ.kg-TSS^{-1} (10.39%) and then by augmenting SE to 151000 kJ.kg-TSS^{-1}, the rate of S_{COD} reduced and attained 8.39%. Regarding US, by augmenting SE, the rate of COD solubilization increased and there was a logarithmic correlation (R^2 = 0.98) between these two parameters.

In Figure 3-43-b ultrasonic, thermal and ozonation treatment are compared when we look at the solubilization of TSS and the specific energy used. Ultrasonic treatment attains highest solubilization of TSS (72.80%) with a relatively medium energy input (200000 kJ.kg-TSS^{-1}) and ozone treatment reaches low solubilization of TSS (from 4.91% to 14.23%) with a low energy input (from 18900 to 151000 kJ.kg-TSS^{-1}). This means that by raising SE, the solubilization rate will increase logarithmically. Figure 3-43-b also illustrates that thermal treatment (40, 60 and 90°C) reaches the medium solubilization with the applied high energy. At this part, no relations were found between specific energy and solubilization of TSS.

Nitrogen solubilization was plotted versus the specific energy applied (Figure 3-43-c). The figure shows that, increasing specific energy, the amount of nitrogen solubilization in the ultrasonic process increases (linearly and R^2 = 0.985) and regarding thermal treatment (90°C, 60°C), although we are in the third and forth phases of the amount of energy, we have a middle

rate of solubilization. In this study, by increasing the specific energy (SE), nitrogen solubilization (S_N) will increase logarithmically too (R^2 = 0.90). Regarding ozonation, the amount of applied energy is not high enough and so is the solubilization. For ozonation treatment, the highest solubilization (17.31%) corresponds to highest SE (151000 kJ.kg-TSS^{-1}), in the other words, the relation between these two parameters is linear.

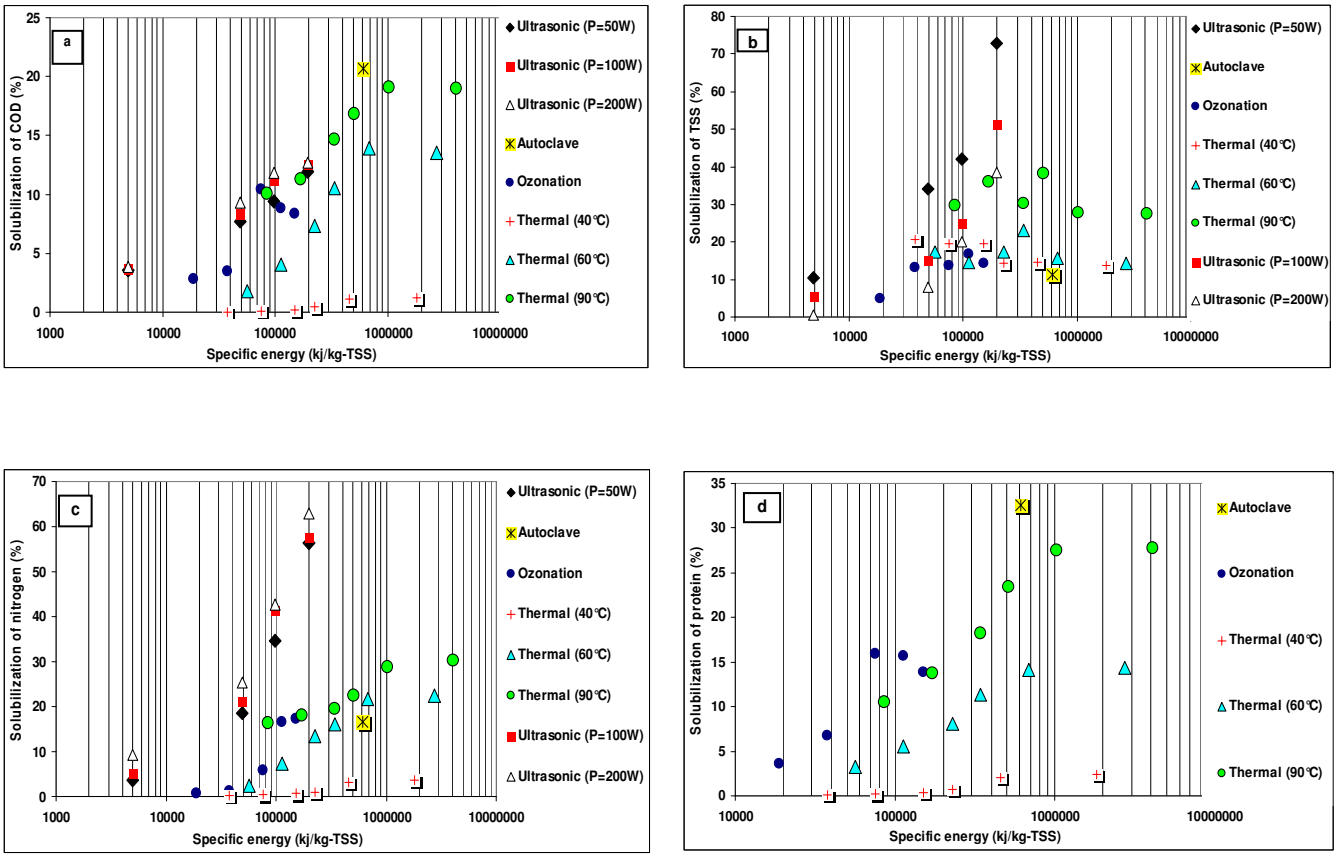

Figure 3-43: Solubilization as a function of the specific energy for various disintegration methods.

Figure 3-43-d shows that in thermal treatment (90°C) the amount of solubilization increases with the increase of applied energy (R^2 = 0.87). Regarding ozone, although applied energy is lower (from 18900 to 151000 kJ.kg-TSS^{-1}) comparing to thermal treatment (from 27800 to 4100000 kJ.kg-TSS^{-1}), the amount of solubilization is better for a temperature higher than 60°C. At thermal treatment, the highest SE corresponds to thermal at 90°C (from 85000 to 4100000 kJ.kg-TSS^{-1}) and thus, this thermal treatment has the highest solubilization of protein (from 10.52% to 27.77%) and this increase is logarithmic.

Regarding the power consumption, thermal and ultrasonic treatments were more suitable than ozonation treatment for the disintegration. An association of one of these physico-chemical

treatments with an activated sludge system is necessary to prove the potential minimization of sludge production and the whole treatment performance. Ultrasound and thermal treatment use more energy. But thermal energy is accessible; it is often cheaper than electrical energy, which is necessary for the other methods.

Part 2

Biological treatment

Study of biodegradability enhancement for pre-treated waste activated sludge

Introduction

In many European countries, the agricultural use of stabilized sludge is already prohibited or is rapidly decreasing due to more stringent regulations. Sludge disposal in landfills will also be strongly limited in the near future, because new legislation allows disposal of sewage sludge only with an organic matter content of less than 5%. The amount of sludge to be incinerated will consequently increase. One way to reduce these disposal costs is to use enhanced biological mineralization, which is positively influenced by sludge disintegration.

Biological methods such as aerobic and anaerobic digestion are widely used for sludge stabilization. Biological stabilization reduces the quantity of sludge to be disposed of, minimizes the offensive odor, and produces useful by-products, such as methane gas (during anaerobic digestion) and soil conditioners. Aerobic or anaerobic digestion of waste activated sludge (WAS), however, is often slow due to the rate limiting cell lysis step (Li and Noike, 1992). This is because the cell wall and the membrane of prokaryotic organisms consist of complex organic materials such as peptidoglycan, teichoic acid, and complex poly-saccharides, which are recalcitrant to biodegradation (Pelczar *et al.,* 1993) and requires a long retention time of 30 to 60 days during biological treatment. Thus, the WAS needs to be pretreated to enhance the digestibility and reduce the retention time.

Sludge disintegration implies floc destruction and cell disruption, which releases solubilized organic matter, improves aerobic or anaerobic degradation and reduces excess sludge production. Floc destruction and cell disruption can be achieved by various methods. The forces applied to solids can be mechanical, chemical, thermal, biological or a combination of these. So far, most full-scale applications have been based on the theses methods.

In this part we will proceed in studying sludge digestion and aerobic or anaerobic biodegradability for different techniques (ultrasound, temperature, ozone) using pilot plant methods. Table 3-28 introduces the characteristic of pretreated samples featuring the highest solubilization rates in the bench scale studies (chapter 3 – part 1) and will undergo the aerobic and anaerobic biological digestion. One of our objectives is to validate the best association of a

specific sludge pretreatment (ultrasonic, ozonation, and thermal treatment) and a biological treatment (aerobic or anaerobic digestion) in regard to biodegradability and sludge reduction improvement. The objectives of the pre-treatment were to improve biodegradability but also to achieve sludge reduction. This mechanism can be due to:

- Uncoupling metabolism in which excess free energy would be directed away from anabolism so that the production of biomass can be reduced. Uncoupled metabolism is observed under some conditions such as : the presence of inhibitory compounds, heavy metals, excess energy source (high S/X ratios), abnormal temperatures and limitation of nutrients (Wei *et al.,* 2003),
- Or to maintenance metabolism: micro-organisms satisfy their maintenance energy requirements rather than producing additional biomass (Wei *et al.,* 2003).

In a second hand, another objective is to qualify this efficacy in terms of energy consumption.

Table 3-28: The characteristics of studied sludge in first and second pilots.

Type of Pilot	Type of treatment	Range of treatment	Type of Pilot	Type of treatment	Range of treatment
Pilot Plant (1) (Aerobic & Anaerobic)	Control -1	Condition STP TSS = 11.66 g/l	Pilot Plant (2) (Aerobic & Anaerobic)	Control -2	Condition STP TSS = 20 g/l
	Ultrasonic	P =50 Watt t = 80 min SE = 205832 kJ/kg-TSS		Thermal (40)	P = 400 Watt T = 40°C t = 60 min SE = 144000 kJ/kg-TSS
	Thermal (90)	P = 900 Watt T = 90°C t = 60 min SE = 555764 kJ/kg-TSS		Thermal (60)	P = 600 Watt T = 60°C t = 60 min SE = 216000 kJ/kg-TSS
	Autoclave	P = 6000 Watt T = 121°C t = 15 min P = 1.5 atm SE = 661602 kJ/kg-TSS		Ozonation	P = 180 (W) t = 60 (min) M O_3 = 0.101 g O_3/g TSS SE = 46286 kJ/kg-TSS

We will compare sludge digestion and biodegradability of the treated sludge with those of untreated sludge in order to better understand the effect of pre-treatment on the sludge.

At the end test results will let us compare sludge obtained from these three pre-treatments along with the control sample (under aerobic and anaerobic conditions), and further choose the most cost effective pre-treatment leading to the highest sludge elimination efficiency.

In all experiments, measurements were done in at least two independent samples. In the corresponding figures, data represent the mean and error bars represent the variability between duplicates.

In this section, the first part presents the results of aerobic digestion after the three types of pretreatments optimized in the last chapter. The second part covers the results of the same samples treated by anaerobic digestion. In the third part, the two biological treatments are compared and discussed and finally in the fourth part, economic evaluation is presented.

5. Aerobic sludge digestion processes

The purpose of aerobic digestion is to stabilize organic matter, to reduce sludge volume, and to eliminate pathogenic organisms. In general, sludge is aerated for 20 day or more. Volatile solids are reduced by biological activity.

The aerobic digestion process is an extension of the extended aeration process. The volatile material in the wastes is digested to a reasonable maximum of up to 45% destruction of volatile solids (Spellman, 2000). The decomposition of solids and re-growth of organisms is maintained until the available energy in active cells and the storage of waste materials are sufficiently low and stable enough for disposal.

In this part, the objective was to understand waste activated sludge modification due to pre-treatment processes (ultrasonic, ozonation and thermal) and its effects on sludge aerobic biodegradability and sludge reduction.

The major concern with sludge digestion was volatile solids reduction and production of soluble organic compounds from the digested solids.

The kinetics and removal efficiencies of the different parameters of interest (COD, BOD_5, nitrogen, phosphorus, proteins, carbohydrates, TSS, VSS …) are presented thereafter.

5.1 Biodegradability improvement for pre-treated sludge

To enhance the biodegradability of the organic matter in sludge, it is necessary to solubilize or hydrolyze this matter prior to aerobic or anaerobic sludge digestion. The solubilization techniques proposed so far include mechanical disintegration using ultrasonic (50W, 80 minutes and 200000 kJ.kg-TSS^{-1}), thermal treatment based Bain-marie (40, 60 and 90°C at 60

minutes) and autoclave method (121°C, 1.5 bar and 15 minutes) and oxidative treatments using ozone (0.101 gO_3.g-TSS^{-1} and 60 minutes), as we have seen in chapter 3, part 1.

The biodegradability enhancement is assessed across C, N, P removal efficiencies and instantaneous specific rate measurement.

5.1.1 Evaluation of the BOD_5 and COD elimination

The methods of improvement of the biodegradability of particular substrate are mainly based on better accessibility of the substrate for micro-organisms. Pre-treatment of sewage sludge by mechanical, chemical, or thermal disintegration can improve the subsequent aerobic digestion due to the release of organics materials into the liquid phase (floc breakage and or sludge disintegration).

5.1.1.1 COD removal efficiency

- **Total COD removal**

The total COD elimination efficiency under aerobic conditions as a function of the pre-treatment (and specific energy) was investigated. Table 3-29 shows that the highest COD_T level in first pilot is attained for the sonicated sample with 81.89% of elimination efficiency (SE = 205800 kJ.kg-TSS^{-1}). The second place is for thermal treated sludge (autoclave = 72.93% and 90°C = 72.16% with high specific energy). In the second pilot the highest elimination efficiency corresponds to ozone pretreatment (73.82% with low specific energy).

COD_T elimination efficiency of different pretreatments was studied as a function of removal yield enhancement compare to the control (Table 3-29). COD removal yield improvement is calculated as the ratio of the removal yield of pre-treated sample (after fermentation) to the removal yield of the control sample of the same pilot plant. The highest COD_T elimination efficiency corresponds to ozonation (1.26 times more than control sample). Thermal treatment (90°C and autoclave) have a much higher specific energy than ozonation but a lower COD_T removal yield. In this work, for the same range of specific energies, the COD_T removal efficiencies are comparable: the lowest COD_T elimination efficiency corresponds to 90°C and autoclave treatments (removal yield enhancements of 1.02 and 1.03 times more than control sample respectively). In the first pilot, the highest COD_T elimination efficiency corresponds to ultrasonic treatment featuring the same efficiency as thermal treatment (60°C) in the second pilot (removal yield enhancement of 15% more than control sample for both treatments).

Ozonation has a much lower specific energy than ultrasonic and thermal treatment (46300 kJ.kg-TSS^{-1}) but its COD_T elimination rate is higher than ultrasonic and thermal treatment (40, 60, 90°C and autoclave). Although the solubilization rate of ozonation is as low as ultrasonic and thermal treatment (only 10.12%) but its elimination efficiency is rather high. It can be concluded that ozonation, with a low applied energy, permit to reach very good COD removal efficiency.

Table 3-29: Elimination efficiency of COD in terms of specific energy and removal yield of improvement in aerobic digester for two series of experiments.

	Control 1	Ultrasonic	Thermal (90°C)	Autoclave	Control 2	Ozonation	Thermal (40°C)	Thermal (60°C)
Total COD Removal yield (%)	70.94	81.89	72.16	72.93	58.53	73.82	63.75	67.25
Removal yield improvement	-	1.15	1.02	1.03	-	1.26	1.09	1.15
Soluble COD Removal yield (%)	72.34	92.28	83.14	88.78	60.99	85.69	72.52	83.44
Particulate COD Removal yield (%)	70.83	72.81	69.62	69.75	58.37	71.90	62.99	64.90
Solubilization (%)	-	42.62	11.35	10.19	-	10.12	3.82	8.14
Specific energy (kJ/kg-TSS)	0.0	205800	555700	661600	0.0	46300	144000	216000

COD_T removal efficiency improvements are thus dependant upon specific energy: it increased with decreasing specific energy (see Table 3-29).

- **Soluble and particulate COD removal**

Particulate and soluble COD removal enhancements were investigated. Figure 3-44 shows the repartition between soluble and particulate COD, after and before digestion. Before digestion, total COD is approximately the same for all samples, and due to pretreatment, soluble portion of COD increases due to pretreatment. For both pilots, COD elimination efficiency for pretreated sample was more than un-pretreated (control) sample. The highest solubilization (before digestion) occurred for sonication treatment (42.62% with SE = 205800 kJ.kg-TSS^{-1}) and the lowest solubilization rate occurred for thermal treatment at 40°C (3.82% with SE = 144000 kJ.kg-TSS^{-1}). Therefore, the highest and the lowest rates of soluble COD removal occurred respectively for sonication (92.28%) and 40°C thermal treatment (72.52%). But the highest COD_S elimination yield corresponds to ozonation processes (1.41 times more than control sample with SE = 46300 kJ.kg-TSS^{-1}).

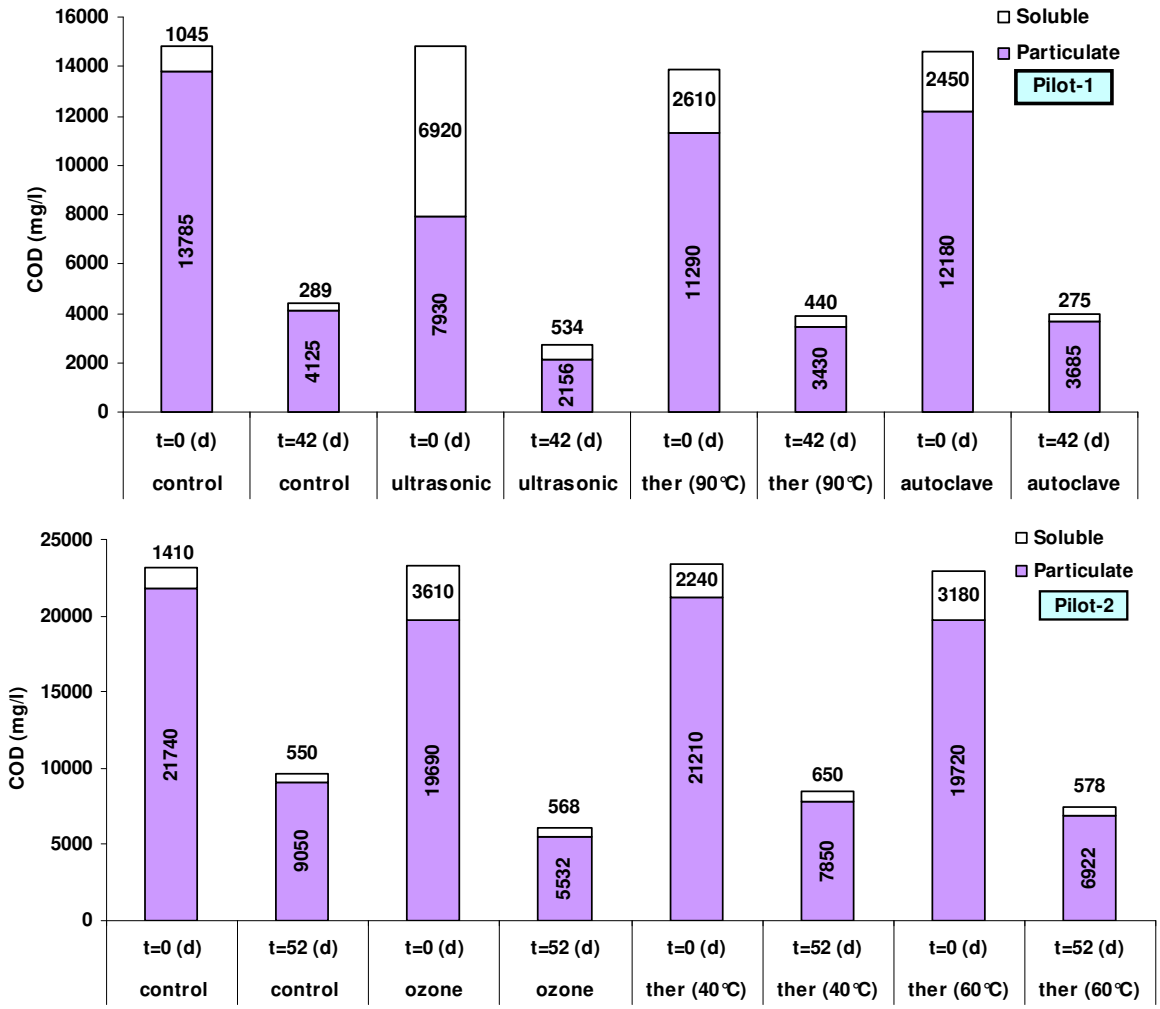

Figure 3-44: Solubilization and biodegradation of COD (soluble & particulate) before and after digestion.

In both soluble and particulate phase, COD elimination efficiency for all samples was higher than control sample and also, the highest removal yield corresponded to sonication in the first pilot and ozonation in the second pilot. Calculating and comparing elimination efficiency of COD_S and COD_P reveal that for all samples, elimination efficiency of COD_S is 14% to 22% more than elimination efficiency of COD_P.

COD_S and COD_P elimination efficiencies of different pretreatments can be classified in terms of removal yield enhancement.

$$COD_S \rangle \underset{1.41}{\text{ozonation}} > \underset{1.37}{\text{thermal (60°C)}} > \underset{1.28}{\text{ultrasonic}} > \underset{1.23}{\text{autoclave}} > \underset{1.19}{\text{thermal (40°C)}} > \underset{1.15}{\text{thermal (90°C)}}$$

The highest COD_S elimination efficiency corresponds to ozonation (85.69% with SE = 46300 kJ.kg-TSS^{-1}). Thermal treatment (90°C and autoclave) have a much higher specific energy than ozonation but a lower COD_S removal yield. Removal yield improvement for thermal treatment

at 90°C and autoclave at 121°C were respectively 1.15 and 1.23 times more than control sample. For ozonation, this improvement is 1.41 times more than control sample. Second and third places go to 60°C thermal treated sample (83.44%) and ultrasonic sample (92.28%) for which removal yield improvements were respectively 1.37 and 1.28 times higher than control sample. At the end of the aerobic digestion, there is still some part of remaining soluble COD.

Removal improvement of COD in particulate phase is like soluble phase with the difference that removal yield improvement for COD_P is less than COD_S. Particulate COD biological elimination improvement can be summarized as follows:

$$COD_P \underset{1.23}{\rangle} \text{ozonation} > \underset{1.11}{\text{thermal}\,(60°C)} > \underset{1.08}{\text{thermal}\,(40°C)} > \underset{1.04}{\text{ultrasonic}} > \underset{1.00}{\text{autoclave}} \geq \underset{0.99}{\text{thermal}\,(90°C)}$$

Both soluble and particulate COD removals are improved by the pre-treatment and especially by ozonation.

- **Dynamics of soluble COD removal efficiency**

The soluble COD elimination efficiency under aerobic conditions was studied during two series of experiments (Figure 3-45). In the first series of experiments the rate of COD elimination (rate and amount of degradation) is quite high during first 12 days and slows down afterwards. This is due to the important amount of soluble COD generated by the pre-treatment processes (ultrasound process and thermal treatment at 90°C and autoclave at 121°C). Thus during digestion process bacteria could quickly absorb organic materials. For second series of experiment the high-speed period lasts 15 days. But for this pilot, COD solubilization was lower, and thus more time is needed for digestion to accomplish.

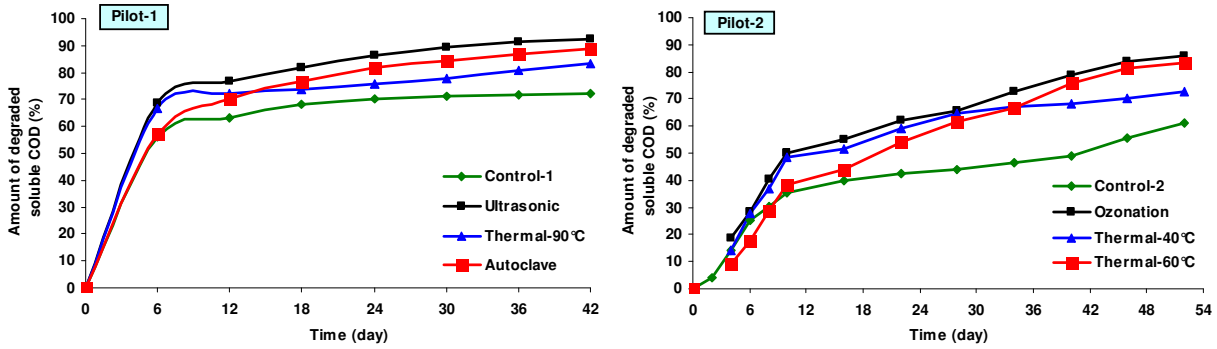

Figure 3-45 : Variation of COD_S in batch reactors during sludge aerobic digestion.

The instantaneous specific rates of soluble COD removal (chapter 2, eqation 11) were calculated to provide a better understanding of soluble COD removal efficiencies under aerobic

conditions. As it is demonstrated on Figure 3-46, the instantaneous specific rates (q_{COD}) for soluble COD removal were positively influenced by sonication, ozonation and thermal treatment.

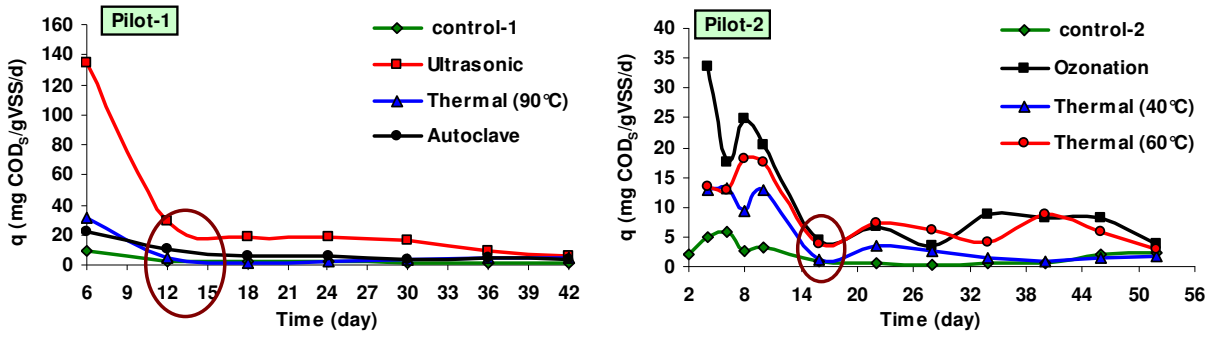

Figure 3-46: Instantaneous specific rates (q_{COD}) for COD_S over time under aerobic condition.

The highest q_{COD} (The specific instantaneous soluble COD consumption rate) for the first pilot corresponded to ultrasonic reactor (134.13 $mgCOD_S.g\text{-}VSS^{-1}.d^{-1}$), and between the 6th and the 9th days, the rate of q_{COD} drastically decreased over the time until 12th to 15th day and decreases gradually to zero afterwards. In this pilot the slope of q_{COD} diminution in ultrasonic reactor is remarkable compared to other samples.

In second pilot, the highest q rate corresponds to ozonation (33.34 $mgCOD_S.g\text{-}VSS^{-1}.d^{-1}$) reactor while the lowest rate is observed on the control sample (3.86 $mgCOD_S.g\text{-}VSS^{-1}.d^{-1}$). In this pilot the q_{COD} increases initially during 5 days and after this period, q_{COD} drastically decreased to reach a very low value (close to 0). The highest q_{COD} decrease happens at 15th day.

Ultrasonic treatment with good level of COD solubilization (42.62%) led to interesting results in terms of COD_S removal yield improvement (≈ 28%) This result is in accordance with previous studies. Yu *et al.* (2008) demonstrated that ultrasonic treatment prior to aerobic digestion led to a considerable soluble COD removal improvement due to enzymatic activity improvement.

The best combination for soluble COD removal improvement was attributed to ozonation treatment followed by an aerobic digestion.

5.1.1.2 BOD_5 removal yield and BOD_5/COD_s ratio

The BOD_5 removal efficiency is studied in terms of specific energy. Figure 3-47 shows the BOD_5 removal efficiency for both pilots under aerobic conditions. It can be seen that the highest BOD_5 removal efficiency after 42 days in pilot-1 and 52 days in pilot-2 of digestion

corresponds to ozonation, thermal (60°C) and ultrasound (> 98%). For other thermal treatments and autoclave, although they required a high SE, their removal elimination was less important and near the control sample. In this study, the rate of BOD_5 elimination for all samples (even control sample) was more than 90%. This suggests that SE has not a determining effect on BOD_5 removal yield.

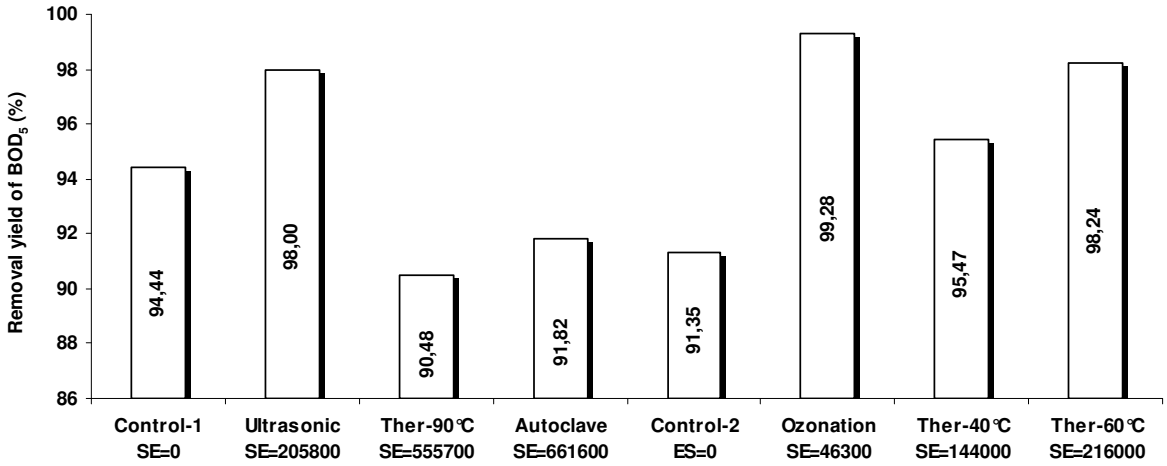

Figure 3-47: BOD_5 removal efficiency vs. specific energy of different digesters in pilots 1 & 2.

Pre-treatment leads to an increase of soluble COD, which is not fully biodegradable. Biodegradability can be defined by the BOD_5/COD_S ratio. During the pretreatment process, sludge flocs are broken, thus organic matter is more accessible to the bacteria and can be more degraded in a shorter time (biodegradability increases).

Biodegradability (BOD_5/CODs) ratios of the second series are in general 20% more than that of the first series. This can be due to different sludge types or digestion conditions. As we can see in Table 3-30, ozone pretreatment has the highest biodegradability efficiency (95.32%, or 38.56% more than the control sample of pilot 1).

Ultrasonic treatment that led to highly biodegradable soluble organic matters (BOD_5/COD_S ratio values were 68% more than control sample), had also a high solubilization rate (61.49%). It means that the enhancement of sludge biodegradability depended upon the kind of pretreatment and the rate of solubilization.

For thermal batch reactor, biodegradability at 40°C, 60°C is comparable to the control but at 90°C, biodegradability efficiency is more than control sample (17%) but less than ozonated or sonicated samples. For thermal treatment (40°C and 60°C), the solubilization efficiency is not very high (respectively 4.55% and 10.02%) and thus the biodegradability enhancement was

also low (≤ 16% more than control sample). Concerning 90°C, although its solubilization was not very high (around 12%) its biodegradability increased to 1.03 times more than 60°C and 3.35 times more than 40°C thermal treatment. We can conclude that increasing the temperature can effectively (compared to solubilization rate) improve the biodegradability.

The biodegradability ratio improvement of autoclave at 121°C (after solubilization) is more important than 90°C thermal treatment, but its biodegradability (after solubilization and digestion) is very low (47.93%). The less important biodegradability of organic compounds of thermally pre-treated sludges can be attributed to the possible actions of the treatment itself on carbohydrates and proteins molecules (i.e. Maillard reactions) leading to less biodegradable compounds (Bougrier *et al.,* 2006).

Table 3-30: The BOD_5/COD_S ratio of sludge and removal yield improvement of BOD_5 compare to the control during digestion for two series of experiments.

	Control 1	Ultrasonic	Thermal (90°C)	Autoclave	Control 2	Ozonation	Thermal (40°C)	Thermal (60°C)
BOD_5/COD_S (%) After solubilization	34.45	57.80	40.23	44.90	65.60	75.21	66.74	68.55
Removal yield improvement	-	1.68	1.17	1.30	-	1.15	1.02	1.05
BOD_5/COD_S (%) After solubilization and digestion	58.56	84.43	73.79	47.93	77.83	95.32	83.86	89.91
Removal yield improvement	-	1.44	1.26	0.82	-	1.22	1.08	1.16

The biodegradability enhancement due to ozone pretreatment was lower than or almost equal to the rate obtained by thermal treatment at 90°C (17%). The biodegradability percentage of 75% is comparable to the results of Bougrier *et al.* (2007) for the same dose of treatment. Ozone is not a selective oxidant, it can react with other reducing materials, and this may lower the oxidation efficiency of activated sludge. Since refractory organic carbon can be released into the effluent after ozonation, the toxicity of those compounds might be responsible for lower biodegradability improvement (Liu, 2003; Bougrier *et al.,* 2006). Sludge biodegradability (BOD_5/COD_S) as a function of ratio improvement can be classified as follows:

$$\left(\frac{BOD_5}{COD_S}\right)\ \underset{1.68}{\text{ultrasonic}} >> \underset{1.30}{\text{autoclave}} > \underset{1.17}{\text{thermal (90°C)}} > \underset{1.15}{\text{Ozone}} > \underset{1.05}{\text{thermal (60°C)}} > \underset{1.02}{\text{thermal (40°C)}}$$

5.1.2 Evaluation of protein and carbohydrate elimination

Proteins are the man building blocs of sludge and there is a fraction of proteins in the exopolymers (EPS= extracellular polymeric substances). Approximately 50% of organic matter is composed of proteins (Stuckey and McCarty, 1979, Li and Noike, 1992). Contrary to carbohydrates, proteins can not be degraded easily (Neyens *et al.,* 2004). In fact most proteins (intracellular compounds) are protected from enzymatic hydrolysis by the cell walls. So, proteins are considered as a good indicator of the biodegradability potential.

The concentration of sugars in the sludge is lower than proteins. 10 to 30% of the organic matter is composed of carbohydrates (Stuckey and McCarty, 1979, Li and Noike, 1992).

5.1.2.1 Protein removal efficiency

- **Total proteins removal**

Total protein removal efficiency was investigated during the two series of experiments (Table 3-31). Concerning total proteins, sonication pre-treatment led to the best improvement in degradation. The removal yield improvement in ultrasound pretreated was higher than other samples in both pilots (1.70 times more than control sample). Protein solubilization and biodegradation efficiency is the most successful among other methods (solubilization: 66.24% and removal yield: 80.36% for total proteins). After sonication, the highest protein solubilization and degradation efficiencies correspond to thermal treatment at 90°C and autoclave (1.53 times more than control for both reactors). However, ozonation and thermal treatment at lower temperatures do not show remarkable solubilization and biodegradation.

Ozone led to less important proteins solubilization (8.97%) but its biodegradability (89.86%) was noticeably high (1.38 times more than control sample). The ozone effect seemed to be limited to solubilization of organic solids (Salhi, 2003) but as a radically oxidant, it can lead to oxidation of organic carbon and increase biodegradability.

For thermal pretreatments (40°C, 60°C and 90°C), proteins solubilization depended on the temperature applied to the sludge. As previously demonstrated by Wang *et al.* (1997) in the same range of temperatures, proteins (and also carbohydrates) solubilization increased with increasing temperature. Thermal treatment at 90°C led to an important proteins solubilization (34.27%) which is similar to the results of Paul *et al.* (2006) for the same range of temperatures.

Table 3-31: Proteins solubilization and elimination efficiency under aerobic conditions.

	Control 1	Ultrasonic	Thermal (90°C)	Autoclave	Control 2	Ozonation	Thermal (40°C)	Thermal (60°C)
Total protein Removal yield (%)	47.32	80.36	72.21	72.31	57.95	65.93	53.42	57.88
Removal yield improvement	-	1.70	1.53	1.53	-	1.14	0.92	1
Soluble protein Removal yield (%)	71.43	93.42	85.69	79.28	64.91	89.86	74.44	89.08
Particulate protein Removal yield (%)	44.43	52.90	64.18	70.47	57.88	63.40	53.12	54.55
Solubilization (%)	-	66.24	34.27	13.65	-	8.97	0.52	8.81

Some pre-treatment (ultrasound, temperature 90°C and autoclave) remarkably improved protein removal while for others (thermal 40°C and 60°C) there is no improvement.

- **Soluble and particulate proteins removal**

Concentration of proteins, before and after aerobic digestion, in particulate fraction and in the supernatant was investigated.

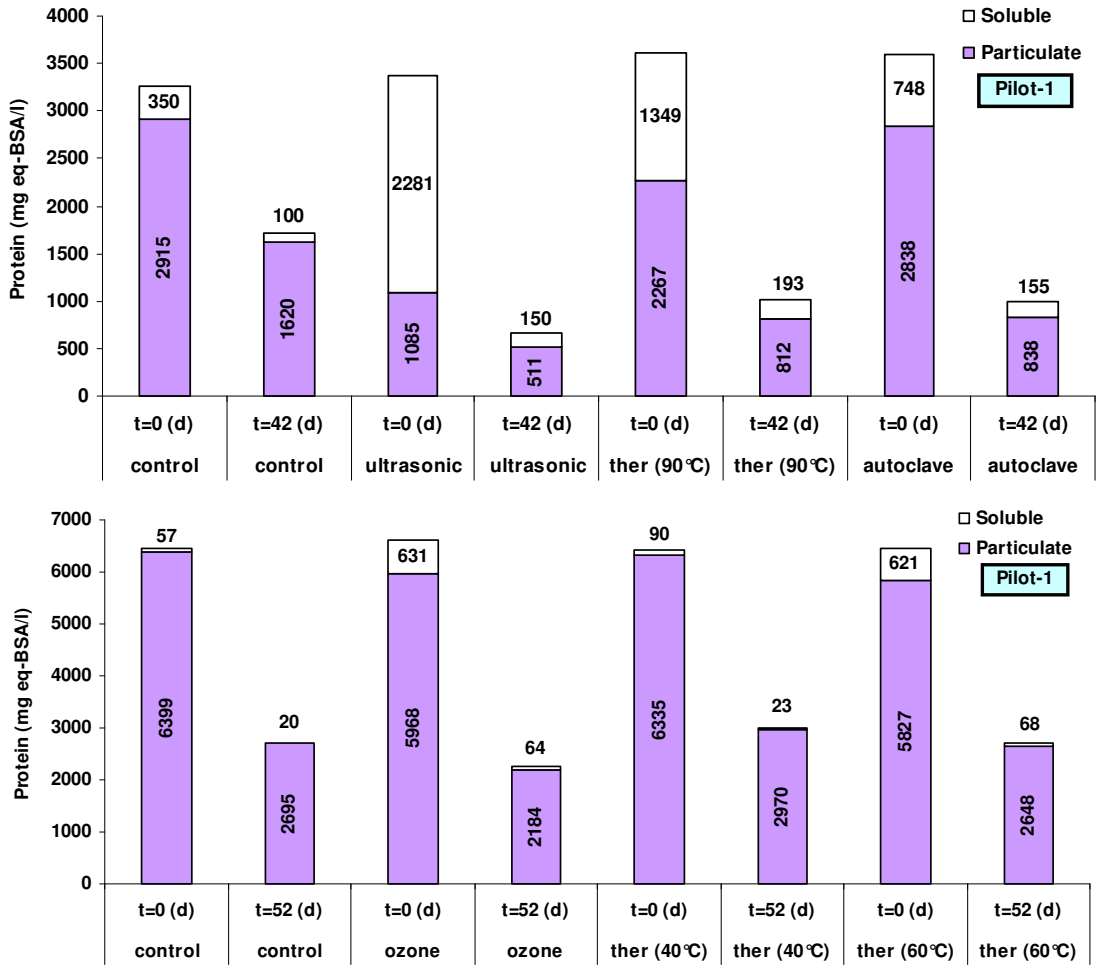

Figure 3-48: Solubilization and biodegradation of protein (soluble & particulate) before and after digestion.

Figure 3-48: indicates proteins repartition in both pilots before and after aerobic digestion. These values are taken after 42 days for the first pilot and 52 days for the second pilot. Elimination efficiency of soluble and particulate protein for different pretreatments can be classified in terms of removal yield enhancement.

$$\text{Protein}_S \rangle \underset{1.38}{\text{ozonation}} \geq \underset{1.37}{\text{thermal}(60°C)} > \underset{1.31}{\text{ultrasonic}} > \underset{1.20}{\text{thermal}(90°C)} > \underset{1.15}{\text{thermal}(40°C)} > \underset{1.11}{\text{autoclave}}$$

The highest solubilization percentage of proteins belong to ultrasonic and thermal treatment at 90°C, while The highest elimination efficiency of soluble protein correspond to ozonation and thermal treated samples at 60°C (1.38 and 1.37 time more than control samples respectively), and also, the lowest improvement is attained by the autoclave and thermal treated sample at 40°C (79.28% and 74.44% respectively).

Although ozone led to lower protein solubilization, but for this dose of ozone, not only the microflocs but also the cell walls were broken leading to the leakage of the intercellular

materials (protein) (Zhao *et al.,* 2007). For a certain level of ozone dose, it can react and break the main cell constituents of proteins to smaller molecular chain compounds (Goel *et al.,* 2003).

In particulate fraction, the highest removal elimination corresponded to autoclave (70.47% = 1.59 times more than sample control) and then to 90°C thermal treatment and ultrasonic (respectively 64.18% and 52.90% = 1.44 and 1.19 times more than control sample). In the second series of experiments, removal yield of particulate protein was near that of control sample. By comparing particulate and supernatant in pilot 1 and 2 we can see that in the first pilot elimination yield of particulate protein is high while in the second pilot elimination yield of soluble protein is high.

$$\text{Protein}_P \rangle \underset{1.59}{\text{autoclave}} > \underset{1.44}{\text{thermal}(90°C)} > \underset{1.19}{\text{ultrasonic}} > \underset{1.10}{\text{ozonation}} > \underset{0.94}{\text{thermal}(60°C)} \geq \underset{0.92}{\text{thermal}(40°C)}$$

High applied energy during pretreatment processes leads to better lysis of organic matters in the particulate phase, and this matters which were formerly slow biodegradable or non biodegradable become more accessible to lysis and decomposition during digestion steps.

- **Dynamics of soluble protein removal efficiency**

The measurement of soluble proteins and carbohydrates removal efficiencies after different pre-treatments can provide a more thorough understanding of the influence of pre-treatment on the digestion processes. Figure 3-49 shows the protein elimination efficiency over the time in both pilots.

In the first series, protein elimination efficiency for sonication is more than other processes. After sonication, thermal treatment (90°C) also yields a high elimination efficiency. The rate of proteins digestion after the autoclave pretreatment is very different from other processes and is inferior to the control sample until day 15. This may be due to the formation of toxic compounds (Maillard's reactions). In fact, autoclave process does not have a high elimination efficiency at the beginning, but after 15 days its elimination of proteins increases to a more important value than the control.

In second pilot (Figure 3-49), ozonation process and thermal treatment at 60°C share the same degradation level. During the first 10 days, all the biodegradation rates are comparable to the control. After 10 days ozone and thermal (60°C) pre-treatment go over the control values.

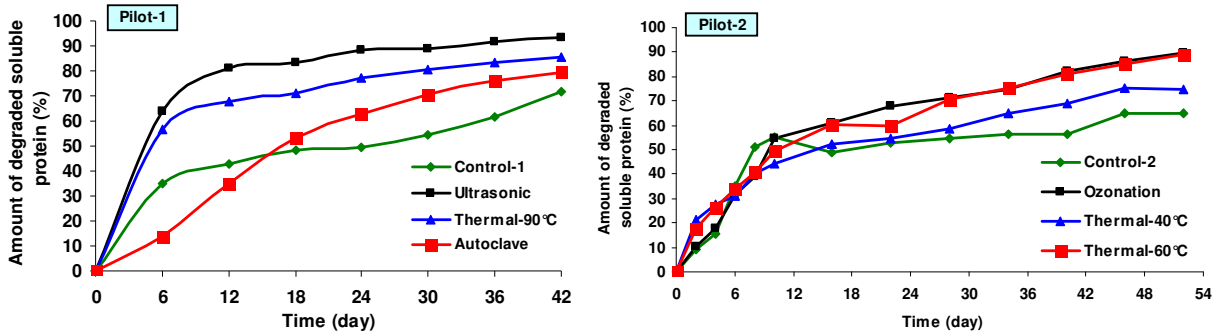

Figure 3-49: Elimination efficiency of soluble proteins in terms of digestion time in aerobic digester.

The instantaneous specific rate values for soluble protein ($q_{protein}$) during aerobic digestion were evaluated. This study shows that the highest rate of $q_{protein}$ (the specific instantaneous soluble protein consumption rate) for the first pilot corresponds to ultrasonic reactor (41.42 mg $protein_S.gVSS^{-1}.d^{-1}$) and was far above the rates of $q_{protein}$ observed in other reactors. In the first series of experiments (pilot 1), the rate of $q_{protein}$ for ultrasonic processes drastically decreased over the time between 6^{th} and 18^{th} day and then sinuously decreased to zero (see Figure 3-50).

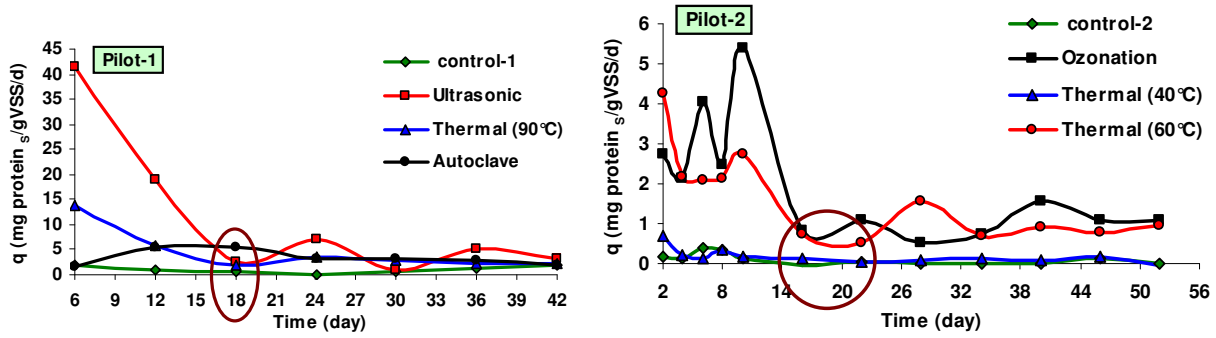

Figure 3-50: Instantaneous specific rates ($q_{protein}$) for soluble protein over time under aerobic condition.

In the second pilot, the values of $q_{protein}$ for ozonation and 60°C thermal treatment are above the control and thermal (40°C) but lower than for the first series and kept quite constant during the first week, then decrease and finally attain their minimum values. For ozonation, the rate of $q_{protein}$ meets its highest value (4.04 mg $protein_S.g\text{-}VSS^{-1}.d^{-1}$) in the 6^{th} day and its minimum (0.82 mg $protein_S.g\text{-}VSS^{-1}.d^{-1}$) in the 16^{th} day. Concerning thermal treatment (60°C), the rate of $q_{protein}$ attains its maximum (4.28 mg $protein_S.g\text{-}VSS^{-1}.d^{-1}$) and minimum (0.52 mg $protein_S.g\text{-}VSS^{-1}.d^{-1}$) values respectively in the 2^{nd} and 22^{nd} days. Autoclave and 40°C thermal treatment showed the same behavior as the control sample (Figure 3-50).

5.1.2.2 Carbohydrate removal efficiency

- **Total carbohydrates removal**

Total carbohydrates elimination efficiencies, removal yield improvement and carbohydrate solubilization for first and second series of experiments are indicated in Table 3-32.

In the first pilot series a high carbohydrate elimination can be observed for control sample as well as pre-treated samples. Ultrasonic, autoclave and 90°C thermal treatment had an elimination efficiency improvement of respectively 1.08, 1.04, and 0.94 compare to the control sample.

For the second pilot, thermal treated sample at 40°C, 60°C and ozone had an elimination efficiency improvement of respectively 1.05, 1.08 and 1.11 compare to the control.

The best carbohydrates removal yield improvement could be attributed to ozone pre-treatment and then ultrasound. In general pre-treatment did not remarkably improve carbohydrates removal yield.

Table 3-32: Carbohydrates solubilization and elimination efficiency under aerobic conditions.

	Control 1	Ultrasonic	Thermal (90°C)	Autoclave	Control 2	Ozonation	Thermal (40°C)	Thermal (60°C)
Total carbohydrate Removal yield (%)	81.71	88.41	76.56	84.73	80.46	89.50	84.42	87.08
Removal yield improvement	-	1.08	0.94	1.04	-	1.11	1.05	1.08
Soluble carbohydrate Removal yield (%)	85.80	96.36	90.74	88.80	66.76	89.86	64.00	80.37
Particulate carbohydrate Removal yield (%)	80.48	77.23	69.63	83.21	81	89.47	85.04	87.38
Solubilization (%)	-	43.43	8.38	5.52	-	7.14	0.30	4.07

By comparing the two series of experiments we can see that however ozone did not lead to a high solubilization rate during pre-treatment steps (7.14%), its removal yield improvement during digestion processes is rather high (1.11 times more than control sample). On the other hand, ultrasonic with a high solubilization rate during pretreatment steps (43.43%) leads to comparable removal yield enhancement compared to ozonation (8 percents more than control). We can see that during digestion processes, ozonation had a more successful performance compared to other pre-treatments (ultrasonic and thermal treatment).

- **Soluble and particulate carbohydrates removal**

Table 3-32 and Figure 3-51, shows that in the first series of experiments, contrary to the second one, the soluble carbohydrates elimination efficiency is higher than total carbohydrates elimination efficiency.

Soluble and particulate carbohydrates repartition before and after digestion are presented in Figure 3-51. The total concentration of carbohydrates is constant whatever the kind of pre-treatment is. At the end of aerobic digestion the main part of soluble and also an important part of particulate carbohydrates are consumed.

For ultrasound, the solubilization rate being high, the soluble carbohydrates elimination efficiencies were also high (96.36%, or 1.12 times more than control sample) but were lower than ozonation (89.86%, or 1.35 times more than control sample).

Solubilization of thermal treatments increased with the treatment temperature, but does not attain high values (min 0.3% and max 8.38%). Soluble carbohydrates elimination efficiency is rather high and increases with temperature while total carbohydrate elimination efficiency is not very high (see Table 3-32). It means that in order to increase solubilization and consequently biodegradability of carbohydrates, higher temperatures must be used. This result is in accordance with Li and Noike (1992) and Bougrier *et al.* (2008) who worked with higher temperatures (170°C) and demonstrated that temperature might have an effect on carbohydrate solubilization.

Concerning ozonation, although the rate of solubilization is low, the removal yields of soluble and total carbohydrates are high (89.86% for soluble and 89.50% for total). The reason is that for a certain level of ozone dose, it can react and break the main cell constituents of polysaccharides to smaller molecular chain compound (Goel *et al.,* 2003).

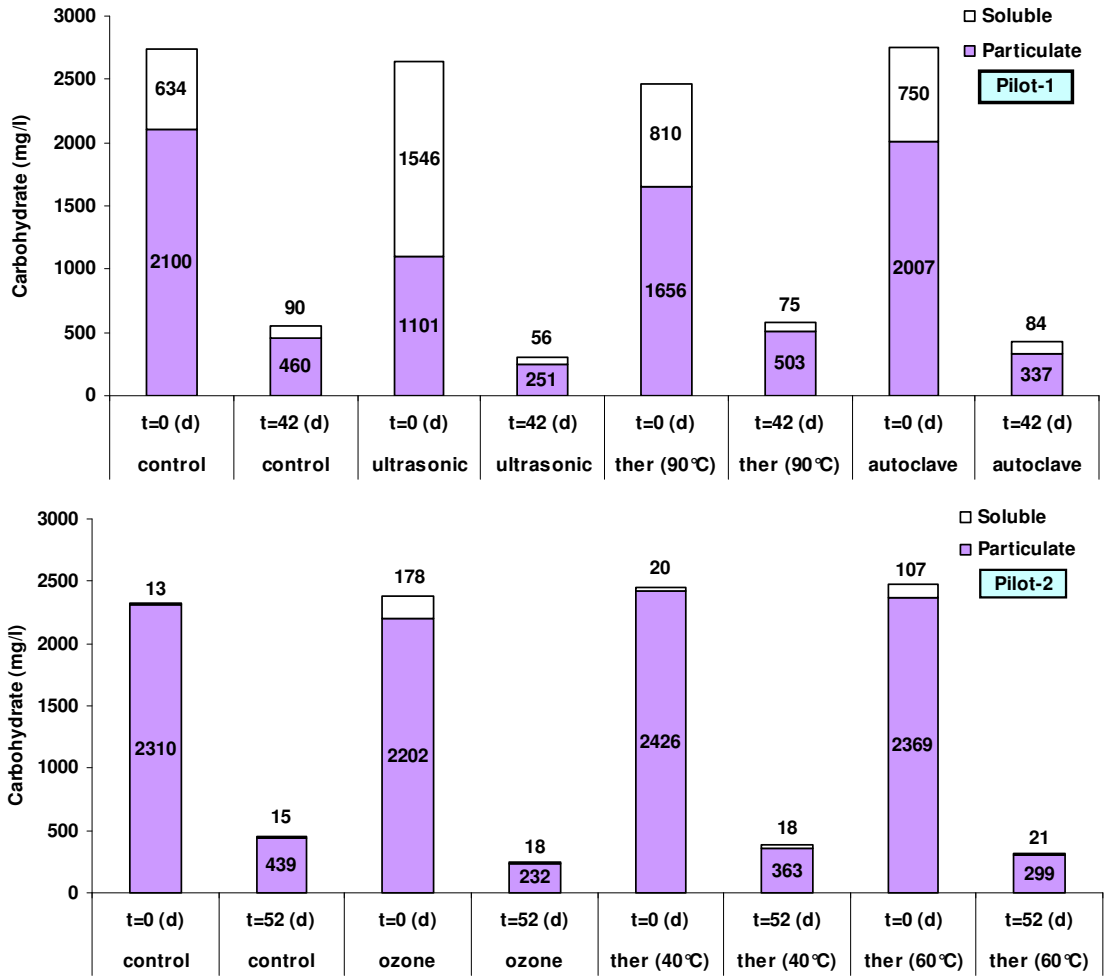

Figure 3-51: Solubilization and biodegradation of carbohydrate (soluble & particulate) before and after aerobic digestion.

The classification of particulate and soluble carbohydrates ozonation and thermal treatment at 90°C produce the highest removal yield improvement. Also removal yield enhancement is higher for soluble carbohydrates compared to particulate carbohydrates.

$$\text{Carbohydrate}_S \rangle \underset{1.35}{\text{ozonation}} > \underset{1.20}{\text{thermal (60°C)}} > \underset{1.12}{\text{ultrasonic}} > \underset{1.06}{\text{thermal (90°C)}} \geq \underset{1.04}{\text{autoclave}} > \underset{0.96}{\text{thermal (40°C)}}$$

$$\text{Carbohydrate}_P \rangle \underset{1.10}{\text{ozonation}} \geq \underset{1.08}{\text{thermal (60°C)}} > \underset{1.05}{\text{thermal (40°C)}} > \underset{1.03}{\text{autoclave}} > \underset{0.96}{\text{ultrasonic}} \geq \underset{0.87}{\text{thermal (90°C)}}$$

- **Dynamic of soluble carbohydrate removal efficiency**

Figure 3-52 shows the biological elimination efficiency of soluble carbohydrates during 42 and 52 days. In this study we observed that carbohydrates were biodegraded with a slower rate compared to proteins and thus it is possible that it does not stabilize after 40 days for low-energy treatments. This point confirms the evolution of the COD described before.

In the first series, biodegradation efficiency improvement of soluble carbohydrates was noticeable for pre-treatment processes such as ultrasound, thermal treatment at 90°C, and autoclave (between 88.80 and 96.38%). The final values are not much different from control sample (85.69%). In the second series soluble carbohydrates removal is greatly improved by ozone and thermal (60°C) treatments.

While the control sample had a carbohydrate elimination efficiency of only 66.76%, this rate raises to 89.86% and 80.37% for ozonation and thermal treatment (at 60°C) respectively. The difference may be due to different sludge types and concentrations (TS = 12g.L^{-1} for the first pilot versus 21.6g.L^{-1} for the second pilot).

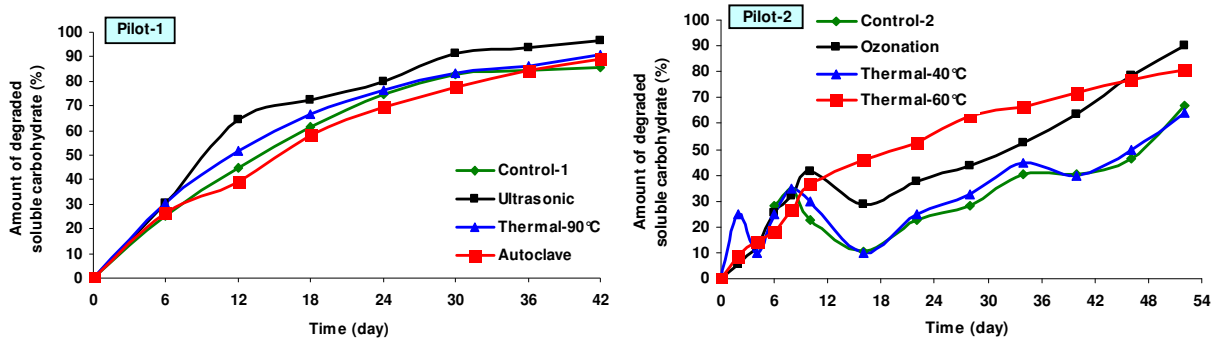

Figure 3-52: Variation of soluble carbohydrate in reactors batch during sludge aerobic digestion.

In this study, values of $q_{carbohydrate}$ (the instantaneous specific rates) for soluble carbohydrates in the both series of experiments were calculated. The results are shown in Figure 3-53. $q_{carbohydrate}$ values and evolutions for thermal (90°C) and autoclave pre-treatment are comparable to the control, while this parameter is much more important for ultrasonic pre-treatment. In the first pilot, $q_{carbohydrate}$ is maximal during the first 12 days, but drastically decreased in the 18th day (from 25.38 to 6.82 mg carbohydrate.g-VSS^{-1}.d^{-1}).

In the second pilot, thermal treated sample at 40°C behaved like control sample whereas ozone and thermal (60°C) pre-treatment led to an important improvement of $q_{carbohydrate}$. The instantaneous specific rates values for soluble carbohydrate of ozone and thermal treatment (60°C) are maximal during the first 10 days and decreased from the 16th day and reached their minimum values. Globally the values for $q_{carbohydrate}$ are less important in the second series than in the first one.

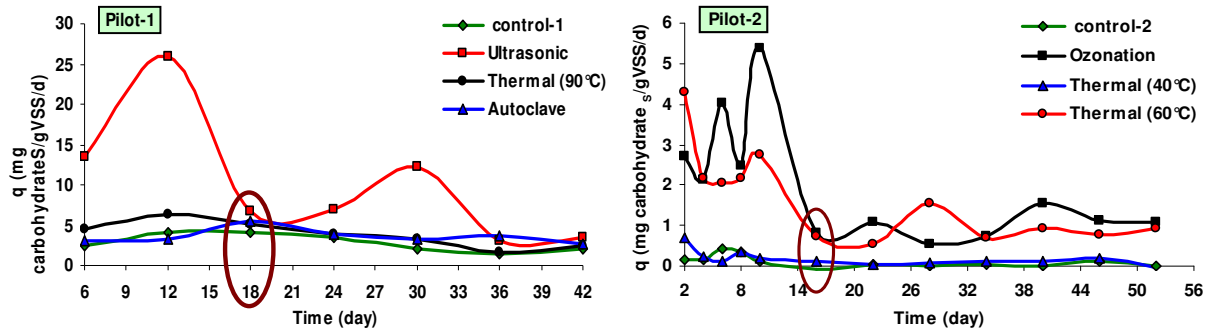

Figure 3-53: Instantaneous specific rates ($q_{carbohydrate}$) for soluble carbohydrate in terms of times in aerobic condition.

A comparison between carbohydrates and proteins digestion processes shows that especially for thermal treatments and second pilot, carbohydrates were biodegraded more than proteins while proteins are more solubilized. This complied with the researches of Barlindhaug and Odegaard, (1996).

5.1.3 Evaluation of nitrogen and phosphorus elimination

Disintegration influences the concentration of organic components in the sludge liquor emerging from the dewatering of the stabilized sludge. The increase in phosphorus is low, compared to the increase in nitrogen. The concentration of ammonia in the sludge water is increased mainly because of the higher degree of degradation of bio-mass containing proteins.

5.1.3.1 Nitrogen removal efficiency

- **Total nitrogen removal**

The highest total nitrogen degradation efficiency was observed on sonicated, thermally treated (60°C and 90°C) and ozonated samples and the highest solubilization rate also corresponds to sonicated and ozonated samples (43.64% and 31.34% respectively).

Ultrasonic (1.23) > Thermal 60°C and 90°C = Ozone (1.12) ≥ Autoclave and Thermal 40°C (1.02)

It means that the highest removal yield corresponds to the pretreatment featuring the highest solubilization rate (Table 3-33). We can summarize total nitrogen biological elimination as follows:

Table 3-33: Nitrogen solubilization and elimination efficiency under aerobic conditions.

	Control 1	Ultrasonic	Thermal (90°C)	Autoclave	Control 2	Ozonation	Thermal (40°C)	Thermal (60°C)
Total nitrogen Removal yield (%)	56.74	69.90	63.33	57.74	54.33	60.77	55.07	60.45
Removal yield improvement	-	1.23	1.12	1.02	-	1.12	1.01	1.11
Soluble nitrogen Removal yield (%)	64.71	75.86	66.74	65.63	61.89	78.10	67.39	82.50
Particulate nitrogen Removal yield (%)	51.82	61.25	59.53	47.22	47.93	44.52	53.81	54.46
Solubilization (%)	-	43.64	24.55	25.45	-	31.34	1.38	13.36

Autoclave and thermal treatment (40°C) did not led to any total nitrogen removal improvement.

- **Soluble and particulate nitrogen removal**

The repartition between soluble and particulate forms of nitrogen before and after digestion is presented in Figure 3-54. Soluble nitrogen is not completely degraded after aerobic digestion, especially in pilot 1. The composition and repartition at the end of the digestion between soluble and particulate forms is quite comparable from one treatment to another. At the end of experiments, there are more particulate forms in the control sample than pretreated samples.

The highest removal improvement for soluble nitrogen corresponded to ozonation and 60°C thermal treatment (1.41 and 1.33 times more than control sample). In this study, removal yield improvement of ultrasonic was 75.86% (1.17 times more than control sample). Removal yield for other samples was not that much different from the control sample.

The highest rate of removal yield enhancement for particulate nitrogen corresponded to ultrasonic and thermal treatment at 90°C (1.18 and 1.15 times more than control sample). Also, removal yield in soluble fraction was higher than particulate fraction.

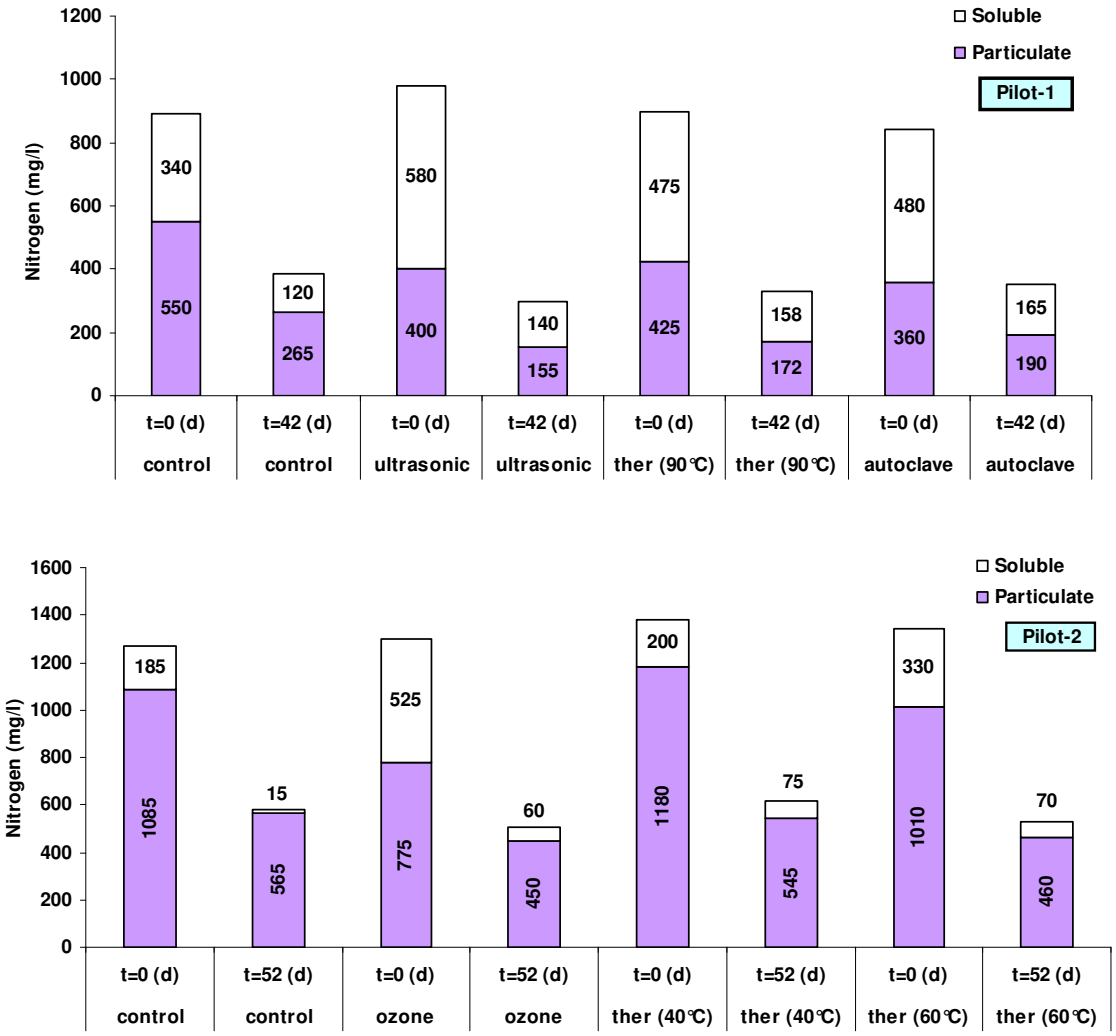

Figure 3-54: Solubilization and biodegradation of nitrogen (soluble & particulate) before and after aerobic digestion.

Particulate and soluble nitrogen biological elimination improvement can be summarized as follows:

$$\text{Nitrogen}_S \rangle \underset{1.41}{\text{ozonation}} > \underset{1.33}{\text{thermal}(60°C)} > \underset{1.17}{\text{ultrasonic}} > \underset{1.09}{\text{thermal}(40°C)} > \underset{1.03}{\text{thermal}(90°C)} \geq \underset{1.01}{\text{autoclave}}$$

$$\text{Nitrogen}_P \rangle \underset{1.18}{\text{ultrasonic}} > \underset{1.15}{\text{thermal}(90°C)} \geq \underset{1.14}{\text{thermal}(60°C)} \geq \underset{1.12}{\text{thermal}(40°C)} > \underset{0.93}{\text{ozonation}} \geq \underset{0.91}{\text{autoclave}}$$

By investigating the classification of soluble and particulate nitrogen, we can see that the highest removal improvement for N_S is produced by ozonation and 60°C thermal treatment and the lowest rates are observed in 90°C thermal and autoclave treatments. But the highest removal enhancement for N_p corresponded to ultrasonic and 90°C thermal treatment and the lowest rates are produced by autoclave and ozonation treatments.

- **Dynamics of soluble nitrogen removal efficiency**

The evolution of soluble nitrogen concentration for the first and the second experiment are totally different. In the first pilot, in which more energetic processes were used to pre-treat samples, nitrogen elimination was globally linear and slow during the first 20 days, speeding up gradually afterwards. However, for second pilot containing samples obtained from less energetic methods, elimination process starts quickly and slows down afterwards (see Figure 3-55).

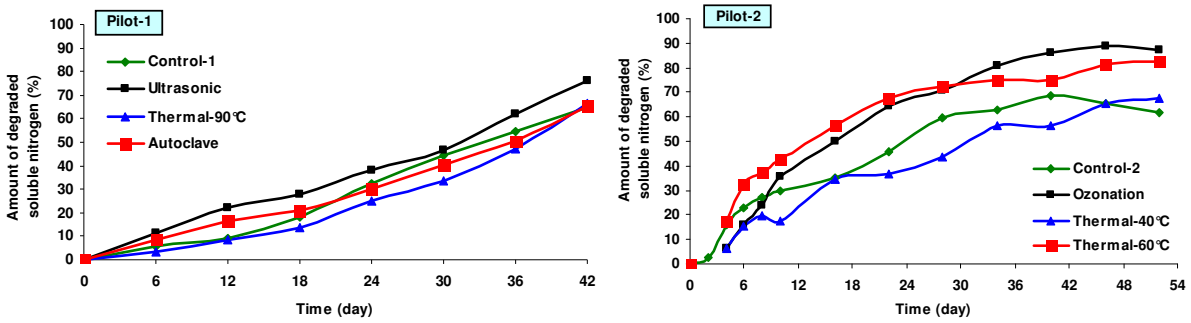

Figure 3-55: Variation of soluble nitrogen in reactors batch during sludge aerobic digestion.

In this study, autoclave and thermal treatment (90°C) has led to high nitrogen solubilization (25.45%, 24.55%, respectively). In other words nitrogen has been transferred from organic solid form into organic soluble phase. In fact during digestion, a great amount of organic and ammoniacal nitrogen in soluble phase has been removed. For second pilot, solubilization has not happened as much as first pilot, but biodegradation efficiency is of the same order as the first pilot. The different pre-treatment have a positive effect on the amount of degraded nitrogen.

5.1.3.2 Phosphorus removal efficiency

- **Total phosphorus removal**

Ultrasonic, thermal and ozonation pre-treatments has led to phosphorus solubilization and have increases the phosphate concentration in organic and mineral forms in soluble phase. Table 3-34 shows the total phosphorus removal yield and its enhancement of outlet samples. During aerobic digestion process, total phosphorus (particulate plus soluble) elimination efficiency for ozonation, thermal treatment at 60°C and sonication is remarkably higher than of control samples (1.51, 1.43 and 1.30 times more than control). In contrary, for autoclave, 40°C thermal treatment, and 90°C thermal treatment, the phosphorus elimination rate is not very high ratio compare to control.

Table 3-34: Elimination efficiency of phosphorus at the end of the aerobic digestion.

	Control 1	Ultrasonic	Thermal (90°C)	Autoclave	Control 2	Ozonation	Thermal (40°C)	Thermal (60°C)
Total phosphorus Removal yield (%)	46.28	59.84	45.13	52.03	23.12	35	24.21	33
Removal yield improvement	-	1.30	0.98	1.12	-	1.51	1.05	1.43
Soluble phosphorus Removal yield (%)	50.00	71.01	52.83	60.71	52.63	67.07	61.22	52.03
Particulate phosphorus Removal yield (%)	44.71	46.32	38.33	44.19	25.12	12.71	26.90	28.97
Solubilization (%)	-	38.82	20	23.53	-	35.11	0.17	21.80

- **Soluble and particulate phosphorus removal**

Regarding soluble and particulate phosphorus removal yield, we saw that the removal yield of P_S is more than that of P_P (Figure 3-56). Moreover, it can be seen that sonication and ozonation pretreatment causes the increase of the removal yield in soluble phosphorus (1.42 and 1.27 times more than control, respectively), while thermal pretreatment (except autoclave) has no considerable impact on the soluble phosphorus removal yield. Autoclave pretreatment causes an increase of 20% in the removal yield of P_S more than control sample.

Pretreatment and digestion do not lead to the increase of the particulate phosphorus removal yield, and the elimination yield is less than 50% in all the reactors.

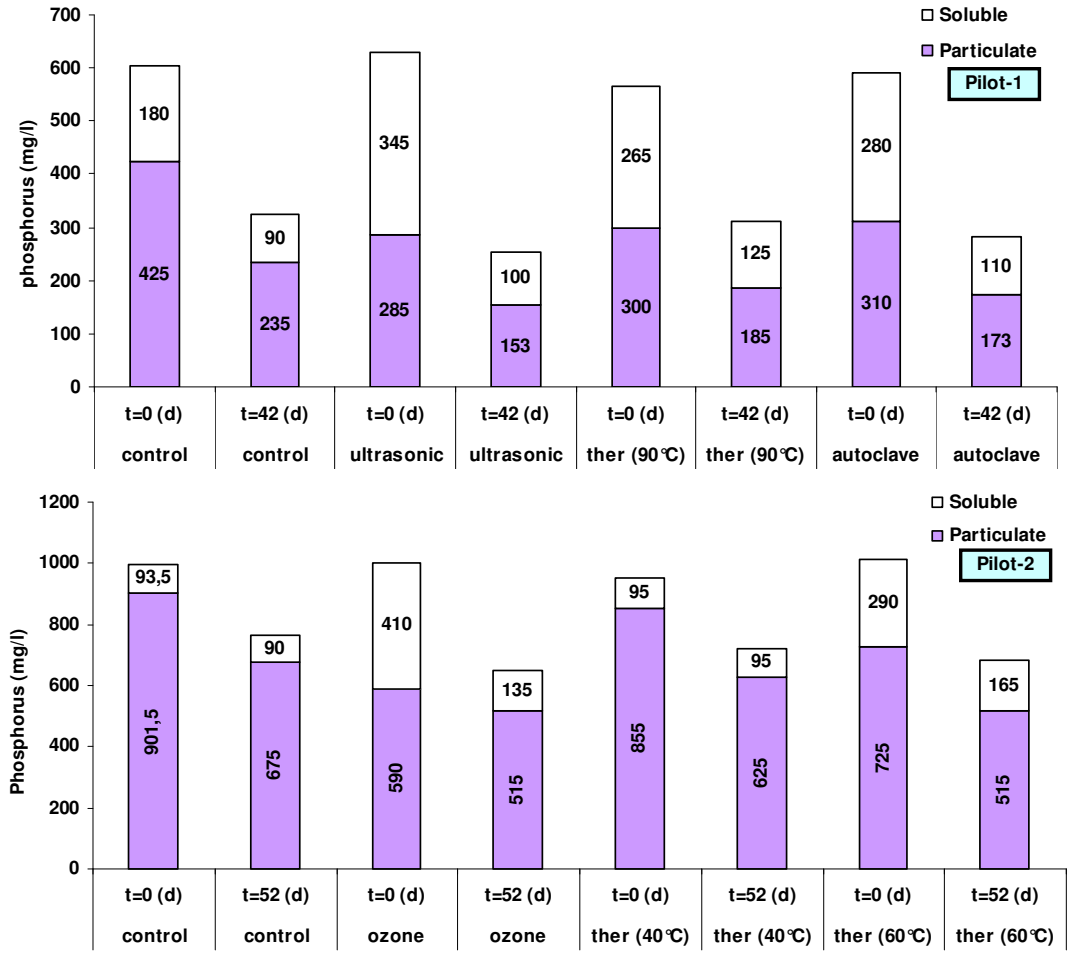

Figure 3-56: Solubilization and biodegradation of phosphorus (soluble & particulate) before and after aerobic digestion.

Regarding classification of P_S and P_P, ultrasonic, ozonation and autoclave treatment have a higher removal yield comparing to thermal treatment, and thermal treatment is not so successful in the elimination of soluble phosphorus. Conversely, low thermal treatment (40°C and 60°C) is more effective than the other methods of pretreatment in the removal of particulate phosphorus.

$$\text{Phosphorus}_S \rangle \underset{1.42}{\text{ultrasonic}} > \underset{1.27}{\text{ozonation}} > \underset{1.21}{\text{autoclave}} > \underset{1.16}{\text{thermal (40°C)}} > \underset{1.06}{\text{thermal (90°C)}} > \underset{0.99}{\text{thermal (60°C)}}$$

$$\text{Phosphorus}_P \rangle \underset{1.15}{\text{thermal (60°C)}} > \underset{1.07}{\text{thermal (40°C)}} > \underset{1.04}{\text{ultrasonic}} > \underset{0.99}{\text{autoclave}} > \underset{0.86}{\text{thermal (90°C)}} > \underset{0.51}{\text{ozonation}}$$

- **Dynamics of soluble phosphorus removal efficiency**

Figure 3-57 show the soluble phosphorus elimination in both pilots. In the sludge digestion process, the highest elimination efficiency corresponds to ultrasonic and ozonation.

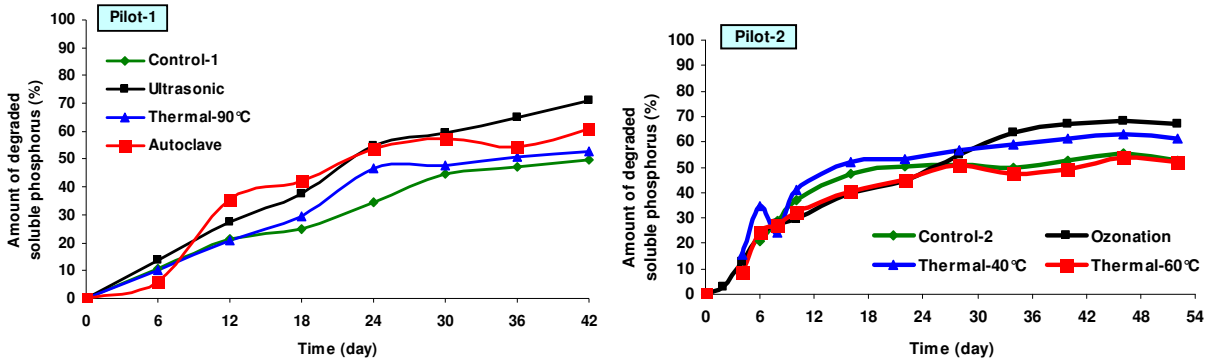

Figure 3-57: Variations of soluble phosphorus in batch reactors during sludge aerobic digestion.

It can also be observed that elimination efficiencies of thermal treated samples (40, 60, and 90°C) are not very different from the control sample (61.22%, 52.03% and 52.83% against about 50% for control sample). In other words thermal treatment had not a noticeable effect on soluble phosphorus elimination.

5.2 Study of improvement in produced sludge reduction

5.2.1 Evaluation of VSS and TSS Elimination in aerobic reactors

The disintegration of the sludge biomass, reflected in a decrease of both total suspended solids (TSS) and volatile suspended solids (VSS) in the treated sludge and the receiving reactors (Weemaes *et al.,* 2000) is one of the key objectives of sludge pre-treatment. A decrease in the ratio of VSS/ TSS of treated sludge has been observed, and accumulation of inorganic solids in the aeration tank was considered negligible (Sakai *et al.,* 1997) and may even be reduced by ultrasonic, thermal and ozonation (Deleris *et al.,* 2002).

5.2.1.1 TSS reduction improvement due to pre-treatment and digestion

Pre-treatment and biological digestion sludge led to sludge reduction due to the solubilization and digestion of total and volatile suspended solids (TSS and VSS).

- **TSS reduction removal efficiency**

Ultrasonic, thermal and ozone sludge treatments induced per se sludge reduction. The relative contribution of the pre-treatment to global sludge reduction differed largely according to the kind of treatment. Ultrasonic pre-treatment contributed in major part to sludge reduction improvement (80% under aerobic conditions and 54% under anaerobic conditions). This observation means that the pre-treatment can considerably reduce the digestion length to reach the TSS removal of the non treated sludge. For thermal treatment the contribution in sludge

reduction is as much important as the temperature is increasing: between 12 and 20% when the temperature varied from 40°C to 90°C. The contribution of ozone pre-treatment (20%) to global sludge reduction was comparable to thermal treatment (90°C). For ozone this result is lower than the sludge reduction obtained by Park and Novak, 2007 (45%) for the same ozone dose. The autoclave treatment led to the less important contribution to TSS global removal (4-5%) leading to the conclusion that the impact of pre-treatment on sludge reduction during digestion is real (15%).

Under aerobic conditions, TSS reduction due only to digestion was between 57% and 67% for all reactors. TSS reduction for pretreated and digested sludge varies between 62.5% and 76%. The results concerning the single step of digestion are different according to the kind of pre-treatment: ultrasound, thermal (90°C, 60°C and 40°C) did not led to an improvement of sludge reduction in the step of aerobic digestion while ozone and autoclave led to respectively 12% and 18% of TSS reduction improvement.

Ultrasound and then thermal treatment at 90°C and autoclave had the highest TSS elimination efficiencies (76.07% for sonication, 67.75% for 90°C and 69.13% for autoclave against 57.29% for control sample). Ozonated sample has an elimination efficiency of 63% after 40 days of digestion; this value attains 71% after approximately 50 days against 57.29% for control sample. Low thermal treatments (40°C and 60°C) have the removal yields of 62.5% and 65%, which does not show a good improvement. (The values of removal yield enhancement are 1.06 and 1.10 times more than control sample).

Under aerobic conditions the maximal TSS removal improvement was 33% for ultrasound, 20% for ozone and thermal treatment (90°C and autoclave), then 10% for thermal treatment at 60°C (Table 3-35). The reasons for ultrasound irradiation accelerating sludge aerobic digestion are that the ultrasound can diminish the flocculation, satisfy the aerobic condition for the microorganism, enhance enzymatic activities and promotes the release of extracellular proteins, polysaccharides as well as the corresponding enzymatic activities (Ding *et al.,* 2006; Yu *et al.,* 2008). Ding *et al.,* 2006; Yu *et al.,* 2008 demonstrated that for ultrasonic pre-treated sludges at lower specific energies (respectively SE = 9500 kJ.kg-TS^{-1} and 112500 kJ.kg-TS^{-1}), TSS removal improvement could reach 40% and 48% after an aerobic digestion.

Ozone represented one the best pre-treatment in terms of TSS removal improvement and energy consumption under aerobic conditions. This result confirmed the interest of ozone used both from TSS removal improvement and energy requirements point of view compare to the

different pre-treatment (Paul *et al.,* 2006; Sievers and Schaefer, 2007; Park and Novak, 2007; Goel *et al.,* 2003). The values of TSS removal improvement (71% and 78.5%) are above the values proposed by Paul *et al.* 2006 (30%) to economically justify a process of sludge reduction and above the results of Sievers and Schaefer, (2007) on full scale application who reached 20-35% and 19% after aerobic or anaerobic stabilization and ozone treatment of 0.05 gO_3.g-TSS^{-1}. Deleris *et al.* (2002) obtained comparable results (70% of reduction of sludge production) with lower ozone dose (ozonation on the recycling loop 0.05 gO_3.g-VSS^{-1}).

Table 3-35: Comparison between TSS removal yield enhancement due to digestion and due to pretreatment plus digestion in aerobic digesters.

	Control 1	Ultrasonic	Thermal (90°C)	Autoclave	Control 2	Ozonation	Thermal (40°C)	Thermal (60°C)
TSS removal yield (%) (During digestion)	57.29	57.30	61.83	67.89	59	65.88	60.53	61.64
Removal yield improvement	-	1	1.08	1.18	-	1.12	1.03	1.04
TSS removal yield (%) (Pre-treatment and digestion)	57.29	76.07	67.75	69.13	59	71	62.5	65
Removal yield improvement	-	1.33	1.18	1.21	-	1.20	1.06	1.10

Different issues could explain the good results of thermal treatment (90°C and autoclave) before aerobic digestion: an important release of organics, an immediate and reversible biological inactivation associated with additional maintenance energy requirements and a potential inert production (Camacho *et al.,* 2005). Thermal treatment at 40°C did not led to significant improvement of sludge reduction. These last results were lower than the results presented in previous studies.

- **Dynamics of TSS removal efficiency**

The TSS elimination efficiency during sludge aerobic digestion process in both pilots after pretreatment (solubilization) was investigated in Figure 3-58.

During the first series of experiments, TSS removal rates have been increasing rapidly for the first ten days and then decreasing slowly. Autoclave, ultrasound and 90°C thermal treatments led to TSS removal improvement during the aerobic processes. The time needed to reach the

level of sludge reduction in the control sample after 42 days can be considerably reduced by the use of pre-treatment.

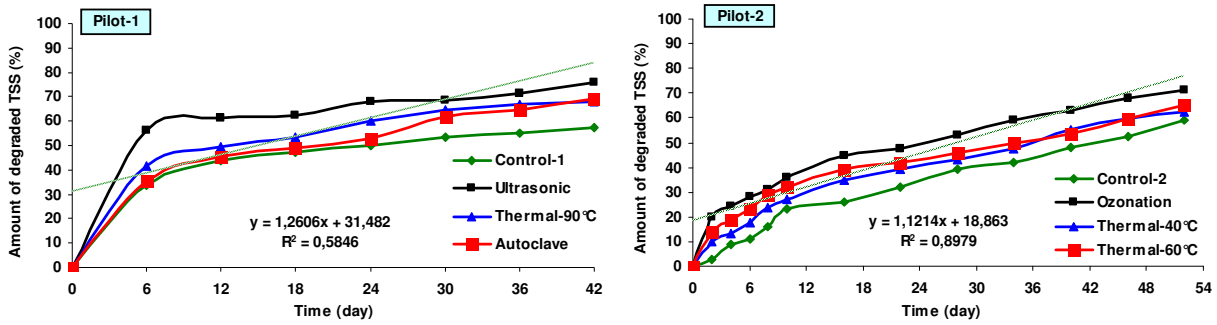

Figure 3-58: Comparison of removal efficiency performance after pre-treatment in aerobic digesters.

In the second series, TSS removal rates increase linearly with time. All of the investigated treatments led to TSS removal improvement. The reduction of the digestion time due to pretreatment is less important in this series (the kinetics are slower).

Linear correlation between TSS removal yield and digestion time after pretreatment and digestion for both series experiments were investigated (R^2 = 0.5846 for pilot 1 and R^2 = 0.8979 for pilot 2. see Figure 3-58).

5.2.1.2 VSS reduction improvement due to pre-treatment and digestion

- **VSS reduction removal efficiency**

VSS removal efficiency, and comparison between the part of digestion and the part of pretreatment & digestion are investigated (Table 3-36). The behavior of removal improvement of VSS is comparable to TSS. During the single step of digestion, ultrasound and thermal treatment did not led to sludge reduction improvement while ozone and autoclave led to a noticeable improvement of sludge reduction respectively 13% and 19% more than control sample. The analysis of the global removal yield improvement (pre-treatment plus aerobic digestion) showed that for ultrasonic and thermal treatment the pre-treatment itself represented the major source of sludge reduction. But with respect to the part of pre-treatment and digestion, we see an increase in efficiency in ultrasonic and thermal treatment (90°C and 60°C) as well as autoclave and ozonation. This means that pretreatment has a good impact on the removal efficiency enhancement of sludge.

Table 3-36: VSS removal yield enhancement with regard to digestion step and both pre-treatment plus digestion condition in aerobic digesters.

	Control 1	Ultrasonic	Thermal (90°C)	Autoclave	Control 2	Ozonation	Thermal (40°C)	Thermal (60°C)
VSS removal yield (%) (During digestion)	66.13	68.81	69.66	78.38	65.03	73.50	66.69	69.08
Removal yield improvement	-	1.04	1.05	1.19	-	1.13	1.03	1.06
VSS removal yield (%) (Pre-treatment and digestion)	66.13	81.46	76.10	79.42	65.03	78.85	68.84	72.71
Removal yield improvement	-	1.23	1.15	1.20	-	1.21	1.06	1.12

Regarding the process of ultrasonic and ozonation, there is a linear correlation between removal yield improvement and solubilization. However, there is no such a relation between autoclave and thermal treatment, and solubilization. This is probably due to the discrepancy in the different mechanisms studied.

- **Dynamics of VSS removal efficiency**

The organic matter removal (VSS) of sludge during the aerobic digestion process shows in Figure 3-59. Organic matter in the sludge, like TSS, decreases in all digesters and sonicated sample shows the most significant decrease. In the second pilot plant, ozonated sample experienced the highest VSS removal.

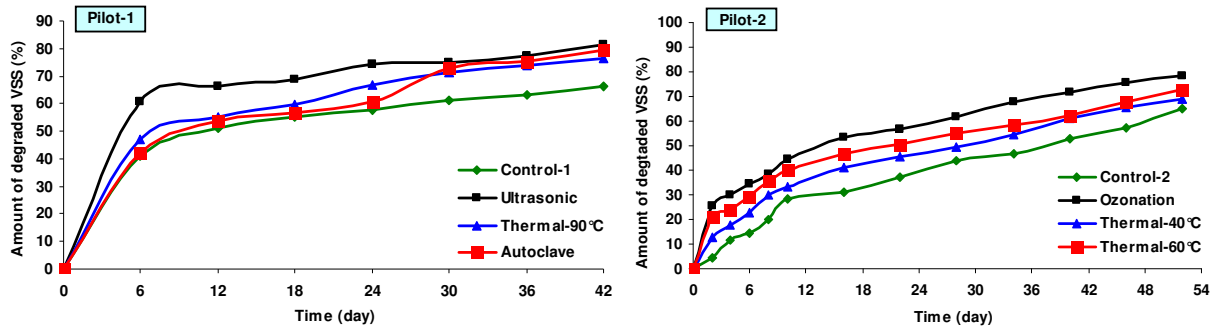

Figure 3-59: Variation of VSS concentration in reactors batch during sludge aerobic digester.

Almost all sludge samples experienced a mineral fraction has been degraded lower than 50% (a minimum rate of 27.90% for autoclaved sample and a maximum of 48.54% for sonicated sample). At the same time, organic fraction of sludge has been degraded more than 65% (a

minimum degradation rate of 68.84% for the thermal treatment at 40°C and a maximum rate of 81.46% for sonicated sample).

In this study the highest TSS, VSS and FSS removal yield improvement in aerobic reactors can be classified as follows:

$$TSS\rangle_{1.33}\ \text{ultrasonic} > \underset{1.21}{\text{autoclave}} \geq \underset{1.20}{\text{ozonation}} > \underset{1.18}{\text{thermal (90°C)}} > \underset{1.10}{\text{thermal (60°C)}}\ \underset{1.06}{\text{thermal (40°C)}}$$

$$VSS\rangle_{1.23}\ \text{ultrasonic} > \underset{1.21}{\text{ozonation}} \geq \underset{1.20}{\text{autoclave}} > \underset{1.15}{\text{thermal (90°C)}} > \underset{1.12}{\text{thermal (60°C)}}\ \underset{1.06}{\text{thermal (40°C)}}$$

$$FSS\rangle_{2.22}\ \text{ultrasonic} > \underset{1.77}{\text{thermal (90°C)}} > \underset{1.27}{\text{autoclave}} > \underset{1.16}{\text{ozonation}} > \underset{1.06}{\text{thermal (40°C)}} > \underset{1.03}{\text{thermal (60°C)}}$$

Sonication led to the highest sludge elimination efficiency (solubilization rate = 46.31%), while the lowest removal yield corresponds to thermal treatment at 40°C with 5% of solubilization (Table 3-37). The ozonated and thermal treated (90°C) samples were solubilized approximately 15% and their removal yield approximately was near to one other. In this study, mineral sludge matters (FSS) were hardly solubilized (a solubilization rate of less than 0.6% in this study) and only the organic sludge matters (VSS) were solubilized (at least 4.82% for autoclave and at most 54.98% for ultrasonic). This complies with results of Bougrier *et al,* (2005) reporting that during sonication with a specific energy of 15000 kJ/kg-TS, mineral matter were solubilized less than 3% while organic matter were solubilized about 29%.

Table 3-37: TSS, VSS and FSS removal yield in term of solubilization with regard to both pre-treatment and digestion condition in aerobic digesters.

	Control 1	Ultrasonic	Thermal (90°C)	Autoclave	Control 2	Ozonation	Thermal (40°C)	Thermal (60°C)
TSS Removal yield (%)	57.29	76.07	67.75	69.13	59.00	71.00	62.5	65.00
VSS Removal yield (%)	66.13	81.46	76.10	79.42	65.03	78.85	68.84	72.71
FSS Removal yield (%)	21.88	48.54	38.80	27.90	38.22	44.52	40.67	39.39
TSS Solubilization (%)	-	46.31	15.52	3.86	-	15.00	5.00	8.75

5.2.1.3 VSS/TSS ratio

Figure 3-60 presents results obtained for the four sludge samples of first series of experiments. For all sludge samples, VSS/TSS ratio decreased after pre-treatment. Therefore, solid concentration in particles decreased and particles became more mineral. In this figure we can

see that the highest solids solubilization corresponds to ultrasonic. At the same time, the least amount of decrease in VSS/TSS has occurred on the sonicated sample (13.19%). This is because during sludge sonication a significant amount of organic compounds are lysed into mineral matters. In Figure 3-60, it can also be observed that the highest rate of decrease in VSS/TSS corresponds to autoclave (32.67%). In other words in sonication process solubilization takes place effectively while autoclaved sample shows a higher biodegradation rate.

The difference between the amount of VSS/TSS in final effluent between control and other samples was not considerable (approximately 22%, 16%, and 19% for ozonation, 40°C, and 60°C against 14% for control sample). It means that ozonation was more successful than thermal treatment at 40°C or 60°C.

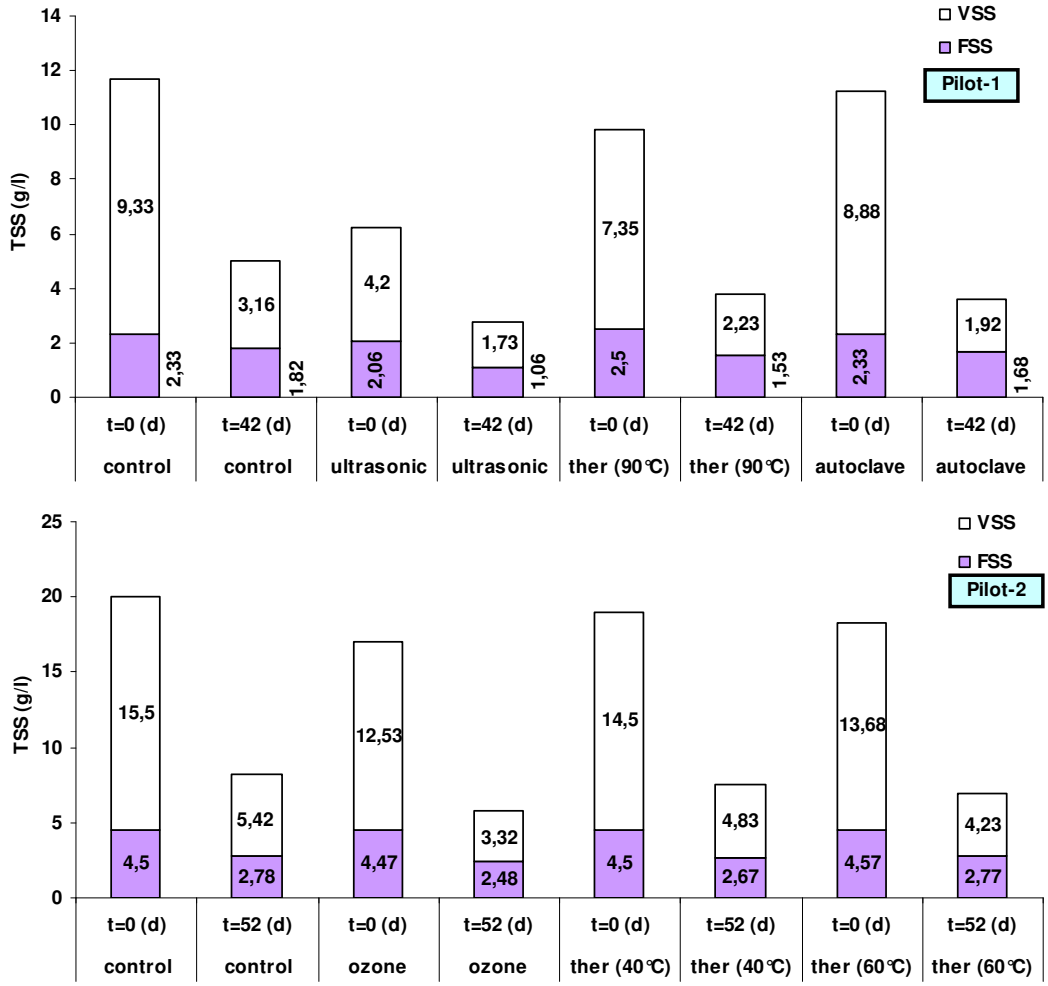

Figure 3-60: Biodegradation of sludge due to different pre-treatments and digestion versus inlet and outlet reactors for both series experiments.

5.3 Conclusion

Different pre-treatments were investigated: ultrasound, thermal and ozone, in order to enhance aerobic sludge biodegradability and production reduction. As demonstrated in chapter 3 – part 1, all of the pre-treatments led to a solubilization of COD, proteins, carbohydrates, total nitrogen and total phosphorus, TSS and VSS. The total, soluble and particulate removal improvement of these parameters were investigated and differed completely from one treatment to another.

The following conclusion can be drawn at the end of the aerobic digestion study:

❁ **Biodegradability improvement**

a) For the total forms

- Total COD removal improvement increased with increasing specific energy and thermal treatment (40°C, 90°C) and autoclave did not led to total COD removal improvement.
- Thermal treatment (40°C, 60°C) did not led to total protein removal improvement, but ultrasound are very efficient with 70% removal improvement.
- Pre-treatments in general did not noticeably improve total carbohydrat removal rates, the same observation can be made for total nitrogen except in the case of ultrasound (removal improvement of 23%).
- Ultrasound, ozone and thermal treatment (60°C) led to remarkable total phosphorus removal improvements (30%, 51%, and 43% respectively) while for other treatments the results are inconclusive.

b) For the soluble forms:

- All the pre-treatments induced a noticeable removal improvement of soluble COD, and proteins.
- Thermal treatments 40°C, 90°C and autoclave did not led to soluble carbohydrates and soluble nitrogen removal improvement.
- 90°C and 60°C Thermal treatments did not led to soluble phosphorus removal improvement.

❁ **Sludge reduction:**

- Ultrasound, Ozone and thermal treatment (90°C) present high sludge reduction improvements after aerobic digestion (respectively 33%, 20% and 18%).

- In the case of ultrasonic treatment the step of pre-treatment represent 76% of the global sludge reduction and the digestion step only 24% which means that the aerobic digestion step can be eliminated or considerably reduced with the use of ultrasound.
- For autoclave, ozone and 90°C thermal treatment, during digestion step represents only 20%, 13.5% and 5% respectively sludge reduction (VSS) improvements after aerobic digestion.
- Thermal treatment at 60°C and 40°C did not led to conclusive results in terms of sludge reduction.

For the majority of the parameters, ultrasound led to the best results in terms of solubilization, and then ozonation and thermal treatments. Surprisingly, for some parameters, the removal improvements did not follow the same order of classification. Investigating the potential relation between solubilization parameter and/or specific energy with removal improvement could led to better understanding of the involved processes. These investigations are given in chapter 4.

6. Anaerobic sludge digestion processes

Compared with aerobic processes the advantages of anaerobic processes lies in the production of an energetic gas (CH_4 + CO_2) and the degradation of non-easily biodegradable substances; On the other hand the disadvantage is slow kinetics. Anaerobic digestion is the standard technique to treat the biological sludge with the benefits of mass reduction, methane production, and improved dewatering properties of the fermented sludge. Due to the rate-limiting step of sludge hydrolysis, anaerobic degradation is a slow process with typical digestion time of 20 or more days (Eastman and Ferguson, 1981), and large digesters are, hence, necessary. Pretreatment-assisted biological sludge degradation has been extensively studied in laboratory, pilot and also in full-scale. Anaerobic degradation is accelerated as a result of disintegration and it is found that digestion time could be reduced.

The objectives of this part are to investigate biodegradability and sludge reduction improvement due to the introduction of ultrasonic, thermal and ozone treatments before anaerobic digestion of sludge.

This study claims that a pre-treatment by means of ultrasound, ozone and thermal treatment have the potential to enhance anaerobic sludge digestion.

6.1 Biodegradability enhancement of pre-treated waste activated sludge

Pre–treatment processes were developed to disintegrate the sludge, solubilize and convert slowly biodegradable organic material to readily biodegradable lower molecular weight compounds. Disintegration techniques can shorten stabilization time and increase the degradation efficiency of the subsequent biological process (Müller, 2001). The amount of sludge that has to be disposed of is reduced because of extended stabilization. The biodegradability improvement due to the pre-treatment is later investigated.

6.1.1 Evaluation of the BOD and COD elimination

During sludge biological elimination process, BOD and COD concentrations decrease. The biodegradability of the sludge is usually expressed as BOD/COD ratio. This parameter determines the ratio of organic biodegradable matter to total organic matter (biodegradable and non biodegradable). This ratio usually increases during solubilization process because biodegradable organic matter (BOD) increases in soluble phase. On the other hand during biological digestion process, biodegradability (BOD/COD) decreases because biodegradable organic matter (BOD) gradually degrades and decreases in soluble phase.

6.1.1.1 COD removal efficiency

- **Total COD removal**

Under anaerobic condition, ultrasound, thermal treatment (90°C), autoclave and ozone improved total COD removal yield (Table 3-38), while thermal treatment (40°C, 60°C) did not led to any improvement. The highest removal yield corresponds to sonicated sample (84.31%) and the lowest elimination efficiency is attained on the thermal (40°C) sample (74.84%). The highest total COD elimination efficiency improvement corresponds to ultrasonic (1.26 times more than control sample) and the lowest total COD removal yield enhancement corresponds to thermal treatment at 40°C sample (1.03 times more than control sample). In this study, the rate of removal yield improvement for autoclave was also considerable (1.22 times more than control sample).

Table 3-38: Elimination efficiency of COD in terms removal yield improvement, solubilization and specific energy in anaerobic digesters.

	Control 1	Ultrasonic	Thermal (90°C)	Autoclave	Control 2	Ozonation	Thermal (40°C)	Thermal (60°C)
Total COD Removal yield (%)	67.16	84.31	75.90	82.23	72.79	79.83	74.84	76.86
Removal yield improvement	-	1.26	1.13	1.22	-	1.10	1.03	1.06
Soluble COD Removal yield (%)	78.47	93.42	86.51	85.71	72.93	89.34	79.55	84.59
Particulate COD Removal yield (%)	66.30	76.36	73.45	81.55	73.70	79.23	74.96	76.19
Solubilization (%)	-	42.62	11.35	10.19	-	10.12	3.82	8.14
Specific energy (KJ/kg-TSS)	-	205800	555700	661600	-	46300	144000	216000

- **Soluble and particulate removal**

COD soluble and COD particulate for both series of experiments were investigated before and after digestion (Figure 3-61).The global COD concentrations are constant whatever the kind of treatment before the anaerobic digestion step is. The repartition of soluble and particulate forms before anaerobic digestion depends upon the kind of pre-treatment.

On the contrary, at the end of the process of anaerobic digestion, the repartition is comparable from one treatment to another. In the control the particulate forms are more predominant. The highest rate of soluble COD removal efficiency was 93.42% for ultrasonic treatment in the first series of experiments and was 89.34% for ozonation in the second series of experiments. The lowest rate of COD_S removal yield for both pilots corresponded to thermal treatment at 40°C (79.55%). For particulate COD we can say that the highest rate of elimination yield was observed on autoclave and ozonation (respectively 81.53% and 79.23%). The lowest rate of particulate COD removal efficiency happened on 40°C thermal treatment (74.96%).Generally, the removal yield enhancement of COD_S in second series of experiments was higher than pilot 1 while the removal yield improvement of COD_P was higher in the first pilot.

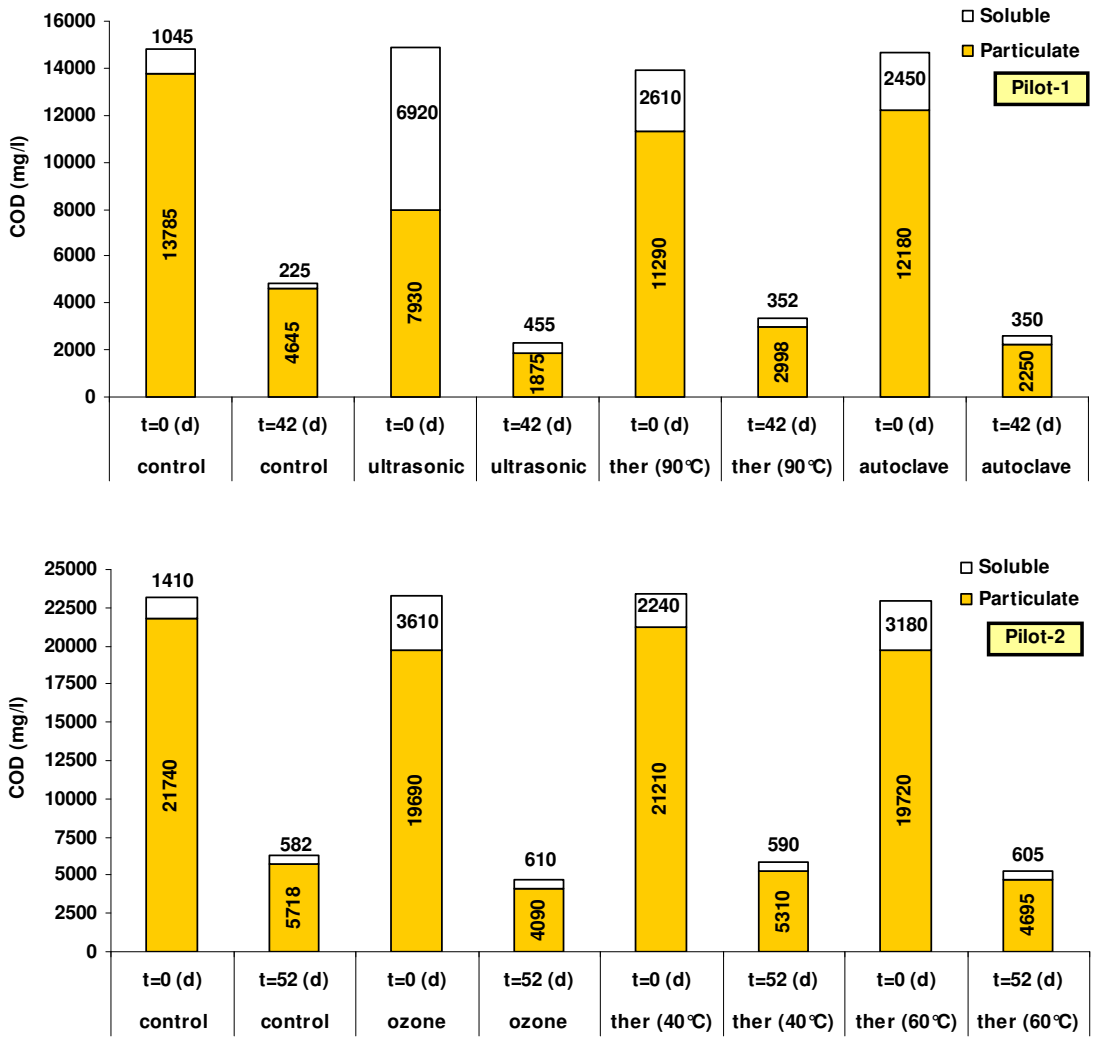

Figure 3-61: Solubilization and biodegradation of sludge before and after digestion.

Soluble COD removal yield improvement for ultrasonic and ozonation were respectively 1.20 and 1.22 times more than control samples. In other words, although they had totally different solubilization rates, they had nearly the same removal enhancement (42.62% for US against 10.12% for O_3).

Soluble and particulate COD removal yield improvement has been summarized as follows:

$$COD_S \underset{1.22}{\rangle} \text{ozonation} \geq \underset{1.20}{\text{ultrasonic}} > \underset{1.16}{\text{thermal (60°C)}} > \underset{1.10}{\text{thermal (90°C)}} \geq \underset{1.09}{\text{autoclave}} = \underset{1.09}{\text{thermal (40°C)}}$$

$$COD_P \underset{1.23}{\rangle} \text{autoclave} > \underset{1.15}{\text{ultrasonic}} > \underset{1.11}{\text{thermal (90°C)}} > \underset{1.08}{\text{ozonation}} > \underset{1.03}{\text{thermal (60°C)}} \geq \underset{1.02}{\text{thermal (40°C)}}$$

Particulate COD removal yield enhancement for first series of experiments was higher than second series analysis. Highest efficiency corresponded to autoclave (1.23 times more than control sample) and the lowest rate was observed for thermal treatment (40°C and 60°C).

- **Dynamics of soluble COD removal efficiency**

The amount of degraded COD (%) and the rate of q_{COD} were evaluated and investigated. Figure 3-62 shows the soluble COD removal elimination efficiency in batch reactors under anaerobic conditions. Elimination efficiency increase very quickly during the first ten days and increases gradually and slowly afterwards.

Therefore:

- The released organic matter is composed by a fraction of easily biodegradable matter and a non easily one,
- An average of 10 to 12 days could be sufficient to treat the major part of this matter

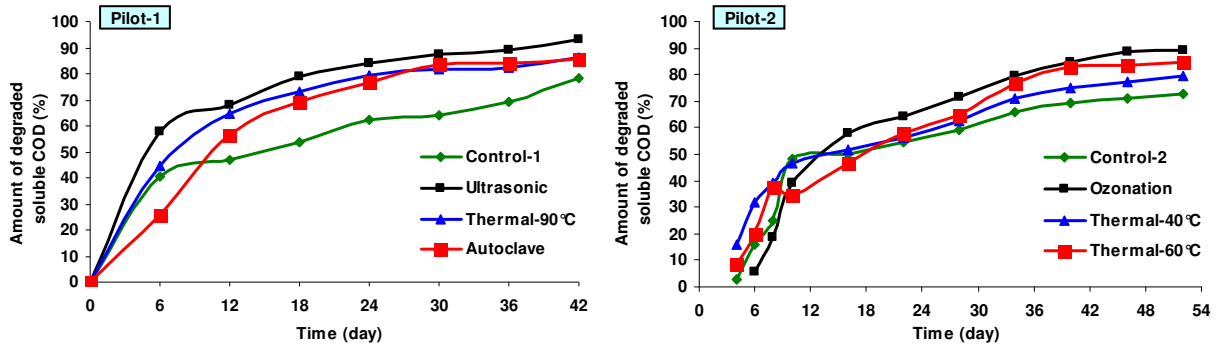

Figure 3-62: Variation of COD in batch reactors during sludge anaerobic digestion.

The global evaluations of q_{COD} were quite similar whatever the kind of pre-treatment. The instantaneous specific rates (q_{COD}) values for soluble COD removal in pilot 1 & 2 for anaerobic condition are represented in Figure 3-63.

In the first pilot, the highest q_{COD} rate occurs on the ultrasonic sample (112.80 mgCOD.g-$VSS^{-1}.d^{-1}$) which decreases strongly during the first week and reaches 36.77 mg $COD.gVSS^{-1}.d^{-1}$. Concerning autoclave and 90°C thermal treatment, this rate increases a little during one week and decreases afterwards to attain a value of 12-13 $mgCOD.g\text{-}VSS^{-1}.d^{-1}$. This decrease continues until 5^{th} week for which this rate meets its minimum. During the last week of experiments, q_{COD} decreases for all reactors. This may be due to the lack of easily biodegradable compounds.

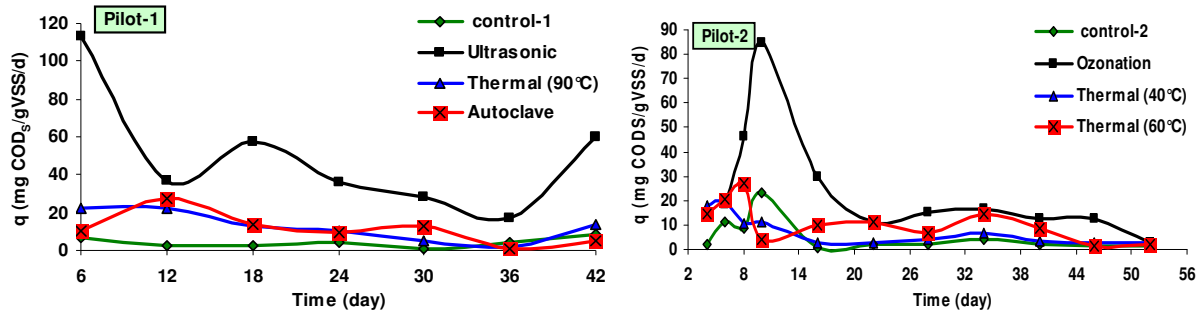

Figure 3-63: Instantaneous specific rates (q) for COD_S in over time under anaerobic condition.

In the second series, the highest q_{COD} corresponds to ozonation reactor in which after 10 days q_{COD} attains its maximum (84.67 mgCOD.g-VSS^{-1}.d^{-1}) and decreases afterward to attain its minimum value of 11.28 mgCOD.g-VSS^{-1}.d^{-1} after 22nd day (86.68% removal yield). For 60°C and 40°C thermal treatments q_{COD} increases during the first week and then it reaches to its lowest amount in the 15th day.

By continuing digestion (after 40 day for pilot 1 and 50 day for pilot 2), the rate of removal yield improvement reaches the same amount (1.20 and 1.22 for US and O_3 respectively).

To conclude, high solubilization rate (e.g. ultrasound) led to a rise in the soluble phase and decreases the particulate phase and consequently **shortens the digestion time and biodegradability**. Therefore, the more solubilization rate is, the higher the velocity (rate) of biodegradation would be in the digester and the less digestion time is required. In this study the soluble COD removal yield for ultrasonic after 12 days attained 67.99% while for ozonation nearly the same value (64.16%). is attained after 22 days.

6.1.1.2 BOD_5 removal yield and BOD/COD ratio

The BOD_5 removal efficiency improvement is studied in Table 3-39. More than 95% of BOD_5 for each kind of treatment is eliminated. The highest removal efficiency improvement belonged to ultrasonic and ozonation (1.05 and 1.04 more than control sample). The lowest removal efficiency corresponded to thermal treatment and autoclave, although these rates are not far away from those obtained by US and O_3.

More generally, the removal efficiency is high either for the control or for the pre-treated samples.

Table 3-39: BOD_5 removal rate for each pre-treatment in terms of specific energy under anaerobic condition.

	Control 1	Ultrasonic	Thermal (90°C)	Autoclave	Control 2	Ozonation	Thermal (40°C)	Thermal (60°C)
BOD_5 Removal efficiency (%)	94.44	99	95.24	96.36	95.56	99.57	97.54	98.99
Removal yield improvement	-	1. 05	1.01	1.02	-	1.04	1.02	1.03
Specific energy (kJ/kg-TSS)	0.0	205800	555700	661600	0.0	46300	144000	216000

The biodegradability of the lysate was also evaluated as a ratio of soluble BOD_5 to soluble COD_S. The enhancement of sludge biodegradability depended on the kinds of pre-treatment. Table 3-40 shows that highest biodegradability after solubilization and before digestion corresponded to ultrasonic pretreatment (68% more than control sample) and the lowest rate corresponded to thermal treatment (40°C and 60°C).

Table 3-40: Removal efficiency of BOD_5/COD_S after and before digestion and removal yield improvement in anaerobic digesters.

	Control 1	Ultrasonic	Thermal (90°C)	Autoclave	Control 2	Ozonation	Thermal (40°C)	Thermal (60°C)
BOD_5/COD_S (%) After solubilization	34.45	57.80	40.23	44.90	65.60	75.21	66.74	68.55
Removal yield improvement	-	1.68	1.17	1.30	-	1.15	1.02	1.05
BOD_5/COD_S (%) After solubilization and digestion	74.19	84.79	68.55	74.55	84.29	96.73	88.57	93.97
Removal yield improvement	-	1.14	0.92	1.00	-	1.15	1.05	1.11

The ratio of BOD_5/COD_S after solubilization and during digestion is reported in Table 3-40. We can see that the highest rate corresponds to ozonation (96.73%). It means that ozonation processes is very successful in sludge digestion. Evaluating total removal efficiency after solubilization and digestion reveals that ultrasonic and ozonation treatment result in high removal yields (84.79% and 96.73% respectively). In order to compare the different pre-treatments, the biodegradability enhancement was calculated. The ratio enhancement for total biodegradability was 15, 14 and 11 percent more than control sample respectively for ozonation, ultrasonic and thermal treatment at 60°C. On the contrary, this ratio for autoclave

and thermal treatment (90°C and 40°C) were not considerably different from the control sample.

Sludge biodegradability (BOD_5/COD_S) as a function of removal efficiency improvement can be classified as follows:

$$\left(\frac{BOD_5}{COD_S}\right) \underset{1.15}{\text{ozonation}} \geq \underset{1.14}{\text{ultrasonic}} > \underset{1.11}{\text{thermal (60°C)}} > \underset{1.05}{\text{thermal (40°C)}} > \underset{1.00}{\text{autoclave}} > \underset{0.92}{\text{thermal (90°C)}}$$

In this classification, it can be seen that the highest values of total improvement after solubilization and digestion belonged to ozonation and ultrasound pretreatments (1.15 and 1.14 times more than control sample). Although autoclave and thermal treatment at 90°C have high biodegradability rates during solubilization, (removal efficiency enhancement = 1.30 and 1.17 times more than control) but after solubilization and digestion, their removal yield improvement is not much more than control sample. For high temperature thermal treatments (90°C and 121°C), the lower biodegradability of organic compounds can be attributed to the possible actions of the treatment itself on carbohydrates and proteins molecules (e.g. millard reaction), leading to less biodegradable compounds (Bougrier *et al.,* 2006).

6.1.2 Evaluation of proteins and carbohydrates elimination

The concentrations of soluble proteins and carbohydrates in the supernatant before and after disintegration were also examined in order to evaluate disintegration.

6.1.2.1 Proteins removal efficiency

- **Total proteins removal**

Final protein elimination efficiency after solubilization and digestion, and removal enhancement under anaerobic conditions were investigated for all pre-treatments. As indicates Table 3-41, the highest total protein removal yield corresponds to sonicated sample (81.25%) and the lowest rate corresponds to thermal treatment at 40°C (60.08%).

Table 3-41: Elimination efficiency of protein in terms of removal yield improvement and solubilization in anaerobic digester.

	Control 1	Ultrasonic	Thermal (90°C)	Autoclave	Control 2	Ozonation	Thermal (40°C)	Thermal (60°C)
Total protein Removal yield (%)	56.81	81.25	69.58	72.67	65.60	73.54	60.08	70.04
Removal yield improvement	-	1.43	1.22	1.28	-	1.12	0.92	1.07
Soluble protein Removal yield (%)	66.86	93.77	88.51	78.21	71.92	86.07	67.74	84.70
Particulate protein Removal yield (%)	55.61	54.93	58.31	71.21	66.58	72.25	61.09	68.47
Solubilization (%)	-	66.24	34.27	13.65	-	8.97	0.52	8.81

The highest value of removal enhancement belongs to ultrasonic (1.43 times more than control sample) and then autoclave, thermal treatment (90°C) and ozonation (respectively 1.28, 1.22 and 1.12 times more than control sample).

- **Soluble and particulate proteins removal**

The biodegradation of soluble and particulate proteins for both series was assessed. Before anaerobic digestion, the soluble fraction of proteins is highly dependant upon the kind of treatment. After anaerobic digestion the main part of soluble proteins are removed and a non negligible part of particulate proteins is still remaining. The solubilization level of sonication process was very high (66.24%), the solubilization rates of thermal treatment at 90°C and ozonation were 34.27% and 8.97% respectively (see Figure 3-64).

Table 3-42: Removal yield and improvement of soluble and particulate proteins after solubilization and digestion under anaerobic conditions.

Pilot plant	Removal yield of soluble protein	Removal yield improvement	Removal yield of particulate protein	Removal yield improvement
Ultrasonic	93.77 (%)	1.40	55.61 (%)	0.99
Thermal (90°C)	88.51 (%)	1.32	54.93 (%)	1.05
Autoclave	78.21 (%)	1.17	71.21 (%)	1.28
Ozonation	86.07 (%)	1.20	72.25 (%)	1.09
Thermal (40°C)	67.74 (%)	0.94	61.09 (%)	0.92
Thermal (60°C)	84.70 (%)	1.18	68.74 (%)	1.03

By investigating protein biodegradation in outlet, it can be observed that a pre-treatment with a higher solubilization rate results in a higher soluble protein biodegradation and a lower

particulate protein biodegradation. For example ultrasonic (with the highest solubilization rate) has the highest soluble protein elimination efficiency (93.77%) and the lowest particulate protein elimination efficiency (54.93%) while thermal (40°C) (with the lowest solubilization rate = 0.52) has the lowest soluble protein removal yield (67.74%) and a high particulate protein elimination efficiency (61.09%). Thermal treatment at 90°C (with 34.27% solubilization) leads to 88.51% of soluble protein removal (less than sonication and more than ozonation) (Figure 3-64 and Table 3-42).

The results of removal yield and elimination improvement for soluble and particulate proteins are resumed in Figure 3-64.

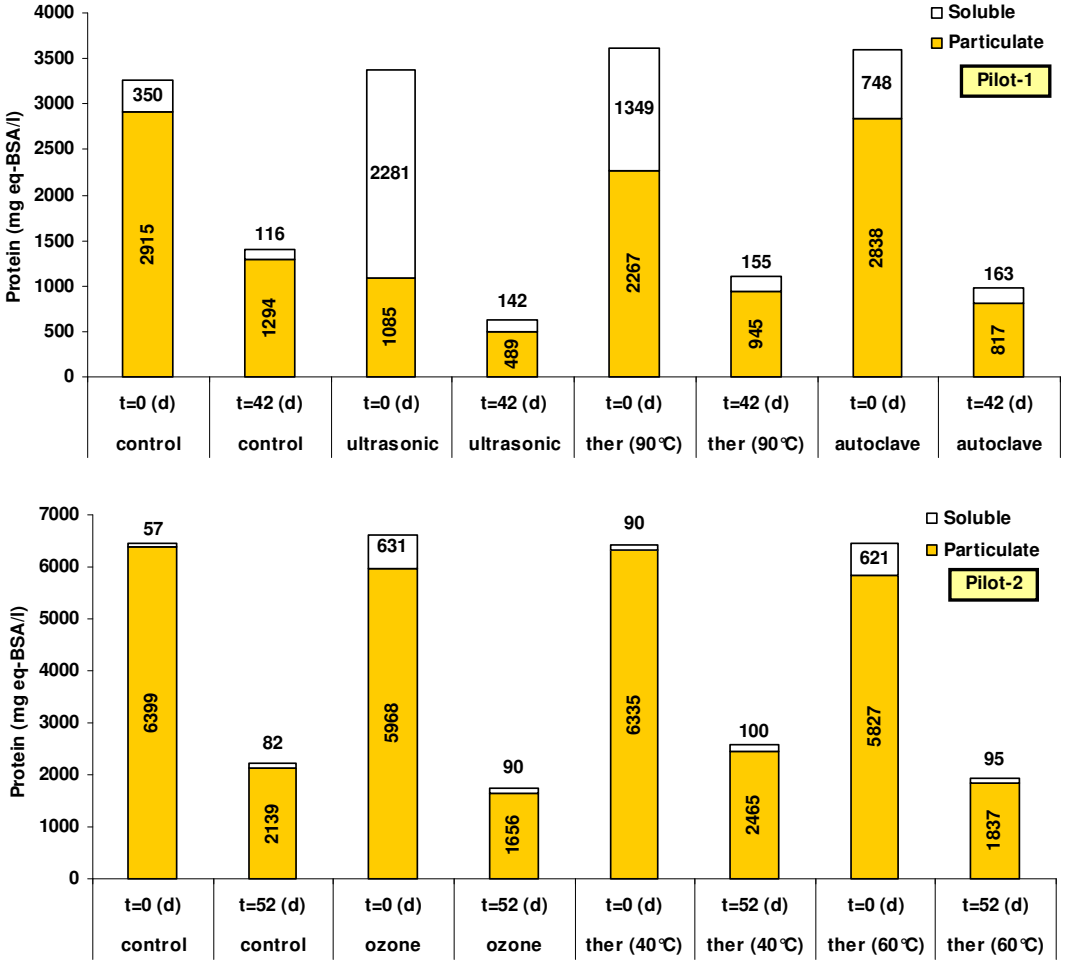

Figure 3-64: Solubilization and biodegradation of protein (soluble & particulate) before and after digestion.

Before anaerobic digestion, the soluble part of protein is highly dependant upon the kind of treatment. After anaerobic digestion the main part of soluble proteins are removed and a non negligible part of particulate proteins is still remaining.

Removal yield improvement for soluble and particulate proteins were calculated and classified as follows. The highest removal yield improvement corresponds to ultrasonic, thermal treatment and autoclave in soluble fraction, and to autoclave and thermal treatments in particulate fraction. In fact in the soluble phase, removal yield increases with solubilization rate.

$$\text{Protein}_S \rangle \underset{1.40}{\text{ultrasonic}} > \underset{1.32}{\text{thermal}(90°C)} > \underset{1.20}{\text{ozonation}} \geq \underset{1.18}{\text{thermal}(60°C)} \geq \underset{1.17}{\text{autoclave}} > \underset{0.94}{\text{thermal}(40°C)}$$

$$\text{Protein}_P \rangle \underset{1.28}{\text{autoclave}} > \underset{1.09}{\text{ozonation}} > \underset{1.05}{\text{thermal}(90°C)} \geq \underset{1.03}{\text{thermal}(60°C)} > \underset{0.99}{\text{ultrasonic}} > \underset{0.92}{\text{thermal}(40°C)}$$

- **Dynamics of soluble proteins removal efficiency**

The soluble protein elimination efficiency in both series is represented in Figure 3-65. Pretreatment led to an improvement of soluble proteins removal rate except for thermal treatment at 40°C for which the yield is comparable to the control sample.

In the first series, soluble protein elimination yield for sonicated and thermal treated samples are nearly the same after 40 days of fermentation. For ultrasonic and thermal treatment (90°C), the maximal soluble proteins removal was attained after 12 days compared to 42 days for the control sample.

In second pilot, ozonated sample and thermal treated sample at 60°C were nearly equally biodegraded. Soluble proteins removal increased linearly with time.

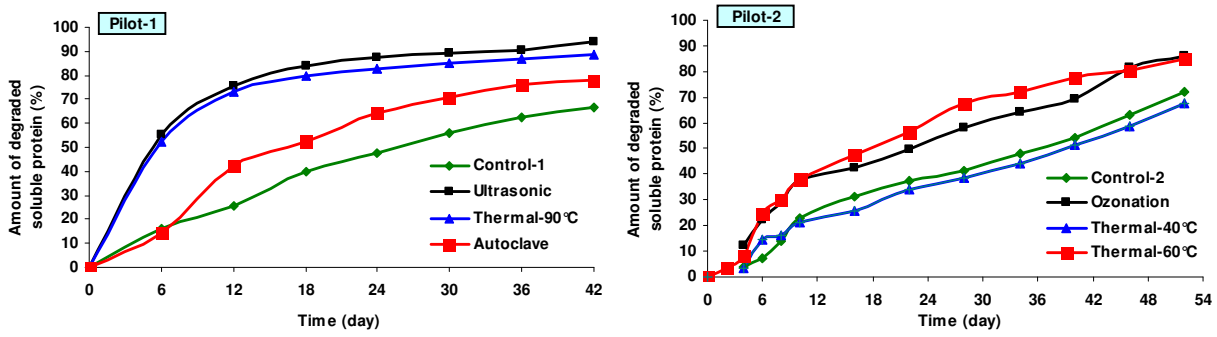

Figure 3-65: Variation of soluble protein in batch reactors during sludge anaerobic digestion.

The instantaneous specific rates for soluble proteins ($q_{protein}$) were investigated for both pilots (Figure 3-66).

In first series of experiments, $q_{protein}$ was high during the first 14 days and decreases afterwards. Ultrasonic treatment led to an important improvement of $q_{protein}$. For thermal treatment (90°C)

this improvement is less important while for autoclave treatment the values are more or less similar to the control sample.

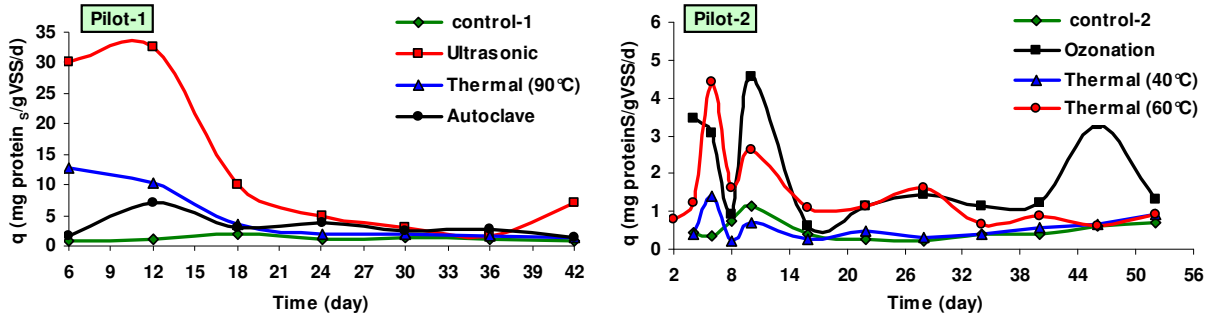

Figure 3-66: Instantaneous specific rates ($q_{protein}$) of soluble proteins over time under anaerobic conditions.

In the second series of experiments, the rate of $q_{protein}$ attains its maximal value during the first 14 days and then decrease. Ozonation and thermal treatment (60°C) led to an improvement of $q_{protein}$ while for thermal treatment at 40°C the value of $q_{protein}$ are similar to the control. Globally, the values for second series are lower than those of the first series.

6.1.2.2 Carbohydrates removal efficiency

- **Total carbohydrates removal**

The results of the final elimination efficiency of total carbohydrates for all pre-treatment methods as well as control sample were investigated. Table 3-43 shows that the removal yields of total carbohydrate at the end of digestion were nearly the same for control sample and other reactors. Compared to control sample, the removal improvements of 7% for Ozonation, 5% for autoclave and thermal (60°C), 2% for ultrasonic and 1% for thermal (40°C) were obtained. Pre-treatment did not lead to noticeable removal yield improvement. For both pilots, biodegradation (soluble and particulate) is very high and nearly equal for all sludge samples including control sample. Thus contrary to proteins, carbohydrates are easily biodegraded and this is in accordance with the researches of Barlindhang and Odegaard, (1996).

- **Soluble and particulate carbohydrates removal**

Solubilization and biodegradation of carbohydrates (soluble and particulate) in the inlet and outlet of both pilots are presented in Figure 3-67. Solubilization rate of first and second pilots are totally different, even for the control sample. This can be explained by the difference of the applied energy during pretreatment and probably the difference in concentration and nature of sludge samples.

Table 3-43: Elimination efficiency of carbohydrates as a function of removal yield improvement and solubilization in anaerobic digesters.

	Control 1	Ultrasonic	Thermal (90°C)	Autoclave	Control 2	Ozonation	Thermal (40°C)	Thermal (60°C)
Total carbohydrate Removal yield (%)	85.59	87.57	80.68	89.66	85.41	91.43	85.94	89.62
Removal yield improvement	-	1.02	0.94	1.05	-	1.07	1.01	1.05
Soluble carbohydrate Removal yield (%)	90.69	94.83	91.60	91.33	77.78	93.24	70.00	87.90
Particulate carbohydrate Removal yield (%)	83.67	77.38	75.60	89.04	85.76	91.28	86.44	89.70
Solubilization (%)	-	43.43	8.38	5.52	-	7.14	0.30	4.07

Carbohydrates repartition between soluble and particulate phase is highly dependant upon the king of pre-treatment. But after anaerobic digestion the repartition is quite similar whatever the kind of treatment and comparable to the control. The main part of soluble carbohydrates is degraded during all anaerobic digestions.

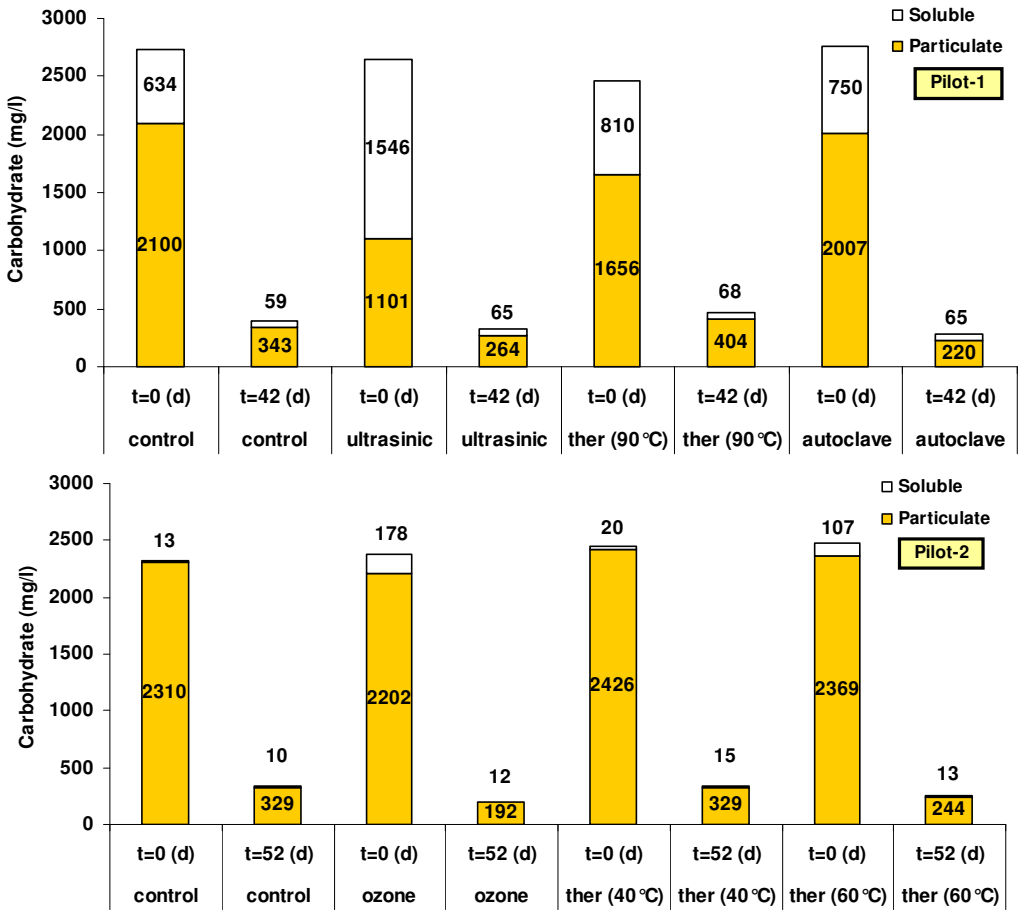

Figure 3-67: Soluble & total solubilization and biodegradation of carbohydrates before and after anaerobic digestion.

For soluble carbohydrate, in the first series of experiments, ultrasonic treatment has a high removal efficiency (94.83%); and in the second series of experiments, ozonation and thermal treatment at 60°C have a high removal yield (93.24% and 87.90%, respectively). But comparing the results of the two pilots, it can be found that the highest yield in soluble carbohydrate corresponds to ozonation, and then to thermal treatment (60°C) and ultrasonic. The amount of yield for ozonation, thermal (60°C) and ultrasonic is 1.20, 1.13 and 1.05 respectively. The other removal yields are close to control sample.

For particulate carbohydrate, the removal yield is lower than that of soluble carbohydrate. Further, autoclave and ozonation have the highest removal yield (6% more than control sample).

Classification of soluble and particulate carbohydrates shows that the maximum removal efficiency improvement for both parameters corresponds to ozonation. Moreover, Table 3-43 shows that ozonation has the highest removal yield enhancement of total carbohydrates (1.07 more than control). Given the results concerning carbohydrates, it can be concluded that ozone reactors has a higher removal yield improvement comparing to the other reactors.

$$\text{Carbohydrate}_S \rangle \underset{1.20}{\text{ozonation}} > \underset{1.13}{\text{thermal (60°C)}} > \underset{1.03}{\text{ultrasonic}} > \underset{1.00}{\text{thermal (90°C)}} \geq \underset{0.99}{\text{autoclave}} > \underset{0.90}{\text{thermal (40°C)}}$$

$$\text{Carbohydrate}_P \rangle \underset{1.06}{\text{ozonation}} = \underset{1.06}{\text{autoclave}} \geq \underset{1.05}{\text{thermal (60°C)}} > \underset{1.01}{\text{thermal (40°C)}} > \underset{0.92}{\text{ultrasonic}} \geq \underset{0.90}{\text{thermal (90°C)}}$$

- **Dynamics of soluble carbohydrates removal efficiency**

The elimination efficiency of soluble carbohydrates in anaerobic batch reactors is showed in Figure 3-68.

In the first series, at the beginning of the digestion process, the velocity (rate) of soluble carbohydrate removal is highest for the sonicated sample and the lowest for the autoclaved sample. The removal efficiency of autoclaved sludge is even lower than the control sample. It suggests the problem of bioavailability of solubilized organic matter after autoclave treatment. Thermal treatment at 90°C behaves like the control sample. At the end of digestion the elimination efficiency of treated and non treated samples are nearly the same (between 90% and 95%).

In the second series, thermal treatment and ozone showed better removal efficiencies than non-treated sludge. Carbohydrates removal after thermal treatment at 40°C is quite similar to non-treated sludge (control) which means no improvement.

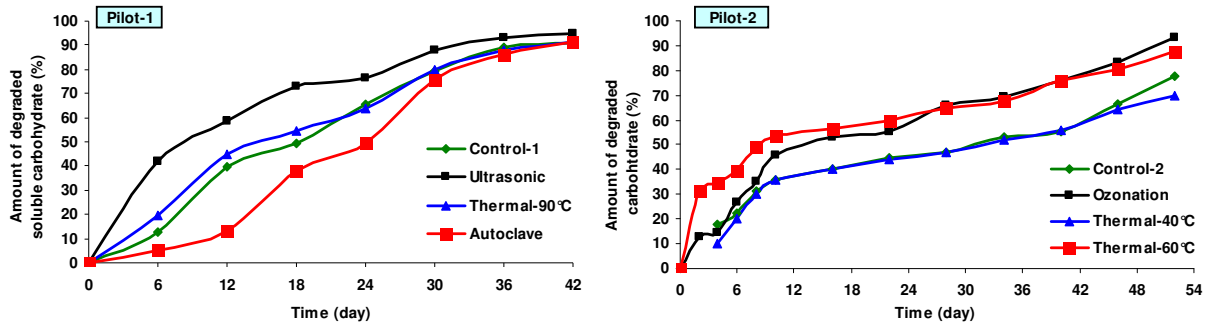

Figure 3-68: Variation of soluble carbohydrate in batch reactors during sludge anaerobic digestion.

The instantaneous specific rates ($q_{carbohydrate}$) are presented in Figure 3-69.

In the first series of experiments, the values of $q_{carbohydrate}$ are maximal for ultrasonic treatment. Thermal treatment (90°C) and autoclave behave like the control which means no improvement of the instantaneous specific rate. The later confirms the expected effect of autoclave and also thermal treatment on carbohydrates potential availability.

In the second series of experiments, ozone treatment led to improvement of $q_{carbohydrate}$ compared to the control sample. The values of thermal treatment at 40°C and 60°C are comparable to the control.

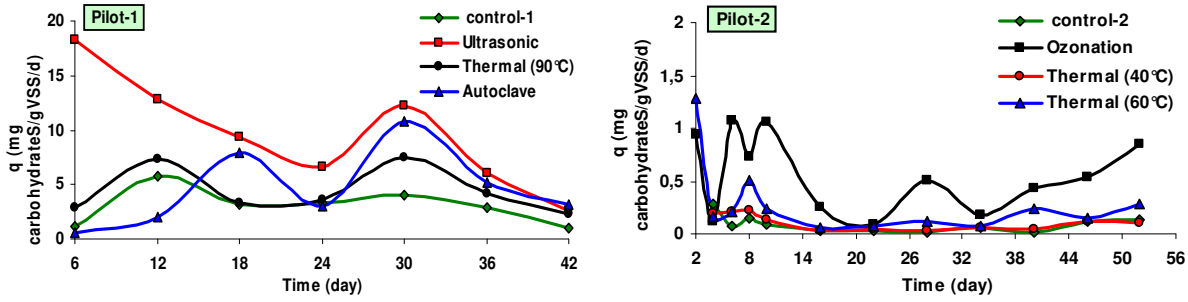

Figure 3-69: Instantaneous specific rates ($q_{carbohydrate}$) for soluble carbohydrate over time under anaerobic condition for both pilot (1 & 2).

6.1.3 Evaluation of nitrogen and phosphorus elimination

Sludge pre-treatment also increased the contents of nitrogen and phosphorus in the solution, and part of organic nitrogen and phosphorus released from the cells could be oxidized to

inorganic nitrogen and phosphorus. Regarding the elimination of nutrition, the feedback of nitrogen and phosphorus within the disintegrated sludge has to be considered.

6.1.3.1 Nitrogen removal efficiency

- **Total nitrogen removal**

The final results of total nitrogen removal efficiency and the removal yields improvement for the both pilots after solubilization and digestion are given in Table 3-44. At this study, the highest rate of the removal yield improvement of total nitrogen corresponds to ultrasonic treatment (16% more than the control sample). The other pre-treatment did not led to noticeable removal improvement compare to the control.

Table 3-44: Elimination efficiency of nitrogen in anaerobic digesters.

	Control 1	Ultrasonic	Thermal (90°C)	Autoclave	Control 2	Ozonation	Thermal (40°C)	Thermal (60°C)
Total nitrogen Removal yield (%)	65.17	75.51	66.67	61.90	59.84	65.38	60.14	62.69
Removal yield improvement	-	1.16	1.02	0.95	-	1.09	1.01	1.05
Soluble nitrogen Removal yield (%)	72.06	81.90	71.58	74.79	87.80	93.18	87.78	89.26
Particulate nitrogen Removal yield (%)	60.91	66.25	61.18	45.00	57.60	49.68	58.05	56.24
Solubilization (%)	-	43.64	24.55	25.45	-	31.34	1.38	13.36

- **Soluble and particulate nitrogen removal**

The soluble and particulate nitrogen after solubilization and digestion were assessed. The repartitions of soluble and particulate forms in the inlet are highly dependant upon the kind of pre-treatment. For example, the rate of nitrogen solubilization for ultrasonic is 43.64% and the rate of removal yield is 81.90% (14% more than the control sample). There is no mineralization phenomenon as the whole total concentration kept constant after the pre-treatments. At the end of anaerobic digestion, the repartition (soluble /particulate) is comparable to the control whatever the pre-treatment. Thermal treatment (40°C) does not have a high solubilization (1.38%), and thus the removal yield of soluble nitrogen is approximately equal to that of the control sample (87.78%). For the other parameters, the value of the removal yields is same as

the control sample (see Figure 3-70). There is a residual part of soluble nitrogen at the end of the anaerobic process.

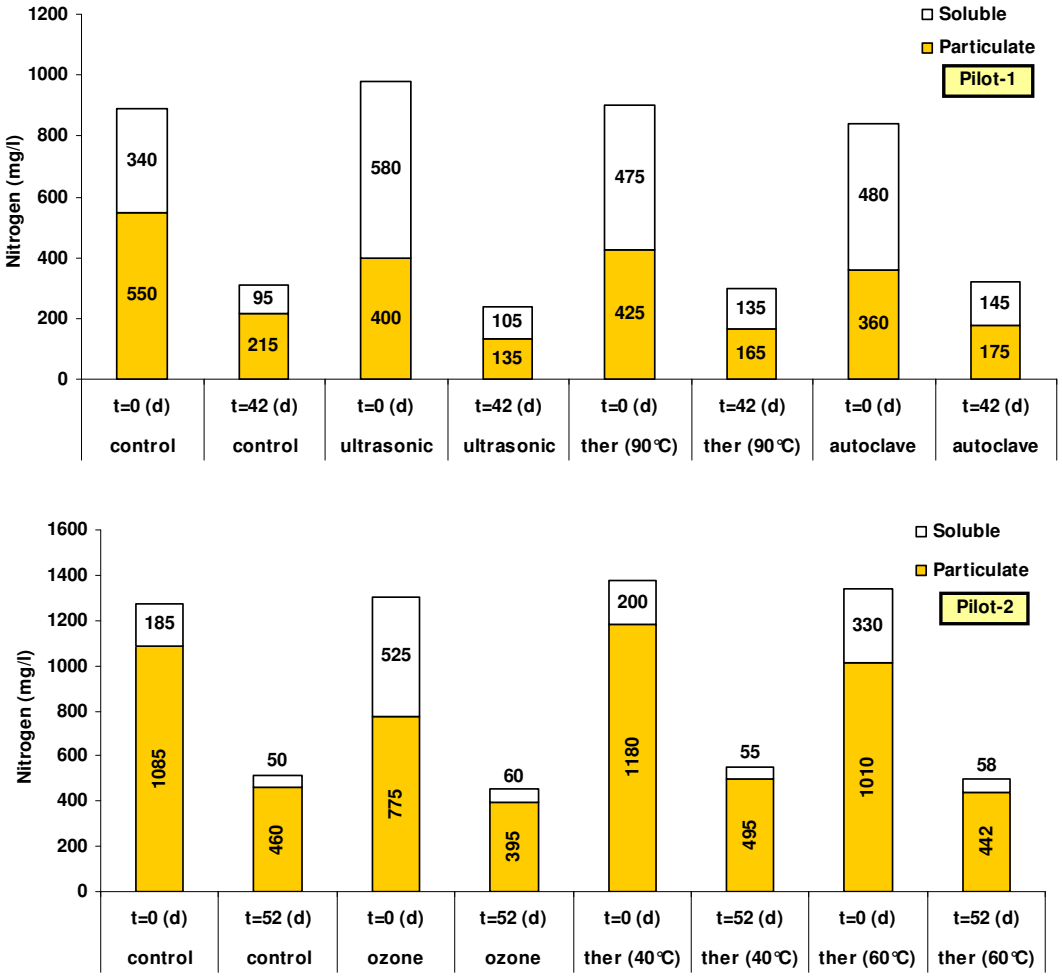

Figure 3-70: Solubilization and biodegradation of nitrogen (soluble & particulate) before and after anaerobic digestion.

The values of elimination efficiency enhancement of soluble and particulate nitrogen can be classifies as follows. It can be seen that the improvement of N_S is 1.14 more than control for ultrasonic. Ozonation, autoclave and thermal treatment at 60°C was 6%, 4% and 2% more than the control sample, respectively.

$$\text{Nitrogen}_S \rangle \underset{1.14}{\text{ultrasonic}} > \underset{1.06}{\text{ozonation}} > \underset{1.04}{\text{autoclave}} > \underset{1.02}{\text{thermal}(60°C)} \geq \underset{1.00}{\text{thermal}(40°C)} \geq \underset{0.99}{\text{thermal}(90°C)}$$

$$\text{Nitrogen}_P \rangle \underset{1.09}{\text{ultrasonic}} > \underset{1.01}{\text{thermal}(40°C)} \geq \underset{1.00}{\text{thermal}(90°C)} \geq \underset{0.98}{\text{thermal}(60°C)} > \underset{0.86}{\text{ozonation}} > \underset{0.74}{\text{autoclave}}$$

In the particulate fraction, only ultrasonic led to a slight removal improvement (1.09 more than control) and the removal yield improvement in the other reactors was not more than that of the

control sample. In general the removal yield of N_P in the first series of experiments was higher than the second series.

- **Dynamics of soluble nitrogen removal efficiency**

Soluble nitrogen elimination efficiency is presented in Figure 3-71. In the first pilot elimination efficiency of sonicated sample is higher than other samples. The soluble nitrogen removal rate increases linearly with time whatever the pre-treatment is. Soluble nitrogen removal rate of thermally treated sludge (90°C and autoclave) behave like the control sample.

In the second pilot, elimination efficiency increases quickly during the first 12 days of digestion. This increase slows down gradually. There is no noticeable difference between the treated and the non treated sludge which means that there is no soluble nitrogen removal improvement due to ozone and low-temperature thermal treatment.

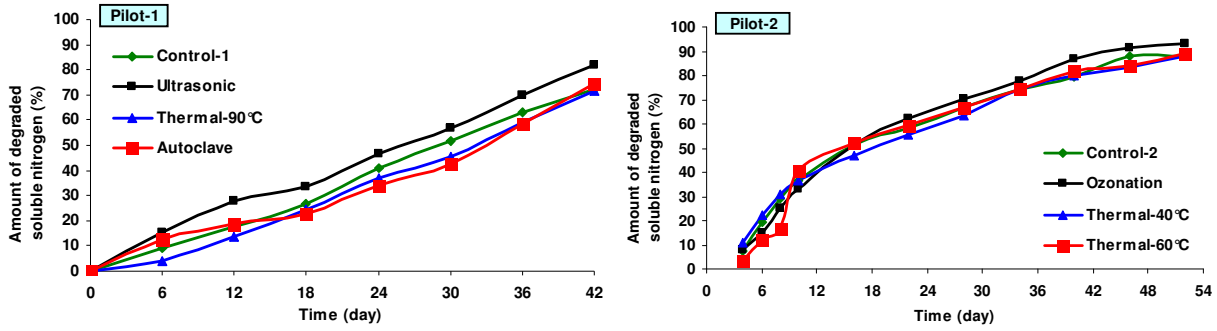

Figure 3-71: Variation of soluble nitrogen in batch reactors during sludge anaerobic digestion.

6.1.3.2 Phosphorus removal efficiency

- **Total phosphorus removal**

The highest solubilization rate corresponded to ultrasound and ozonation (38.82% and 35.11% respectively) and therefore the best results in terms of total phosphorus removal yield can be attributed to ultrasound and ozonation (respectively 29% and 35% more than control sample). Autoclave and thermal (60°C) led to lower improvements (11% and 28% more than control sample respectively) while thermal treatment 40°C and 90°C did not led to noticeable enhancement of total phosphorus removal.

Table 3-45: Elimination efficiency and removal yield improvement of phosphorus in anaerobic digester.

	Control 1	Ultrasonic	Thermal (90°C)	Autoclave	Control 2	Ozonation	Thermal (40°C)	Thermal (60°C)
Total phosphorus Removal yield (%)	50.41	65.08	50.44	55.93	28.14	38	27.37	35.96
Removal yield improvement	-	1.29	1.00	1.11	-	1.35	0.97	1.28
Soluble phosphorus Removal yield (%)	58.33	75.36	58.49	64.29	58.76	66.79	58.42	58.11
Particulate phosphorus Removal yield (%)	47.06	52.63	43.33	48.39	42.87	26.27	43.86	40.97
Solubilization (%)	-	38.82	20	23.53	-	35.11	0.17	21.80

- **Soluble and particulate phosphorus removal efficiencies**

Total phosphorus content of sludge was constant whatever the kind of treatment before anaerobic digestion. As for other parameters the soluble part of phosphorus is highly dependant upon the kind of treatment. At the end of the anaerobic digestion, an important part of soluble phosphorus is not degraded. The repartition between soluble and particulate composition is quite similar whatever the kind of treatment and close to the control.

Elimination efficiency of particulate phosphorus is higher in first pilot than in second pilot (see Figure 3-72). In fact ultrasonic treatments of the first pilot, have a high mineralization rate as well as a high solubilization rate. In other words these processes lead to a high biodegradation rate (43%-53%). However in second pilot (reactors containing ozonated, 40°C and 60°C thermal treated samples) soluble organic matters were well degraded, but particulate matters were not biodegraded efficiently (25% to 43%).

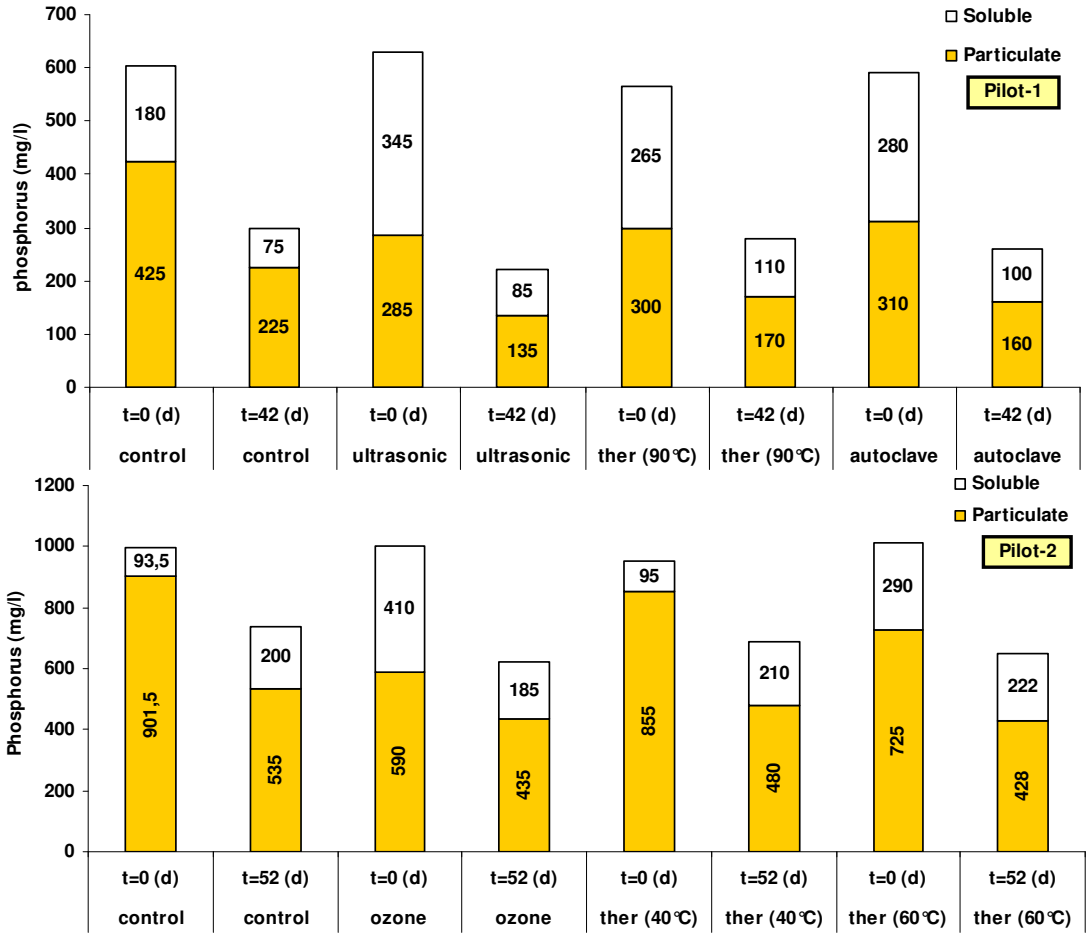

Figure 3-72: Solubilization and biodegradation of phosphorus (soluble & particulate) before and after anaerobic digestion.

Thus the following inequality can be concluded for the soluble and particulate phosphorus elimination efficiencies:

$$\text{Phosphorus}_S \rangle \underset{1.29}{\text{ultrasonic}} > \underset{1.14}{\text{ozonation}} > \underset{1.10}{\text{autoclave}} > \underset{1.00}{\text{thermal}\,(90°C)} \geq \underset{0.99}{\text{thermal}\,(60°C)} = \underset{0.99}{\text{thermal}\,(40°C)}$$

$$\text{Phosphorus}_P \rangle \underset{1.12}{\text{ultrasonic}} > \underset{1.08}{\text{thermal}\,(40°C)} > \underset{1.03}{\text{autoclave}} \geq \underset{1.01}{\text{thermal}\,(60°C)} > \underset{0.92}{\text{thermal}\,(90°C)} > \underset{0.65}{\text{ozonation}}$$

The highest removal yield improvement for soluble phosphorus corresponded to ultrasonic and ozonation and the lowest rate corresponded to thermal treatment. In particulate fraction, the highest elimination efficiency belonged to ultrasonic and thermal treatments while the lowest rate was observed on the ozonated sample.

- **Dynamics of soluble phosphorus removal efficiency**

The dynamics of soluble phosphorus elimination in anaerobic batch reactors is presented in Figure 3-73. The phosphorus removal rate increases quite linearly with time.

In the first series, sonicated sample is better biodegraded than other samples (75.36%). Removal yields of 90°C thermal treatment and autoclave are near the control sample (see Figure 3-73, pilot-1).

In the second pilot, the impact of pre-treatment on soluble phosphorus removal cannot be clearly demonstrated. At the end of the anaerobic processes, ozonated sample seems to be better biodegraded than others (66.79%). In this pilot phosphorus elimination of thermal treatments at 40°C and 60°C is not very different from control sample (58.42% and 58.11% against 58.76% for control). Thus ultrasound and ozone were more successful in phosphorus removal than thermal treatment. Thermal treatment has not a significant effect on phosphorus elimination.

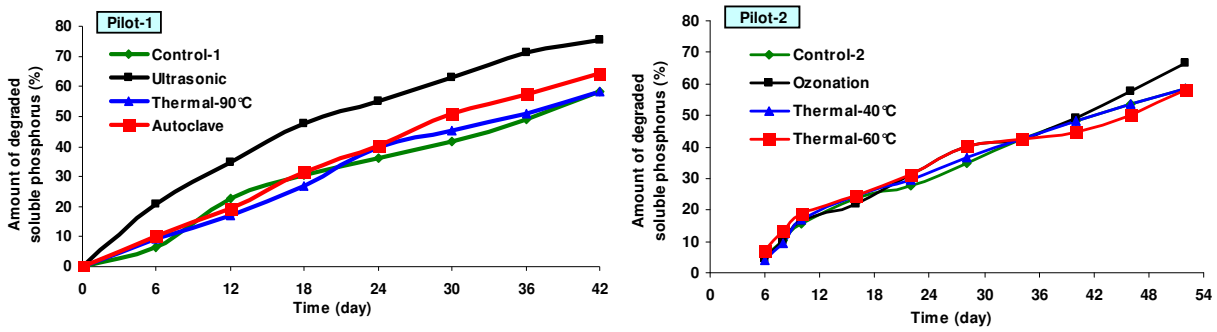

Figure 3-73: Variation of soluble phosphorus in batch reactors during sludge anaerobic digestion.

6.2 Sludge biodegradability improvement under anaerobic condition

Options for improvement of the anaerobic treatment process are further development of physical, chemical, thermal or combined physical/chemical/thermal pre-treatment processes, aimed at disintegration of the sludge prior to sludge digestion in order to increase the biogas production and to reduce the total amount of organics in the final sludge residue and therefore also the total amount of sludge residue.

Bougrier *et al.* (2005) reported that pre-treatment led to an increase of sludge biodegradability, but sludge does not become fully biodegradable. The rise of solubilization rate during pretreatment also leads to an increase in biogas production.

Anaerobic treatment (digestion) is aimed to produce biogas from the sludge and to improve the stability of the sludge and dewatering properties. The biogas can be used for electricity generation and for heating. With the standard digestion technologies in general 40–60% of the

organic matter is mineralized, strongly dependent on the type of sludge and the performance of the anaerobic digestion process. A substantial increase of biogas production can be obtained by applying a proper pre-treatment step, such as hydrothermal heating, microwave heating, ultrasonic heating, use of ozone, use of enzymes, use of liquid jets, pre-treatment (hydrolysis) with sodium hydroxide, high performance pulse techniques, wet oxidation and supercritical oxidation as a pre-treatment step (Camacho *et al*., 2002; Dohányos *et al*., 2000; Goel *et al*., 2003; Müller, 2002; Neis *et al*., 2000; Weemaes *et al*., 2000).

6.2.1 Biogas production

Anaerobic digestion is the breakdown of organic material by micro-organisms in the absence of oxygen. Biogas is generated during anaerobic digestion - mostly methane and carbon dioxide - this gas can be used as a chemical feedstock or as a fuel. Therefore, batch anaerobic digestion tests were realized in order to choose the best treatment. Figure 3-74 (pilot 1 and 2) presents accumulation results of batch anaerobic digestion tests. All pre-treatments allowed a biogas production equal or higher than for untreated sludge. Obviously the organic compounds transferred by pre-treatment from the sludge solids into the aqueous phase were readily biodegradable.

- **Quantitative evaluation of biogas production**

In first pilot, ultrasonic leads to the highest sludge biogas production. Biogas production starts within 24 hours after beginning the digestion process. This delay is about 3 days for the case of thermal treatment. For all pretreatments, the biogas production is very high during the first two weeks of experiment and after the 15^{th} day, biogas production decreases.

In second pilot, biogas production of ozonated sample, is some how different from other samples. For all other samples, biogas production speed is initially high and slows down afterwards, while for ozonated sample this phenomenon is observed with approximately five days of latency. Biogas production for other samples slow down after 15 days while for ozonated sample this happens after 20 days. This could be due to inhibitory conditions (too much ozone remained in the soluble phase), to the formation of refractory compounds, to not well-adapted inoculums or to ozone consumption by reduced compounds of the sludge.

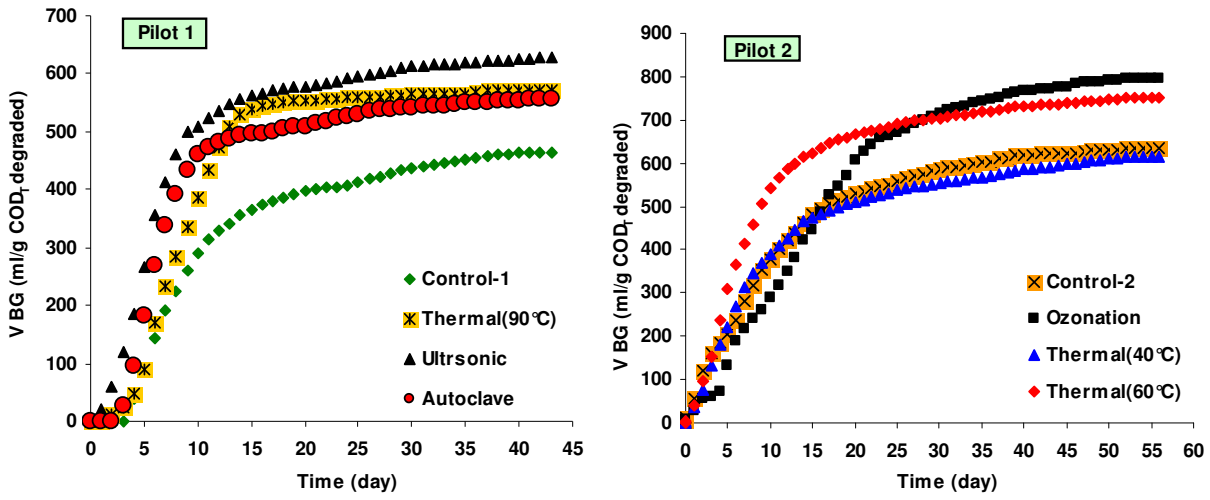

Figure 3-74: Volume accumulation of biogas production from different pre-treatment in anaerobic fermenter.

Biogas production enhancement was also evaluated as the specific ratio of milliliters of produced biogas per milligram of soluble COD biodegraded (Figure 3-75). In the first pilot, biogas production for sonication and thermal treatment is very high during the first week of digestion. This production decreases during the second week. From the 15th day on, biogas production becomes very low (During this period pretreated sludge is not totally biodegraded). Biogas production is negligible from 35th day on. Referring to Figure 3-62 and Figure 3-84, it can be seen that in the first pilot, biodegradation of COD, BOD, and VSS does not evolve significantly after the first 35th day of process.

In the first pilot, biogas production for thermal treated sample starts three days after sonicated sample. This latency may be due to the lack of required digestion conditions, and inappropriate reactor adaptation to the environmental conditions.

In the second pilot, thermal treated sample at 60°C has the highest biogas production rate, while the 40°C thermal treated sample has the same behavior as the control sample (there is no biogas improvement for the 40°C sample compared to control sample). For the ozonated sample, the most of biogas is produced in a period of 15 days (from the fifth day to the 20th day), and the biogas production is decreased afterwards. In this pilot we can see that biogas production is approximately halted after the 40th day.

The biogas production attained its maximum value after 20 days for the first pilot and after 30 days in second pilot. Thus it can be suggested that biodegradation of soluble carbon in the first pilot was more successful and effective compared to the second one. Pre-treatment makes the

substrate more quickly and effectively available to the bacteria and consequently shortens the rate- limiting step. As a result, to reach the same biogas production as for non-treated sludge, could be reduce the digestion time of pretreated sample to half (see Figure 3-75).

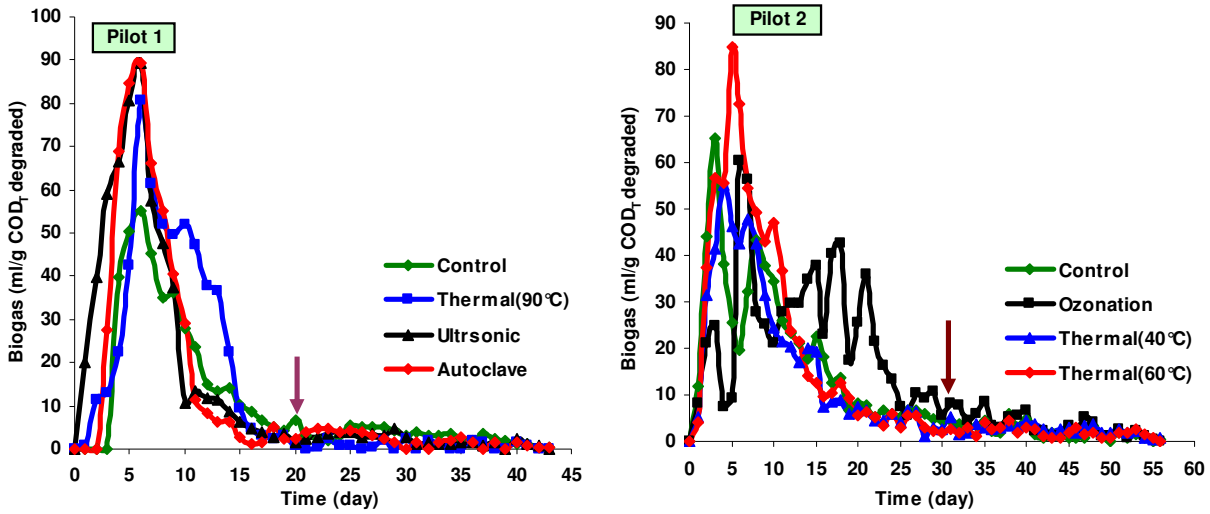

Figure 3-75: Instantaneous biogas to soluble COD yield (mL/mg-COD$_S$) during anaerobic digestion.

The driving parameters of biogas enhancement and biogas yield were investigated. Table 3-46 indicates biogas enhancement (the ratio of produced biogas to biogas production of control sample), the volume of produced methane, biodegradability rate, and increased biogas production to versus control sample (V_{sample}-$V_{control}/V_{sample}$). In this table it can be seen that biogas enhancement and biodegradability of sonicated sample is higher than other samples (69.65% increase compared to control sample). This is due to high solubilization rate of ultrasonic pretreatment. The more solubilization rate is, the higher biodegradability and biogas production would be. In this study, the biogas production and biodegradability of thermal treatment (90°C, 60°C, and autoclave), are nearly the same and are near the ozonated sample (30% to 45% increase compared to control sample).

The biogas production of control sample will reach 400 ml in first pilot and 535 ml in second pilot after 21 days. SRT (sludge retention time) in ultrasonic must be 6 to 7 days for biogas production to attain the same amount. This time is 8 to 11 days for thermal treatment (60°C, 90°C, and autoclave) and 17 days for ozonation and 25 days for 40°C thermal treatment.

Table 3-46: Biogas production enhancement and biodegradability in pilot plant 1 & 2.

Pilot plant (1)	Control-1	Ultrasonic	Thermal (90°C)	Autoclave
Biogas enhancement	1	1,70	1.30	1.45
Biogas yield (ml biogas/g-COD_T)	464.86	627.4	572.51	556.52
COD total biodegraded (%)	67.16	84.31	75.9	73.47
Increased volume of produced biogas (%) versus control	-	69.65	30.45	46.60
Total amount of biogas (ml)	4630	7855	6040	6695

Pilot plant (2)	Control-2	Ozonation	Thermal (40°C)	Thermal (60°C)
Biogas enhancement	1	1.38	1.01	1.24
Biogas yield (ml biogas/g-COD_T)	634.01	795.43	615.67	751.99
COD total biodegraded (%)	72.79	79.83	74.84	76.86
Increased volume of produced biogas (%) versus control	-	38.49	1.14	23.89
Total amount of biogas (ml)	10683	14795	10805	13235

Final volume of produced biogas in pilot 2 (after 52 day) was more than pilot 1 (after 42 day), but removal efficiency improvement in the first pilot was higher than second pilot. This could be due to different sludge type and concentration (TS = 12 $g.L^{-1}$ for pilot 1 and 21.6 $g.L^{-1}$ for pilot 2). It can be concluded the following relation for the biogas production enhancement and biodegradability in both pilot plants:

$$\underset{1.70}{\text{ultrasonic}} > \underset{1.45}{\text{autoclave}} > \underset{1.38}{\text{ozonation}} > \underset{1.30}{\text{thermal(90°C)}} > \underset{1.24}{\text{thermal(60°C)}} > \underset{1.01}{\text{thermal(40°C)}}$$

In first pilot, sonication which showed the highest solubilization rate had also the highest biogas production enhancement (1.7 times more than control sample). Biogas enhancement for ultrasonic treatment was comparable to the results of Bougrier *et al.* (2006). (in which lower specific energy but higher input power were used) and Kim *et al.* (2003).

The enhancement in biogas production obtained by ozone treatment (1.38 times increase compared to control sample for an ozone dose of 0.1 gO_3/g-TSS) was better than the results of Bougrier *et al.* (2006) with an ozone dose of 0.16 gO_3/g-TS (1.25 times higher than untreated sludge), but lower than the biogas enhancement obtained by Battimelli *et al,* (2003) for which the best result was obtained for 0.15 gO_3/g-TS (2.4 times increase compared to untreated sludge). This increase was completely linked to the sludge solubilization.

Thermal treatment especially at 90°C led to the best results in terms of biogas enhancement (30.45% for 90°C, 23.89% for 60°C, and only 1.14% for 40°C). Biogas enhancement at 90°C was considerably less than the results obtained by Bougrier *et al.,* (2008) at 95°C (70% biogas enhancement) but was more satisfactory than some other studies, for example Barjenbruch and Kopplow, (2003) obtained 16% and 21% of enhancement respectively at 80°C and 90°C. For thermal treatment at 60°C, biogas improvement was comparable to the results of Gavala *et al.* (2003) obtained at 70°C (26%) but was lower than biogas improvement obtained by Climent *et al.,* (2007) at 70°C (58%). In this study, biogas production at 40°C was approximately the same as control sample (only 1.01 times more than control sample).

Autoclave pre-treatment led to higher biogas improvement compared to other works: Barjenbruch and Kopplow, (2003) and Kim *et al.,* (2003), cited in Bougrier *et al.,* (2008) obtained respectively 20% and 32% of biogas enhancement in the same conditions.

❁ Qualitative evaluation of biodegradability enhancement

The biodegradability of pretreated sludge could be evaluated via the calculation of the volume of produced biogas, V_{BG} (mL) and biogas specific rate production (q_{BG}). The calculation of instantaneous specific rates of biogas production (q_{BG}) allowed a more accurate understanding of the mechanisms of biogas production.

In this study, biogas specific rate production (q_{BG}) was investigated in both pilots (Figure 3-76). At the beginning of the digestion, all the pre-treatment led to q_{BG} enhancement compare to the control. It can be observed that in the first pilot, q_{BG} for ultrasonic and autoclave decreases quickly during the second week. For all three reactors (ultrasonic, autoclave and thermal 90°C), q_{BG} attains its minimum value after 20 days (20.55, 7.84, and 11.40 mL BG.g-VSS^{-1}.d^{-1} respectively).

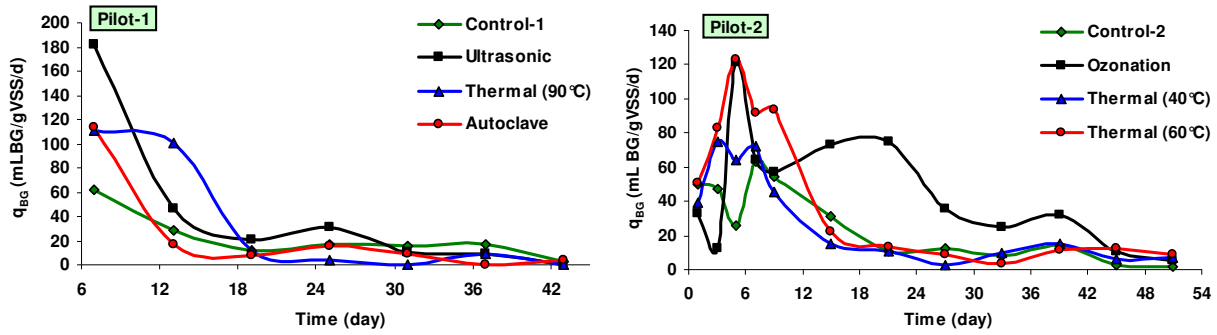

Figure 3-76: Biogas specific rate production (qBG) in termes of biogas production time.

For the second pilot, for all reactors q_{BG} increases during the first week and decreases afterwards. For thermally treated samples at 60 and 40°C q_{BG} is completely decreased after 20 days (13.07 and 10.27 mL BG.g-VSS^{-1}.d^{-1} respectively and then decreased to zero).

Y (mL biogas.mg-COD_S^{-1}) is another kinetic parameter that can express the relation between organic matters and biodegradable matters and volume of produced biogas. Figure 3-77 presents Y, in terms of mL produced biogas to mg soluble COD, for the both pilots and the anaerobic condition. It can be seen in Figure 3-77 that Y values for pre-treated samples is less than that of control (untreated) samples. Therefore, it can be concluded that the increase of produced biogas is due to the increase of released COD in pretreatment.

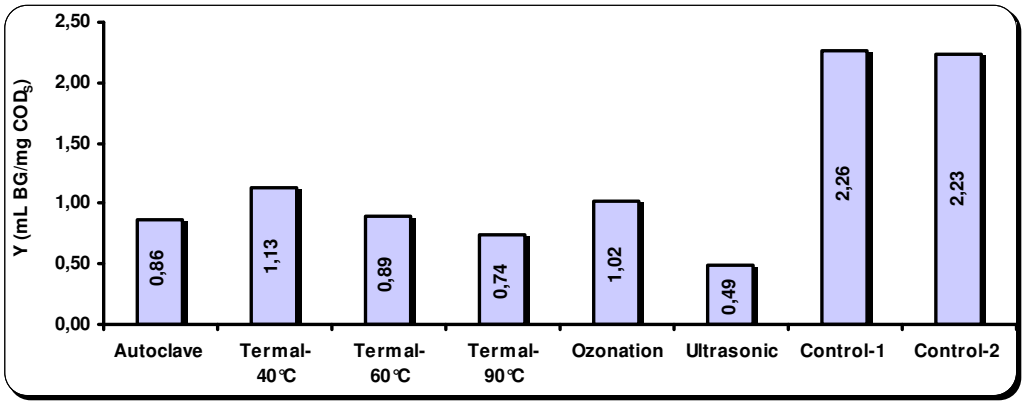

Figure 3-77: Y (mL biogas.mg-COD_S^{-1}) as a function of pretreatment method under anaerobic conditions.

The link between VSS and biogas enhancement was investigated. In Figure 3-78, Y values are calculated as mL produced biogas to g-VSS (volatile suspended solids).

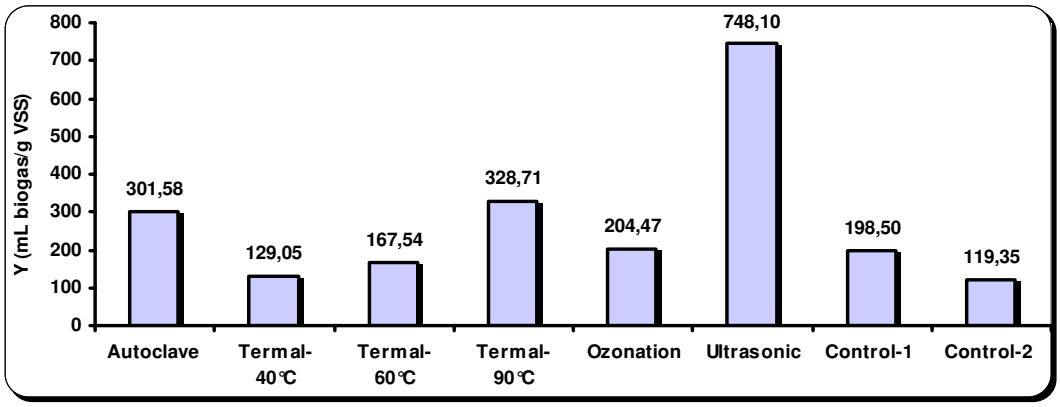

Figure 3-78: Y values (mL biogas.gVSS^{-1}) as a function of total biogas production on as a function of pre-treatment method under anaerobic conditions.

In this figure, the minimum of Y corresponds to the control (untreated) samples, and the maximum value corresponds to sonication. This means that there is a direct relationship between VSS reduction and biogas production.This result is in accordance with the work of Thiem *et al.* (1997) who examined the effect of ultrasound pre-treatment on VS destruction during anaerobic digestion of municipal sludge (53% primary sludge and 47% secondary sludge).

The effect of pretreatment on sludge and the increase of production of biogas can be summarized as follows:

$$\text{Biogas} \rangle \text{ultrasound} > \text{thermal}\,(90°\text{C}) \geq \text{autoclave} > \text{ozonation} > \text{thermal}\,(60°\text{C}) > \text{thermal}\,(40°\text{C})$$

6.2.2 The relationship between solubilization and biogas production processes

All the pre-treatment led to an improvement of solubilization of organic matter which implies a subsequent increase in biogas production as demonstrated before. The establishment of correlation between solubilization level and biogas production improvement whatever the kind of treatment could be of interest for the management of sludge reduction processes prior to anaerobic digestion.

- **Biogas enhancement and carbohydrate and proteins solubilization**

Solubilization led to an increase in biodegradability rate and biogas production. Measuring protein and carbohydrate concentrations after pre-treatment provides us with a better understanding of removal yield of digestion processes. In this study, the relationship between carbohydrate and protein solubilizations and biogas enhancement was investigated (Figure 3-79).

For low temperatures (40°C) which solubilization rate is low (less than 1%), the biogas enhancement rate is also low (less than 1.2%). By increasing temperature, the solubilization rate and biogas enhancement increase. We have:

Thermal (90°C) > (60°C) > (40°C)

The highest biogas production corresponds to ultrasonic pretreatment (70% biogas enhancement and 45-65% solubilization rates of the two parameters). In general, it can be observed that higher protein and carbohydrate solubilizations lead to more biogas production.

But ozone and autoclave show a different behavior. Although the solubilization rates of the two parameters are higher than thermal treatment at 90°C, the rate of biogas production is about 21% (for ozone) and about 34.5% (for autoclave) more than 90°C thermal treatment. Thus we can say that in this study, biogas enhancement cannot be linearly correlated to proteins and carbohydrates solubilizations but a logarithmic relationship with $R^2 = 0.87$ for protein and $R^2 = 0.74$ for carbohydrate can be observed.

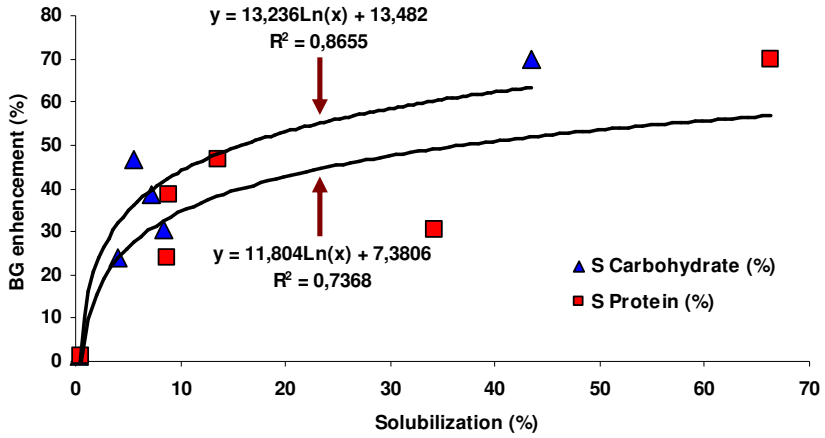

Figure 3-79: Biogas enhancement as a function of carbohydrates and proteins solubilization for different pre-treatments.

Previous studies stated that for the same kind of pre-treatment (e.g. ultrasound) biogas production could be linearly correlated to COD solubilization (Bougrier, 2005) or carbohydrates and proteins solubilization (Wang *et al.,* 1999). Some authors mentioned that proteins solubilization after thermal treatment could be prejudicial to biogas production (Bougrier, 2005). Cui and Jahng (2006) demonstrated that the enhancement of biogas production and the quality of biogas were improved by proteins partial removal (50%) after pre-treatment (sonication, thermal treatment) and before anaerobic digestion.

- **Y (mL BG.mg-COD_S^{-1}) and COD, proteins and carbohydrates solubilization**

Effect of biodegradability can be studied by total yield of biogas production (Y) which is the ratio of biogas to soluble COD (mL BG.mg-COD_S^{-1}). Relationship between solubilization parameters ($S_{protein}$ and $S_{carbohydrate}$) and total yield of biogas production (Y) were also investigated. In this study, Y is inversely proportional to solubilization rate. In Figure 3-80 we can see that Y has linearly decreasing with increasing rate of initial soluble protein and carbohydrate.

The reason that Y decreased with the increase of solubilization may be the formation of refractory compounds, formation of non-effective or less effective compounds (for biogas production), and additional maintenance energy requirements (cellular maintenance) (Dziurla *et al.,* 2005)

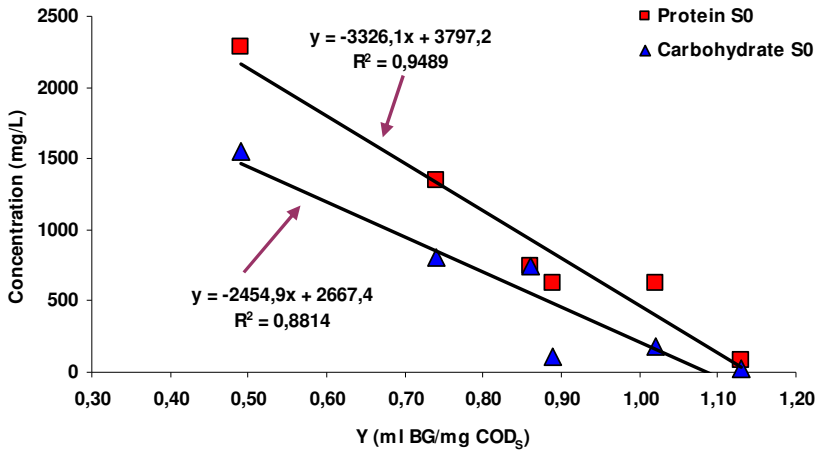

Figure 3-80: Variation of the total yield of biogas to soluble COD as a function of proteins or carbohydrates contents.

A reduction of Y was already observed by Camacho *et al.* (2005) after thermal treatment at 95°C. This reduction was attributed to additional maintenance energy requirements. Even at low ozone doses, Dziurla *et al.* (2005) demonstrated a decrease in the respiratory activity probably due to the alteration of the membrane permeability (COD is used for cellular maintenance).

6.2.3 Biogas production enhancement

The effectiveness of anaerobic digestion was assessed across the evaluation of the global conversion yield (Y = biogas to soluble COD). Previous studies show that biogas production can be linearly correlated to COD solubilization (Bougrier, 2005), carbohydrates and proteins solubilization (Wang *et al.,* 1999). At this study, the relation between soluble COD and biogas yield was investigated. In Figure 3-81, one can see a logarithmic tendency ($R^2 = 0.69$) between soluble COD and Y (mL biogas.mg-COD^{-1}). We can infer from the diagram that the production of biogas increased logarithmically with the decrease of soluble COD; the reason is the impact of solubilization, and consequently the process of digestion.

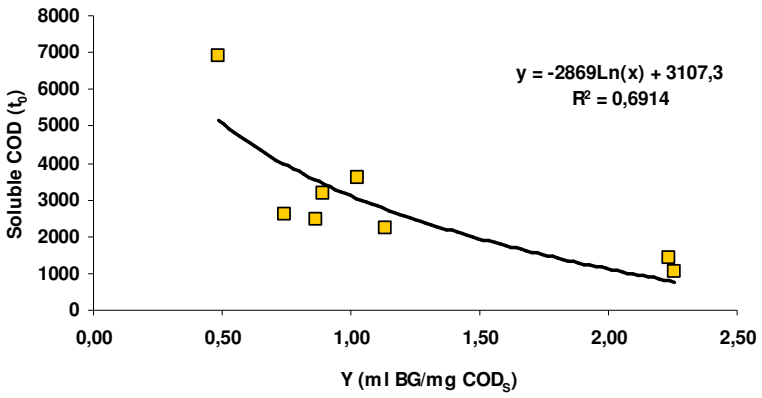

Figure 3-81: Values of Y (mL.mg-COD_S^{-1}) as a function of soluble COD.

6.3 Study of sludge reduction improvement under anaerobic conditions

Understanding the mechanisms induced in the reduction of sludge production with pre-treatment combined with biological process, requires investigation of its physicochemical and biological effects.

By the determination of the observed sludge production rates or efficiencies on a control sample and on samples treated with ultrasonic, ozonation and thermal treatment, it is possible to estimate the reduction of sludge production (RSP) on TSS, VSS.

6.3.1 Evaluation of VSS and TSS concentration

Processes can be applied in combination with the existing biological treatments to reduce excess sludge production (ESP). The chosen combined process aimed at sludge disintegration can be placed either on the wastewater treatment process or in the sludge treatment process (e.g., combined to anaerobic digestion). In all cases, treated sludge is sent back to a biological reactor for further degradation of the organic material. Thus, the use of the disintegration techniques mainly aims at improving the sludge VSS and TSS biodegradability while solubilizing the sludge mineral matter.

Table 3-47 indicates the final TSS, VSS and FSS removal efficiencies of samples in both pilot plants. These tables show that VSS elimination efficiency at the end of digestion process for ultrasonic is higher than ozonation and thermal treatment. The same results are obtained for FSS elimination. It means that the VSS elimination efficiency of sonicated sample is high and the VSS removal yield of 90°C thermal treatment and ozonation are not very different (≈ 10%). For the mineral matter elimination of sludge (FSS), sonication and ozonation led to nearly

equivalent results while thermal treatment was less successful than them in mineral matter removal. These tables also show that VSS removal was more successful than FSS removal.

Table 3-47: Elimination efficiency of TSS, VSS and FSS in anaerobic digester for both pilot 1 & 2.

	Control 1	Ultrasonic	Thermal (90°C)	Autoclave	Control 2	Ozonation	Thermal (40°C)	Thermal (60°C)
TSS Removal yield (%)	72.13	86.11	76.42	75.99	66	78.50	69.50	73.00
VSS Removal yield (%)	81.99	92.50	86.60	86.07	72.19	84.71	75.68	79.87
FSS Removal yield (%)	32.26	60.52	35.62	35.62	44.67	57.11	48.22	49.33
VSS Solubilization (%)	-	54.98	21.22	4.82	-	19.16	6.45	11.74

Figure 3-82 shows the TSS (VSS+FSS) rate for inlet (t = 0) and outlet (t = 42d and 52d) samples under anaerobic conditions. Before digestion process, the highest solubilization rate corresponds to sonication process (46.31%). 90°C thermal treatment and ozonation lead to a solubilization rate of 15.52% and 15% respectively. It is important to note that the amount of FSS is nearly the same after pretreatment process regardless of the pretreatment method. On the other hand, the amount of VSS decreases more or less depending on the pretreatment method. Obtained VSS solubilization rates were 54.98% for US, 21.22% for thermal treatment at 90°C, 19.16% for O_3, 11.74% for 60°C, 6.45% for 40°C, and 4.82% for autoclave.

During the digestion process in both pilots, TSS rate decreased dramatically for all processes (See Table 3-47, and Figure 3-82). As it can be seen in Figure 3-82, the decrease of VSS accounted for the most of TSS decrease (70%-90%). Thus the mineral matters in sludge (FSS) are not efficiently eliminated (less than 60%) compared to organic matters (VSS). These results comply with the findings of Bougrier *et al,* (2005).

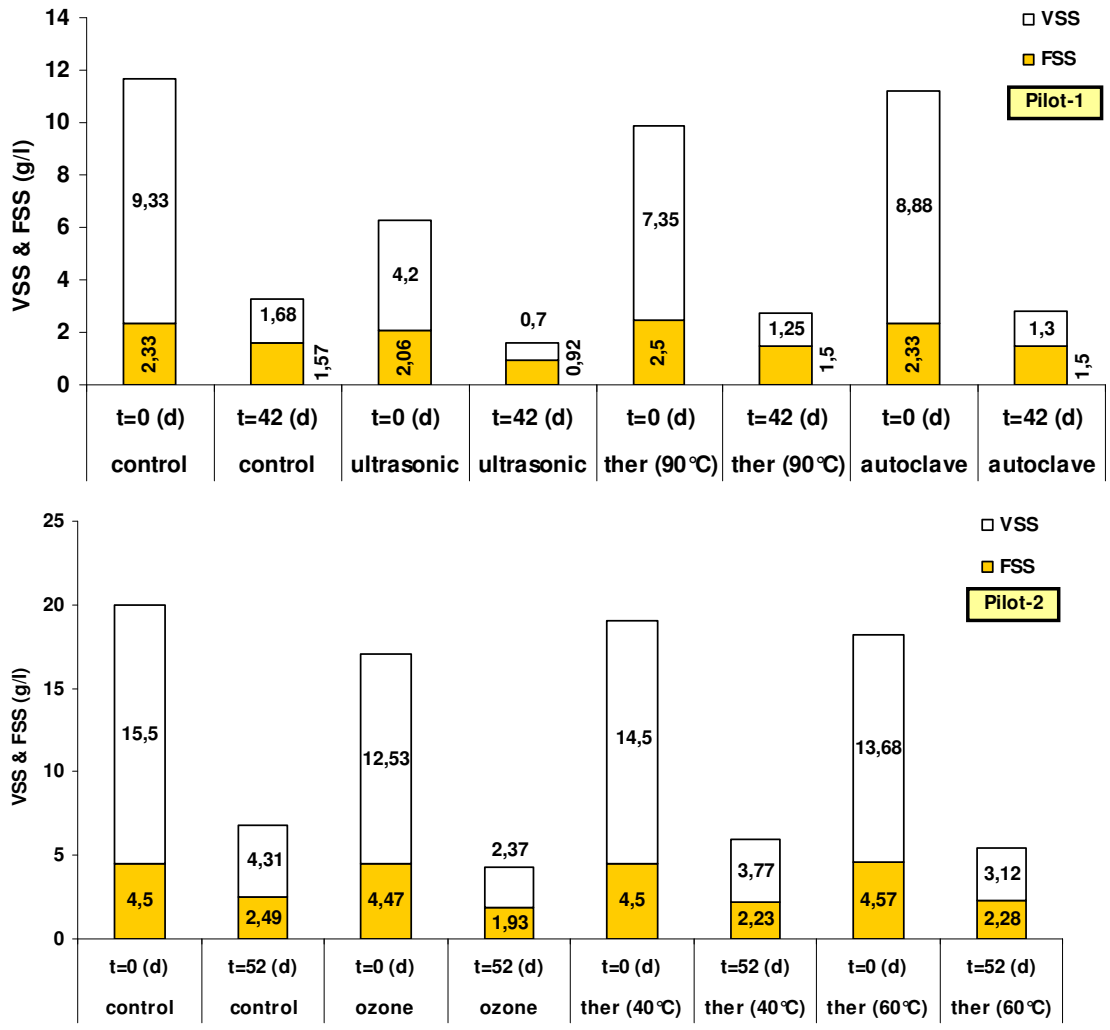

Figure 3-82: Sludge reduction rate (TSS & VSS) before and after digestion.

Sludge reduction improvements were globally lower than the results found in the literature after anaerobic digestion. Kim *et al.* (2003) obtained 89% and 56% of sludge reduction improvement for an SRT = 7 respectively after ultrasound and autoclave treatment, Bougrier *et al.* (2006) demonstrated a TSS removal improvement of 80% at a higher temperature (170°C). During digestion, TSS removal yield of ozonated sample was higher than other samples (1.13 times or 13% more than of control sample).

6.3.1.1 Sludge reduction due to pre-treatment and digestion in anaerobic reactors

a) TSS elimination improvement due to pre-treatment and digestion

Sludge usually decreases during digestion steps and pretreatment leads to better TSS reduction. Table 3-48 investigates TSS removal yield. The part of anaerobic digestion and pre-treatment in regard to sludge reduction were investigated. In this study, anaerobic digestion was

noticeably more successful than aerobic digestion: sludge removal yield values are higher than under aerobic conditions.

In this table it can be seen that for all reactors, the rate of TSS removal efficiency (except for control samples) is higher for pretreatment and digestion than digestion alone. In this study, in the part of pre-treatment + digestion, the values of TSS removal yield improvement for ultrasonic and ozonation treatments were higher than other reactors (1.19 times more than control sample). The level of sludge reduction reach the control value (at the end of the process) after only 6 days which means a considerable reduction of digestion time.

Table 3-48: TSS removal yield and relative contributions of pre-treatment and digestion steps under anaerobic condition.

	Control 1	Ultrasonic	Thermal (90°C)	Autoclave	Control 2	Ozonation	Thermal (40°C)	Thermal (60°C)
TSS removal yield (%) (during digestion)	72.13	74.12	72.08	75.02	66	74.71	67.89	70.41
Removal yield improvement	-	1.03	1	1.04	-	1.13	1.03	1.07
TSS removal yield (%) (Pre-treatment and digestion)	72.13	86.11	76.42	75.99	66	78.50	69.50	73
Removal yield improvement	-	1.19	1.06	1.05	-	1.19	1.05	1.11

The dynamics of TSS removal efficiencies after pretreatment and during digestion were investigated for both pilots. Figure 3-83 shows the TSS elimination efficiency for all pre-treatment methods as well as control sample. The total values range of TSS removal yield is increased from 66% to 86.11% under anaerobic condition. Ultrasonic and then ozonation lead to the highest TSS elimination efficiency (19 percent more than control sample) while thermal treatments were not very successful in TSS removal. TSS removal yield for thermal treatments (except thermal treatment at 60°C) were not very different than that of control sample.

In the first series, thermal treatment (90°C) and autoclave behave more or less like the control while ultrasound led to great improvement of TSS removal. In the second series, thermal treatment at 40°C and 60°C behave more or less like the control sample while ozone led to considerable improvement of TSS removal.

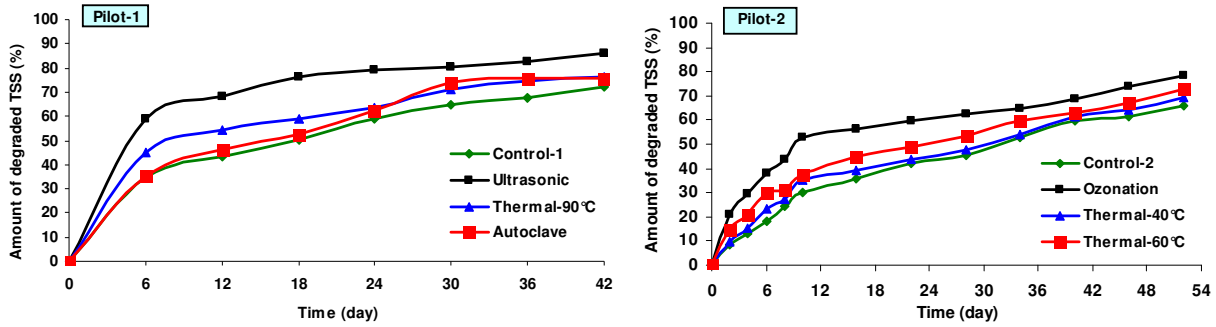

Figure 3-83: Comparison of TSS elimination efficiency for ultrasonic, thermal, autoclave, ozonation and control sample under anaerobic condition.

In fact, thermal treatment (40°C, 90°C and autoclave) did not led to significant improvement of sludge removal (TSS degradation improvement for 40°C = 5%, 90°C = 6%, and 121°C = 5%) which confirms the results of Barjenbruch and Kopplow, (2003). For thermal treatment (60°C) the rate of removal yield was 11% higher than control sample.

b) VSS elimination improvement due to pre-treatment and digestion

VSS elimination efficiency and VSS removal yield improvements under anaerobic digestion were evaluated. Table 3-49 shows the VSS removal yield of different pretreatments after solubilization and digestion with to removal yield of VSS after digestion in both pilots.

Table 3-49: VSS removal yield and relative contributions of pre-treatment and digestion steps under anaerobic condition.

	Control 1	Ultrasonic	Thermal (90°C)	Autoclave	Control 2	Ozonation	Thermal (40°C)	Thermal (60°C)
VSS removal yield (%) (during digestion)	81.99	83.33	82.99	85.36	72.19	81.09	74	77.19
Removal yield improvement	-	1.02	1.01	1.04	-	1.12	1.03	1.07
VSS removal yield (%) (Pre-treatment and digestion)	81.99	92.50	86.60	86.07	72.19	84.71	75.68	79.87
Removal yield improvement	-	1.13	1.06	1.05	-	1.17	1.05	1.11

It can be seen that the pretreated sample with the highest VSS solubilization rate (ultrasonic with 54.98%), had the highest VSS degradation (92.5%). 90°C thermal treatment and ozonation were solubilized at mostly equal rates (21% and 19%), thus they have a nearly equal biodegradability rate (86.60% and 84.71%). Also 40°C and 60°C thermal treatment, which led

to lowest solubilization rates (11.47% and 6.45%), had the lowest biodegradation rates (79.87% and 75.68%).

Some authors mentioned that improvement of VSS removal after pre-treatment during anaerobic stabilization can be correlated with VSS solubilization (goel *et al.,* 2003). Figure 3-84 shows the VSS concentration during the digestion process in the anaerobic batch reactors. We can see that in the first pilot ultrasonicated sample and for the second pilot ozonated sample had the highest VSS elimination rates.

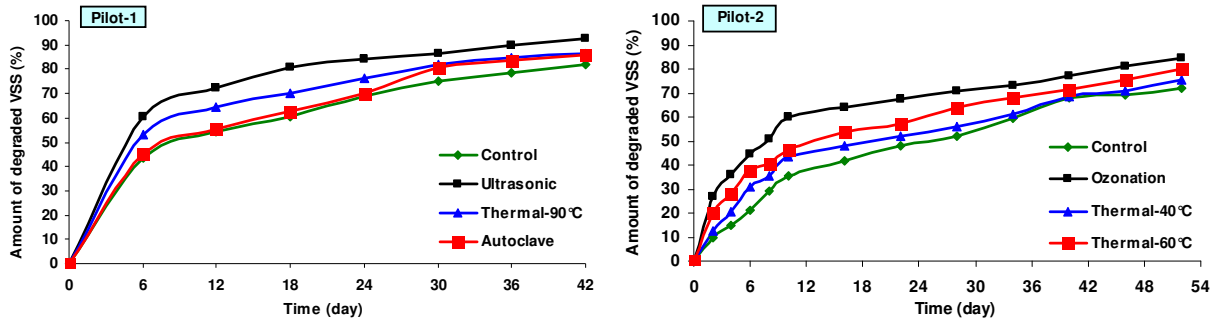

Figure 3-84: Variation of VSS removal yield in both reactors batch during sludge anaerobic digestion.

In this study, the removal yield of ozonation was 17% and ultrasound 13% more than control sample. The rate of elimination efficiency of thermal treatment was approximately the same as the control sample.

6.3.1.2 TSS/VSS ratio

The ratio of TSS/VSS for anaerobic digestion process is shown in Figure 3-85. This figure shows that TSS/VSS ratio decreases over digestion time. In the first pilot VSS/TSS decreases to 51.69% for control sample, 43.21% for ultrasonic, 45.45% for thermal treatment at 90°C, and 48.15% for autoclave process. In other words the elimination efficiency was about 40%. In the second pilot this ratio decreases to 63.38% for control sample, 55.12% for ozonated sample, 57.78% for thermal treated sample at 60°C, and 61.80% for 40°C thermal treated sample. In other words elimination efficiency of reactors in the second pilot plants was about 25%.

In conclusion, in the first pilot plant sonication treatment was the most efficient treatment in terms of matter biodegradation and thermal (90°C and autoclave) led to almost the same results. At the same time in the second pilot plant, the decrease in VSS/TSS is nearly the same for ozonated sample and 60°C thermal treated sample and for both cases is less than VSS/TSS decrease of sonicated sample and 90°C thermal treated sample.

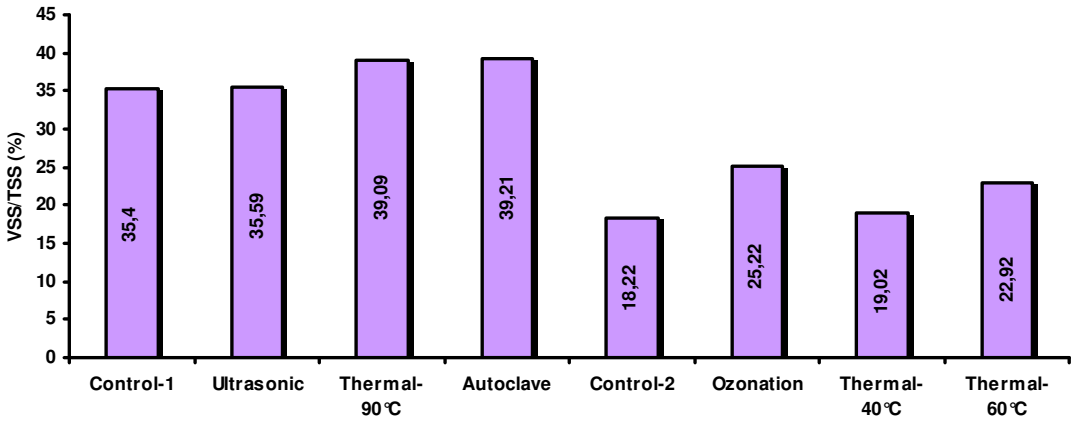

Figure 3-85: The ratio of VSS/TSS for different pre-treatment for pilot 1 & 2 and after anaerobic digestion.

Globally, in elimination of TSS and VSS, we can see that ozonation and ultrasonic have highest removal yields. In this study, thermal treatment did not feature a high elimination rate. It worth mentioning that the TSS and VSS removal yield improvement for 60°C thermal treatment was higher than autoclave and thermal treatment at 90°C (11% for 60°C thermal treatment against 6% for 90°C thermal treatment and 5% for autoclave, all more than control sample). It can be conclude that the use of low temperature pre-treatments (< 90°C), leads to a successful sludge removal and the efficiency does not increase with the temperature. Paul *et al,* (2006) demonstrated that by heating sludge at temperatures lower than 90°C, a part of the sludge minerals can be released by de-sorption or floc destruction but no increase in the intrinsic biodegradability occurs.

The pre-treatment in term of sludge reduction after anaerobic digestion can be classified as followed:

$$TSS \rangle \underset{1.19}{\text{ozonation}} = \underset{1.19}{\text{ultrasonic}} > \underset{1.11}{\text{thermal}\,(60°C)} > \underset{1.06}{\text{thermal}\,(90°C)} \geq \underset{1.05}{\text{autoclave}} = \underset{1.05}{\text{thermal}\,(40°C)}$$

$$VSS \rangle \underset{1.17}{\text{ozonation}} > \underset{1.13}{\text{ultrasonic}} > \underset{1.11}{\text{thermal}\,(60°C)} > \underset{1.06}{\text{thermal}\,(90°C)} \geq \underset{1.05}{\text{autoclave}} = \underset{1.05}{\text{thermal}\,(40°C)}$$

6.4 Conclusion

The increase of sludge biodegradability, biogas production and sludge reduction after sludge anaerobic digestion of solubilized sludge were studied. The following conclusions can be drawn:

❁ **Biodegradability improvement**

a) For the total forms

- Thermal treatment (40°C and 60°C) did not lead to total COD and total proteins removal yield improvement.
- Ultrasonic pre-treatment led to an important total proteins removal improvement of 43%.
- The removal yields of total carbohydrates and somehow total nitrogen (except for ultrasound) were not improved by pretreatments.
- Thermal treatment (90°C and 40°C) did not lead to total phosphorus removal improvement.

b) For the soluble forms

- All pre-treatments (excepting thermal 40°C) induced a noticeable removal improvement of soluble COD, and proteins.
- Thermal treatments 40°C, 90°C, autoclave and ultrasound did not lead to soluble carbohydrates removal improvement.
- The pre-treatments (except for ultrasound) did not induce a noticeable removal improvement of soluble nitrogen.
- Thermal treatments (40°C, 60°C and 90°C) did not lead to soluble phosphorus removal improvement.

c) Biogas

- The pre-treatment processes are effective in increasing biogas production.
- A logarithmic relation can be established between carbohydrates and proteins solubilization and biogas production enhancement.
- The highest biodegradability and biogas production was observed for ultrasonic (70% more than control), and then for autoclave, ozonation, thermal treatment at 90°C and 60°C (respectively 45%, 38%, 30%, and 24%).

- The biogas to soluble COD conversion yields of pre-treated sludge are lower than those of control sample, they decrease linearly with increasing initial concentration of soluble proteins and carbohydrates.

❁ **Sludge reduction improvement**

- The values of sludge reduction are higher under anaerobic conditions than under aerobic conditions.
- The best sludge reduction improvement can be attributed to ozone and ultrasonic pre-treatment (20% of improvement), for thermal treatments (40°C, 60°C, 90°C and autoclave) the results are less spectacular.
- In the case of ultrasonic treatment the respective contribution of pre-treatment and anaerobic digestion in sludge reduction improvement are equal (50%).
- In the case of ozonation, the digestion step represents 80% of total sludge reduction improvement and the pre-treatment step only 20%.

As in the case of aerobic digestion, it is difficult to establish a link between specific energy and/or solubilization and removal improvement. Investigating the potential relationship between solubilization parameters and/or specific energy with removal improvement could lead to better understanding of the anaerobic digestion after pre-treatment. These investigations are given in chapter 4.

7. Comparison of aerobic and anaerobic digestions

In this study, two series of pilots for biological digestion under aerobic and anaerobic conditions were used. Pilot 1 consisted of samples from ultrasonic, thermal (90°C), and autoclave as well as control sample. Pilot 2 consisted of samples from ozonation, thermal (40°C), and thermal (60°C) as well as control sample. It is important to mention that the test results for many parameters (e.g. removal yield) for control sample in first and second pilots were totally different. This could be due to the following reasons:

- There was a large interval of time between the operations of the two pilots. Pilot 1 started on 01/03/2007 while pilot 2 started on 24/11/2007.
- Quality of sampled sludge (before digestion) may be totally different in winter and summer.

- The concentration of sludge used in pilots was different. (Pilot 1: TS = 12 g/L and Pilot 2: TS = 21.6 g/L).

Therefore in order to obtain the most accurate results, it was necessary to compare the elimination efficiencies of each treated sample only with the control sample of the same pilot.

7.1 Comparison of biodegradability improvement

The biodegradability improvement of aerobic and anaerobic digestion is compared thereafter. As stated in the above section, it could be interesting for the setting up of aerobic and anaerobic digestion after pre-treatment to find "driving" parameters which predict the performances of the digestion step. The objectives of this chapter are double:

1) Comparing the removal improvement for different parameters and determining the best kind of digestion (aerobic anaerobic) and thus the best combination (pre-treatment and treatment),

2) Investigating the potential relations between biodegradability improvement and solubilization and/or specific energy input.

7.1.1 Comparison of removal yield

In most biological wastewater treatment process such as activated sludge process, though they have been recognized to be effective for organic wastewater treatment, a large amount of excess sludge derived from microbial growth has been problematic. Such excess sludge produced from the biological process has been generally digested either aerobically or anaerobically. To enhance the biodegradability of sludge cells, it is necessary to solubilize or hydrolyze the sludge cells prior to aerobic or anaerobic sludge digestion.

7.1.1.1 Soluble COD removal improvement

- **COD**

The COD_T elimination efficiencies (COD biodegradability) in the outlet of batch reactors were studied under aerobic and anaerobic conditions. We can see that for all pretreatments, COD biodegradation is more efficient under anaerobic conditions (at least 13.38% for ultrasonic and at most 34.34% for autoclave). The only exception is control sample of first pilot for which COD elimination of aerobic reactor is 12.99% more than that of anaerobic reactor (see Table 3-58).

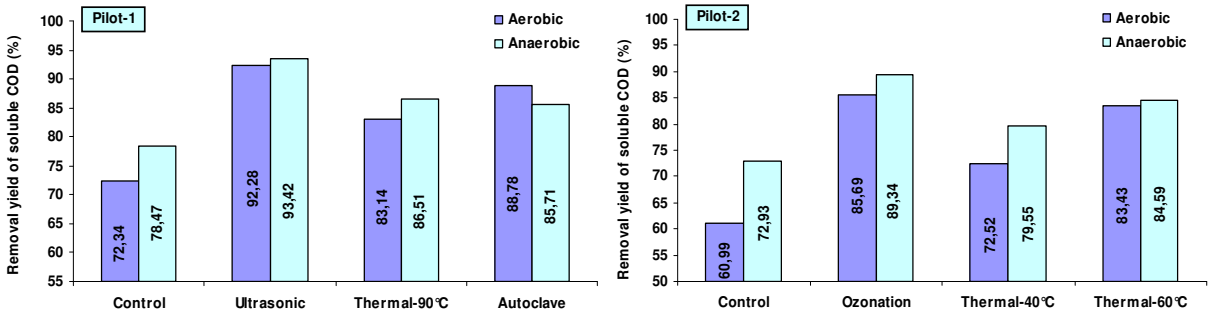

Figure 3-86: Comparison of removal yield of soluble COD in aerobic and anaerobic condition.

Soluble COD elimination efficiency of samples undergone different pretreatments showed in Figure 3-86. We can see that except for autoclave of first pilot, soluble COD elimination efficiency is higher under anaerobic conditions. However, the difference is not usually very significant (excepting untreated sample in second reactor). It means that by pre-treating sludge, elimination efficiency of aerobic and anaerobic reactors will be roughly the same. In other words, pretreatment minimizes the difference between aerobic and anaerobic biological elimination of soluble COD.

Soluble COD elimination efficiency can describe the difference between aerobic and anaerobic reactors in terms of COD_S removal improvement. The removal yield enhancement of COD_S under aerobic condition is more than anaerobic condition for all pretreatments. This difference in ozonation and ultrasonic pretreatment is more considerable than thermal treatment (Table 3-50). This means that in soluble COD elimination, the best combination for biodegradability improvement was attributed to ozonation treatment prior to aerobic digestion (41%).

Table 3-50: Removal yield of soluble COD under aerobic and anaerobic conditions.

	Control 1	Ultrasonic	Thermal (90°C)	Autoclave	Control 2	Ozonation	Thermal (40°C)	Thermal (60°C)
	Aerobic							
Soluble COD Removal yield (%)	**72.34**	**92.28**	**83.14**	**88.78**	**60.99**	**85.69**	**72.52**	**83.44**
Removal yield enhancement	**-**	**1.28**	**1.15**	**1.23**	**-**	**1.41**	**1.19**	**1.37**
	Anaerobic							
Soluble COD Removal yield (%)	**78.47**	**93.42**	**86.51**	**85.71**	**72.93**	**89.34**	**79.55**	**84.59**
Removal yield enhancement	**-**	**1.20**	**1.10**	**1.09**	**-**	**1.22**	**1.09**	**1.16**

- **BOD**

Variations of soluble BOD_5 before and after digestion in aerobic and anaerobic digesters were investigated (Figure 3-87). It can be seen that except for control sample of the first pilot, soluble BOD_5 removal yield is higher under anaerobic conditions than under aerobic conditions. In the second experiments, the removal yield of BOD_5 for anaerobic conditions is higher than that of aerobic conditions. For ozonation, both reactors yield the same elimination efficiency. Generally, anaerobic reactors are more successful in soluble BOD_5 elimination compared to aerobic reactors.

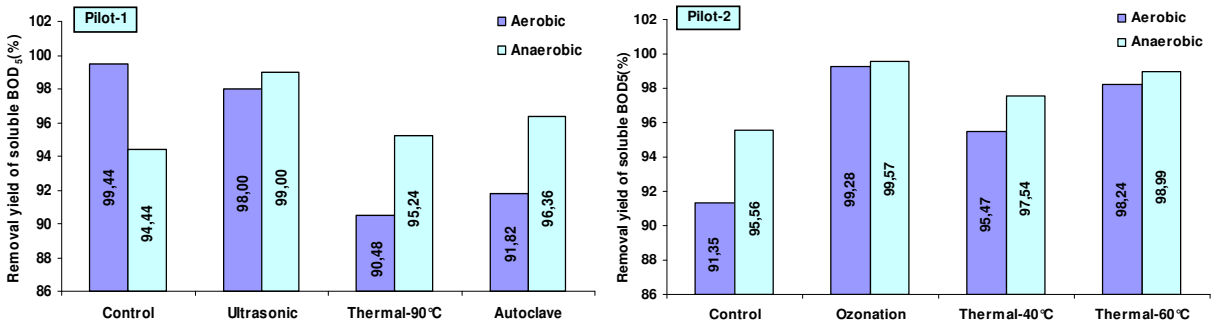

Figure 3-87: Comparison of removal yield of soluble BOD_5 in aerobic and anaerobic condition.

Table 3-51 presents results obtained for soluble BOD_5 removal yield enhancement. For all pretreatments samples, removal yield of BOD_5 under both aerobic and anaerobic conditions is higher than 90% and there is no remarkable difference between them and control sample.

Table 3-51: Removal yield improvement of soluble BOD_5 under aerobic and anaerobic conditions.

	Control 1	Ultrasonic	Thermal (90°C)	Autoclave	Control 2	Ozonation	Thermal (40°C)	Thermal (60°C)
	Aerobic							
Soluble BOD_5 Removal yield (%)	94.44	98.00	90.48	91.82	91.35	99.28	95.47	98.24
Removal yield enhancement	-	1.04	0.96	0.97	-	1.09	1.05	1.08
	Anaerobic							
Soluble BOD_5 Removal yield (%)	94.44	99.00	95.24	96.36	95.56	99.57	97.54	98.99
Removal yield enhancement	-	1.05	1.01	1.02	-	1.04	1.02	1.03

In the first pilot, the highest removal yield improvement corresponded to ultrasonic pre-treatment under anaerobic conditions (1.05% times more than control sample) and in the

second series of experiments, the heist rate belonged to ozonation and 60°C thermal treatment under aerobic condition (respectively 9% and 8% more than control sample).

7.1.1.2 Proteins and carbohydrates removal improvement

- **Proteins**

Variations of total proteins after digestion (in the outlet of reactors) in aerobic and anaerobic digestion were investigated. In first pilot protein biodegradation is nearly the same for aerobic and anaerobic reactors. The only significant difference is observed on control sample (18.02%). In the second pilot, anaerobic reactors are somehow more successful than aerobic reactors. We can The results are not very far apart, the differences are 18.20% for control sample, 22.33% for ozonation, 14.30 for 40°C, and 28.87 for 60°C thermal treatment (Table 3-58).

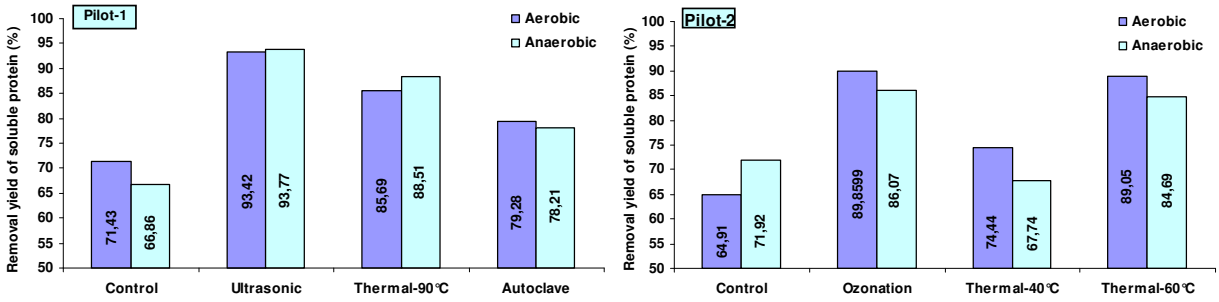

Figure 3-88 : Comparison of removal yield of soluble protein under aerobic and anaerobic conditions.

As we can see in Figure 3-88, except for sonicated sample, 90°C thermal treated sample, and control sample of second pilot, soluble protein biodegradation is a little higher under aerobic condition than under anaerobic conditions. It means that anaerobic digestion is not successful in soluble protein elimination.

Table 3-52: Removal yield of soluble protein under aerobic and anaerobic conditions.

	Control 1	Ultrasonic	Thermal (90°C)	Autoclave	Control 2	Ozonation	Thermal (40°C)	Thermal (60°C)
	Aerobic							
Soluble protein Removal yield (%)	**71.43**	**93.42**	**85.69**	**79.28**	**64.91**	**89.86**	**74.44**	**89.08**
Removal yield enhancement	**-**	**1.31**	**1.20**	**1.11**	**-**	**1.38**	**1.15**	**1.37**
	Anaerobic							
Soluble protein Removal yield (%)	**66.86**	**93.77**	**88.51**	**78.21**	**71.92**	**86.07**	**67.74**	**84.70**
Removal yield enhancement	**-**	**1.40**	**1.32**	**1.17**	**-**	**1.20**	**0.94**	**1.18**

Soluble protein removal yield improvement can describe the difference between aerobic and anaerobic reactors. In the first series of experiments, the removal yield enhancement of soluble protein for anaerobic conditions is higher than aerobic conditions while in the second series of experiments, the removal yield of soluble protein for aerobic conditions is higher than anaerobic conditions (see Table 3-52).

- **Carbohydrates**

The elimination efficiencies of soluble carbohydrates for different samples are shown in Figure 3-89. In the first pilot elimination efficiencies of aerobic and anaerobic reactors for all pretreatment are nearly the same. But in the second pilot elimination efficiency of soluble carbohydrates for control sample and 40°C and 60°C treated samples is remarkably higher under anaerobic conditions. Thus anaerobic reactors are more successful in carbohydrates elimination.

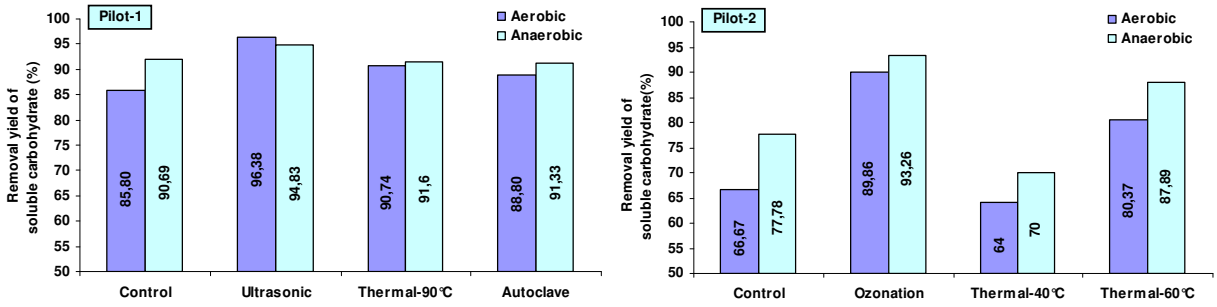

Figure 3-89: variations of soluble carbohydrate before and after digestion under aerobic and anaerobic digestion.

As it can be seen in Figure 3-89, in carbohydrate biodegradation process, for all sludge samples excepting sonicated sample, elimination efficiency of anaerobic reactors are a little higher than aerobic reactors. Thus anaerobic reactors are more successful in carbohydrates elimination.

The removal yields of soluble carbohydrate for both aerobic and anaerobic digestions are considerable while the improvement of elimination efficiency of aerobic conditions is higher than that of anaerobic conditions (Table 3-53).

Table 3-53: Removal yield of soluble carbohydrate under aerobic and anaerobic conditions.

	Control 1	Ultrasonic	Thermal (90°C)	Autoclave	Control 2	Ozonation	Thermal (40°C)	Thermal (60°C)
	Aerobic							
Soluble carbohydrate Removal yield (%)	85.80	96.36	90.74	88.80	66.67	89.86	64.00	80.37
Removal yield enhancement	-	1.12	1.06	1.03	-	1.35	0.96	1.20
	Anaerobic							
Soluble carbohydrate Removal yield (%)	90.69	94.83	91.60	91.33	77.78	93.26	70.00	87.90
Removal yield enhancement	-	1.05	1.01	1.01	-	1.20	0.90	1.13

7.1.1.3 Nitrogen and phosphorus removal improvement

- **Nitrogen**

Nitrogen elimination efficiency of all samples is higher under anaerobic conditions than under aerobic conditions (see Figure 3-90). In other words for soluble nitrogen, anaerobic reactors are more successful than aerobic reactors.

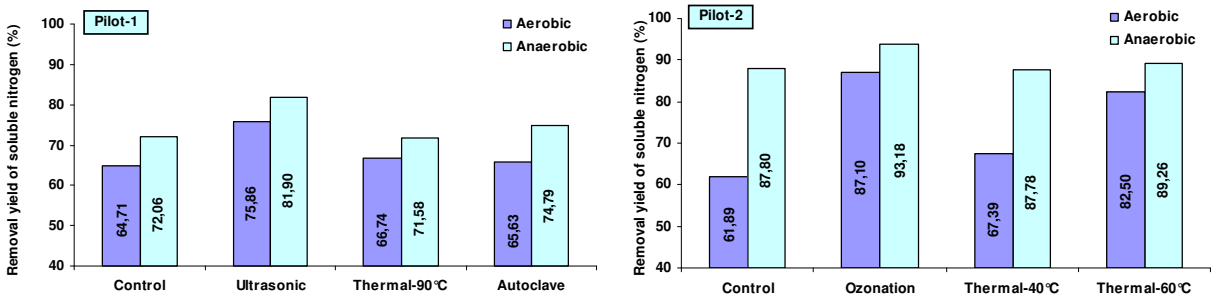

Figure 3-90: Comparison of removal yield of soluble nitrogen soluble in aerobic and anaerobic condition.

The Total nitrogen removal efficiencies (N_T biodegradability) in the outlet of batch reactors under aerobic and anaerobic conditions, for all pretreatments, total nitrogen biodegradation is more efficient under anaerobic conditions (at least 5.66% for thermal (90°C) and at most 19.48% for control sample in first pilot) see Table 3-58.

The removal yield of soluble nitrogen for ozonation and thermal treatment at 60°C under aerobic conditions is more considerable than anaerobic conditions. For other parameters, differences are not very noticeable (see Table 3-54).

Table 3-54: Removal yield of soluble nitrogen under aerobic and anaerobic conditions.

	Control 1	Ultrasonic	Thermal (90°C)	Autoclave	Control 2	Ozonation	Thermal (40°C)	Thermal (60°C)
	Aerobic							
Soluble nitrogen Removal yield (%)	64.71	75.86	66.74	65.63	61.89	78.10	67.39	82.50
Removal yield enhancement	-	1.17	1.03	1.01	-	1.41	1.09	1.33
	Anaerobic							
Soluble nitrogen Removal yield (%)	72.06	81.90	71.58	74.79	87.80	93.18	87.78	89.26
Removal yield enhancement	-	1.14	0.99	1.04	-	1.06	1.00	1.02

- **Phosphorus**

The variations of total phosphorus removal yield in anaerobic reactors compared to aerobic reactors were investigated for all samples (Table 3-58). Phosphorus elimination rate is higher under anaerobic digestion compared to aerobic digestion. The difference of biodegradation under aerobic and anaerobic conditions is higher in first pilot than in second pilot (7-13% for first pilot against 4-6% for second pilot).

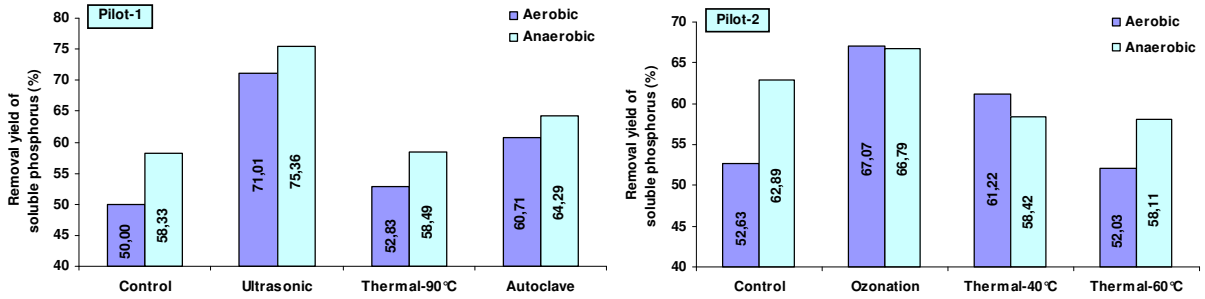

Figure 3-91: Comparison of removal yield of phosphorus soluble in aerobic and anaerobic condition.

As we can see in Figure 3-91, in first pilot, for all pretreatment samples, the elimination efficiency of soluble phosphorus is higher under anaerobic conditions than under aerobic conditions. In second pilot this phenomenon is not observed. For 40°C thermal treated sample elimination efficiency of aerobic digestion is a little higher than anaerobic digestion. For ozonation, both reactors yield the same elimination efficiency.

Table 3-55: Removal yield of soluble phosphorus under aerobic and anaerobic conditions.

	Control 1	Ultrasonic	Thermal (90°C)	Autoclave	Control 2	Ozonation	Thermal (40°C)	Thermal (60°C)
	Aerobic							
Soluble phosphorus Removal yield (%)	50.00	71.01	52.83	60.71	52.63	67.07	61.22	52.03
Removal yield enhancement	-	1.42	1.06	1.21	-	1.27	1.16	0.99
	Anaerobic							
Soluble phosphorus Removal yield (%)	58.33	75.36	58.49	64.29	58.76	66.79	58.42	58.11
Removal yield enhancement	-	1.29	1.00	1.10	-	1.13	0.99	0.99

As it can be seen in Table 3-55, for all parameters (except for thermal treatment at 60°C) the removal yield enhancement of soluble phosphorus under aerobic conditions is more than anaerobic conditions. This difference in ultrasonic pretreatment is more considerable than ozonation and thermal treatment. The best removal improvement either under aerobic or anaerobic conditions can be attributed to ultrasonic pre-treatment.

7.1.2 Research of correlation between removal improvement and input energy/solubilization

The optimal management of biodegradability improvement requires a more important insight in the link between solubilization parameters or specific energy input and removal rate. These correlations will allow the users to determine in advance the performance of the process only with solubilization parameters even thought the solubilization processes are not the same.

- **Correlation with solubilization parameters**

For each removal rate of interest, a correlation was establish or not with a corresponding solubilization parameter. The results are reported in Table 3-56. In this approach the different mechanisms involved during the pre-treatment step are not really taken into account. It is a global strategy to find some general “driving” parameters of the aerobic and anaerobic processes.

Table 3-56: Correlation between removal yield improvements and corresponding solubilization parameters.

	Aerobic		Anaerobic	
	Removal yield improvement			
	Soluble COD	Total COD	Soluble COD	Total COD
Solubilization of COD	No relation	No relation	Exponential relation $R^2 = 0.25$	Exponential relation $R^2 = 0.72$
	Soluble Protein	Total Protein	Soluble Protein	Total Protein
Solubilization of protein	No relation	Exponential relation $R^2 = 0.71$	Exponential relation $R^2 = 0.82$	Exponential relation $R^2 = 0.82$
	Soluble Carbohydrate	Total Carbohydrate	Soluble Carbohydrate	Total Carbohydrate
Solubilization of carbohydrate	No relation	No relation	No relation	No relation
	Soluble Nitrogen	Total Nitrogen	Soluble Nitrogen	Total Nitrogen
Solubilization of nitrogen	No relation	Exponential relation $R^2 = 0.41$	Linear relation $R^2 = 0.67$	No relation
	Soluble Phosphorus	Total Phosphorus	Soluble Phosphorus	Total Phosphorus
Solubilization of phosphorus	Linear relation $R^2 = 0.81$	Linear relation $R^2 = 0.35$	Linear relation $R^2 = 0.62$	Linear relation $R^2 = 0.66$
	Total suspended solids (TSS)		Total suspended solids (TSS)	
DD_{COD}	Exponential relation $R^2 = 0.91$		Linear relation $R^2 = 0.34$	
	Removal yield improvement of COD_S		Removal yield improvement of COD_S	
BOD/COD (Biodegradability)	Linear relation $R^2 = 0.58$		Linear relation $R^2 = 0.39$	
	-		Y (mL-Biogas.mg-COD^{-1})	
Soluble COD	-		Logarithmic relation $R^2 = 0.69$	

It was possible for some parameters to establish linear, logarithmic or exponential correlation between solubilization and removal improvement, but for others it was not possible. The more important correlations are developed in the following part.

- **Correlations with specific energy input**

The specific energy input is an important parameter of sludge solubilization and thus removal improvement. As before, in this approach the different mechanisms involved during the pre-treatment step are not really taken into account. It is a total strategy to find some general "driving" parameters of the aerobic and anaerobic processes.

It is possible to calculate for each kind of treatment the specific energy. In the following figure the different removal improvement are plotted as a function of specific energy input.

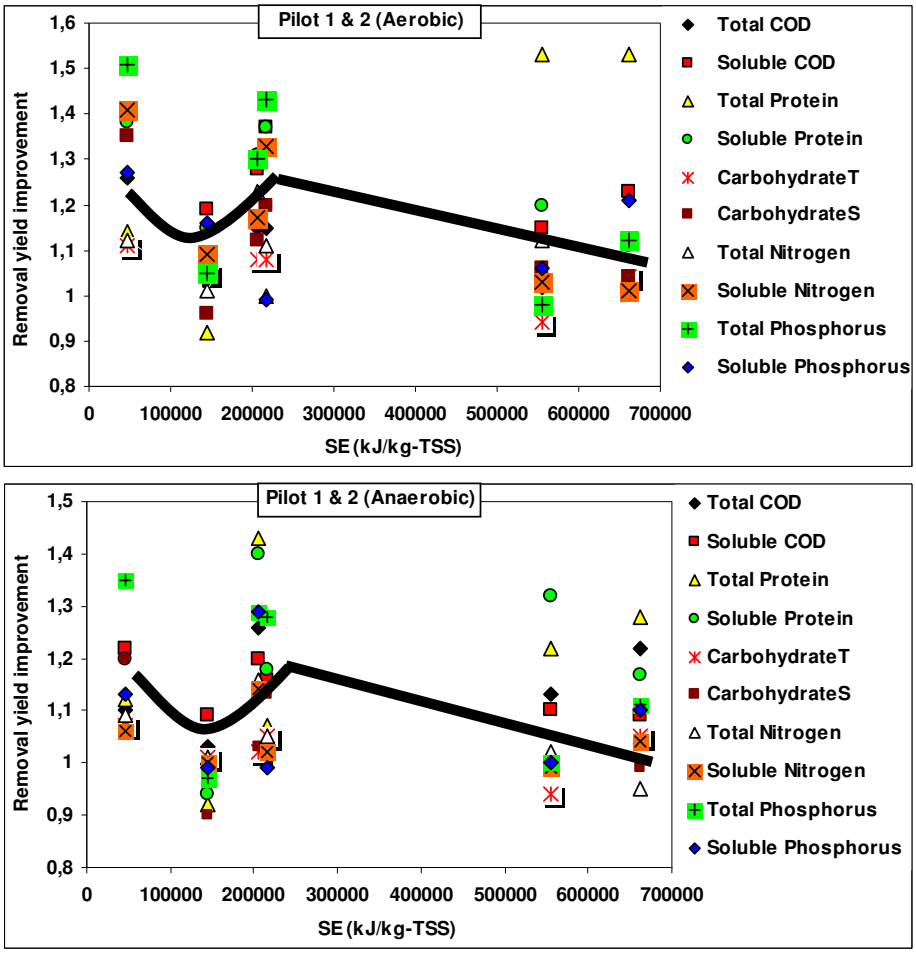

Figure 3-92: Correlation between removal yield improvement and specific energy under aerobic and anaerobic conditions.

The general tendency is plotted with bold lines. It was not possible to find real correlations with specific energy. For all the removal improvement except proteins, the values seemed to decrease with increasing specific energy (Figure 3-92).

7.1.2.1 Correlations between solubilization and soluble COD removal improvement

Different kinds of correlation were drawn in order to find the possible driving parameters of soluble COD removal.

In this study, all types of pre-treatment lead to increased elimination of soluble COD and sonication has the highest elimination efficiency (93.42% under anaerobic condition and 92.28% under aerobic condition). Figure 3-93 shows the correlation between COD, protein and carbohydrate solubilization rates with Soluble COD removal improvement under aerobic and anaerobic conditions. It can be observed that it was not possible to establish a clear correlation between soluble COD removal and solubilization parameters (COD, protein and carbohydrate)

but under anaerobic conditions this correlation is somehow established. For both pilots, the improvement of increased exponentially with increasing solubilization of soluble COD, proteins and carbohydrates. This increase is more significant in pilot 1 (ultrasonic, thermal at 90°C, and autoclave) compared to pilot 2 (thermal at 40°C, 60°C and ozonation).

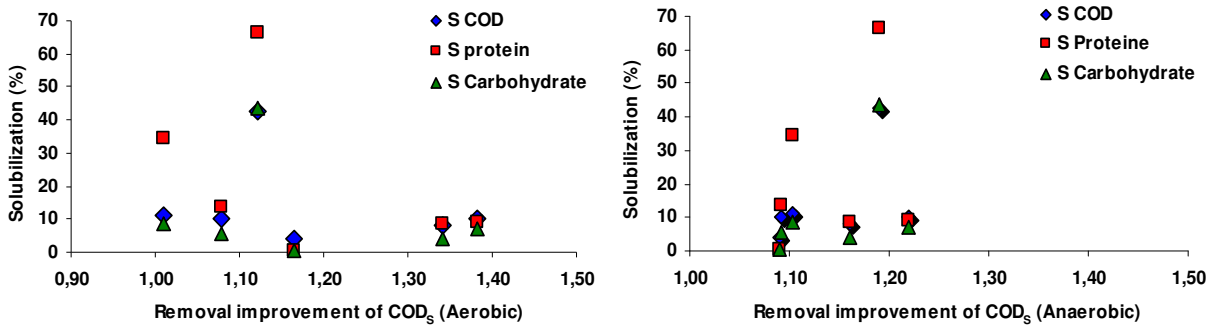

Figure 3-93: Solubilization of COD, proteins and carbohydrates versus soluble COD removal improvement under aerobic and anaerobic conditions.

BOD_5/COD_s ratio is a good indicator to determine whether or not pre-treatment processes are successful in improving aerobic and anaerobic digestion. The BOD_5/COD_s is traced versus Soluble COD removal improvement in Figure 3-94. We can see that biodegradability increases somewhat linearly with COD removal improvement.

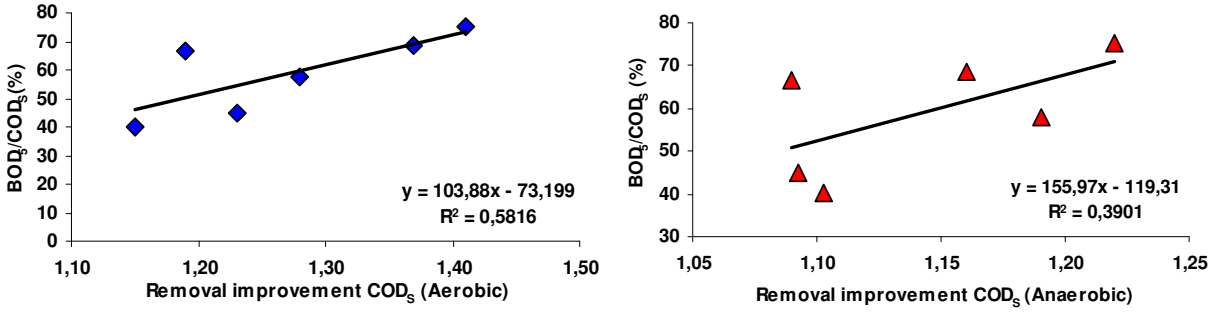

Figure 3-94: Correlation between BOD_5/COD_S ratio and soluble COD removal improvement under aerobic and anaerobic conditions.

7.1.2.2 Nitrogen and phosphorus removal improvement

- **Nitrogen**
  - ***Aerobic conditions***

Figure 3-95 shows the relation between solubilization rate and elimination efficiency enhancement in soluble. It can be seen that there is no linear relation between soluble nitrogen

removal and nitrogen solubilization. The lack of linear correlation between solubilization and removal yield improvement in the soluble nitrogen means that pretreatment processes and solubilization did not lead to an increase in soluble nitrogen removal yield (under aerobic conditions).

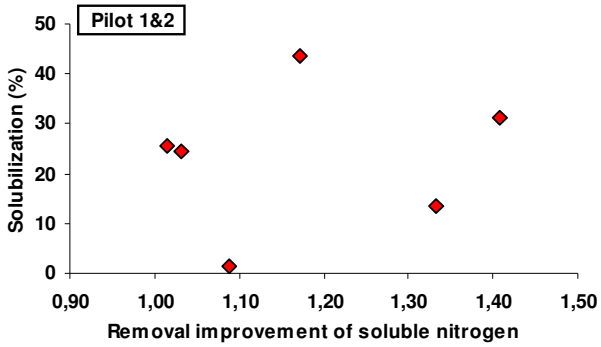

Figure 3-95: Nitrogen solubilization after pre-treatment versus removal yield improvement of soluble nitrogen under aerobic conditions.

* ***Anaerobic conditions***

The correlation between nitrogen solubilization and removal improvement of soluble nitrogen is plotted in Figure 3-96. Sonication leads to a higher solubilization rate than other samples (43.64%). As a result, the highest biodegradation rate during the fermentation corresponds to sonicated sample (75.51%) see Table 3-44. The lowest biodegradation rates correspond to thermal treatments at 40°C and 60°C. Also solubilization rate and biodegradation of thermal treatment at 90°C and ozone pretreatment are approximately equal. In this study, soluble nitrogen increased linearly with increasing the rate of nitrogen solubilization (R^2 = 0.67), therefore we can say that solubilization of nitrogen led to an increase of soluble nitrogen removal efficiency under anaerobic conditions.

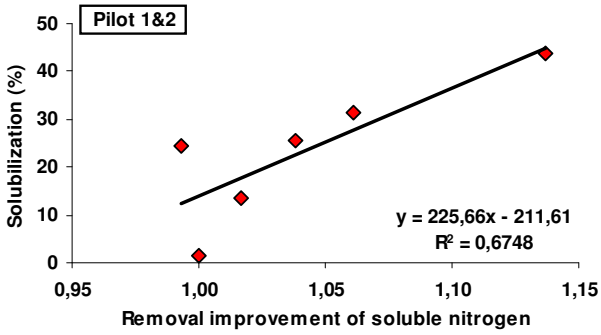

Figure 3-96: Correlation between nitrogen solubilization (after pre-treatment) and removal yield improvement for soluble and total nitrogen under anaerobic condition.

- **Phosphorus**

  * ***Aerobic conditions***

Relationship between solubilization and removal yield improvement (after solubilization and before digestion) for P_S and P_T were investigated. It can be seen that in Figure 3-97, for soluble phosphorus, a clear linear relation exists between solubilization and removal yield improvement (R^2 = 0.81) while weak linear correlation is observed for total phosphorus (R^2 = 0.35). It means that when the solubilization rate is high, the rate of soluble phosphorus and consequently the removal yield improvement will also increase.

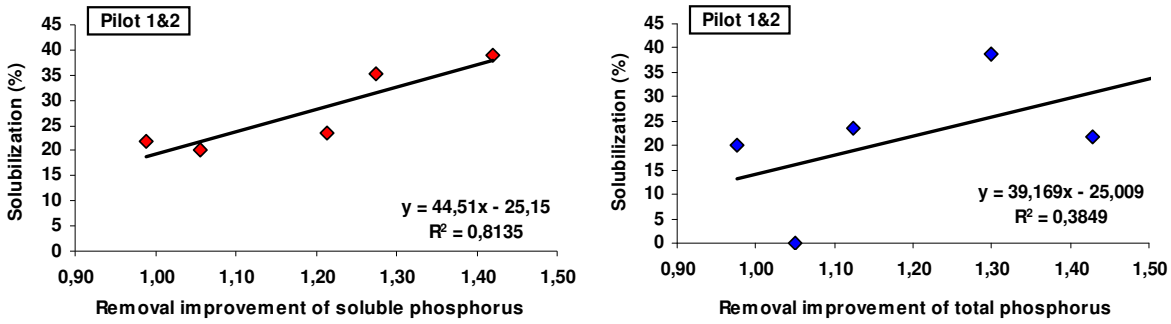

Figure 3-97: Correlation between phosphorus solubilization and removal yield improvement (after pre-treatment) for soluble and total phosphorus under aerobic condition.

  * ***Anaerobic conditions***

Relationship between solubilization and removal efficiency improvement of soluble and total phosphorus was investigated. Figure 3-98 shows this correlation after pretreatment in outlet (t = f) compared to inlet (t = 0) for both pilots. At this figures, we can see that soluble and total phosphorus increased linearly with increasing rate of phosphorus solubilization ($R^2 \approx 0.65$ for soluble and total phosphorus).

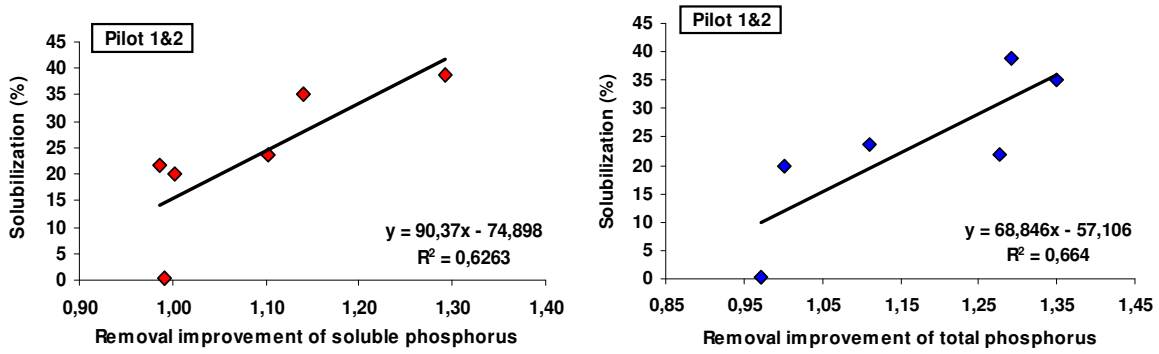

Figure 3-98: Correlation between phosphorus solubilization (after pre-treatment) and removal yield improvement for soluble and total phosphorus under anaerobic condition.

7.2 Comparison of sludge reduction improvement

7.2.1 Removal improvement

As it was expected, the sludge reduction, measured in term of VSS reduction, TS and VS solubilization which seams to be good indicators of per se sludge reduction, increased with the increasing input energy. Figure 3-99 shows the TSS digestion efficiency for all digestion processes. By comparing the removal efficiency of anaerobic and aerobic reactors (outlet) it can be noticed that anaerobic process results in more efficient sludge elimination (VSS and FSS).

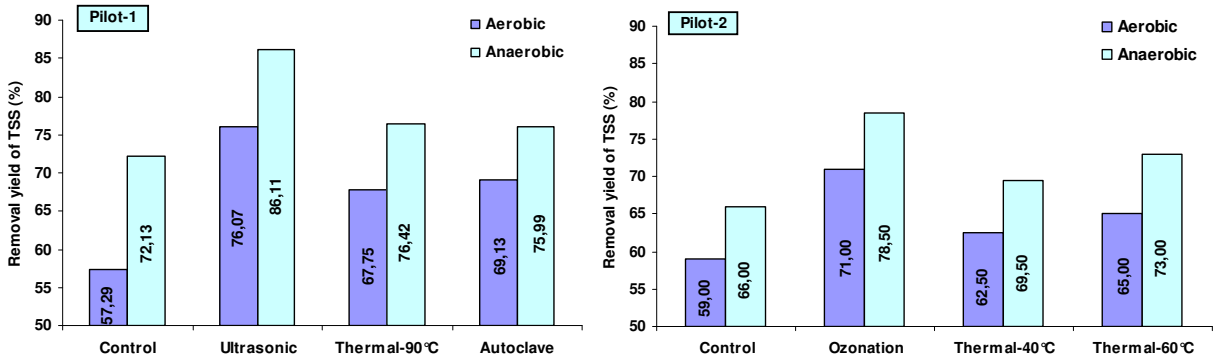

Figure 3-99: variations of total suspended solids (TSS) before and after digestion in aerobic and anaerobic digestion.

In this study TSS biodegradation of reactor containing sonicated sample under anaerobic conditions is 41.94% more than aerobic conditions. This difference is 26.86%, 25.86%, 22.86%, and 22.22% for 90°C, ozonated, 60°C, and autoclaved samples (see Table 3-58).

Table 3-57: Removal yield of total suspended solids under aerobic and anaerobic conditions.

	Control 1	Ultrasonic	Thermal (90°C)	Autoclave	Control 2	Ozonation	Thermal (40°C)	Thermal (60°C)
	Aerobic							
TSS removal yield (Pre-treatment and digestion) (%)	57.29	76.07	67.75	69.13	59	71	62.5	65
Removal yield enhancement	-	1.33	1.18	1.21	-	1.20	1.06	1.10
	Anaerobic							
TSS removal yield (Pre-treatment and digestion) (%)	72.13	86.11	76.42	75.99	66	78.50	69.50	73
Removal yield enhancement	-	1.19	1.06	1.05	-	1.19	1.05	1.11

We can conclude that anaerobic process is much more successful in TSS and VSS elimination than aerobic process. By comparing the removal efficiency improvement of anaerobic and aerobic reactors it can be seen that in all parameters (except thermal treatment at 40°C and 60°C) the removal efficiency enhancement of TSS under aerobic condition is more than anaerobic condition. And this difference in first pilot is more considerable than second pilot (Table 3-57).

7.2.2 Research of correlations between sludge reduction improvement and solubilization

The anticipation of sludge removal efficiency could be of interest for the setting up of pre-treatment before aerobic or anaerobic digestion. Solubilization parameters could be interesting "driving" parameters as measured very early in the process.

Relationship of carbohydrates, proteins, and COD solubilization rates with sludge removal improvement under aerobic conditions was not linear; TSS removal improvement increased exponentially with solubilization (Figure 3-100). Under anaerobic conditions it was not possible to establish a clear link between solubilization parameters and sludge reduction improvement.

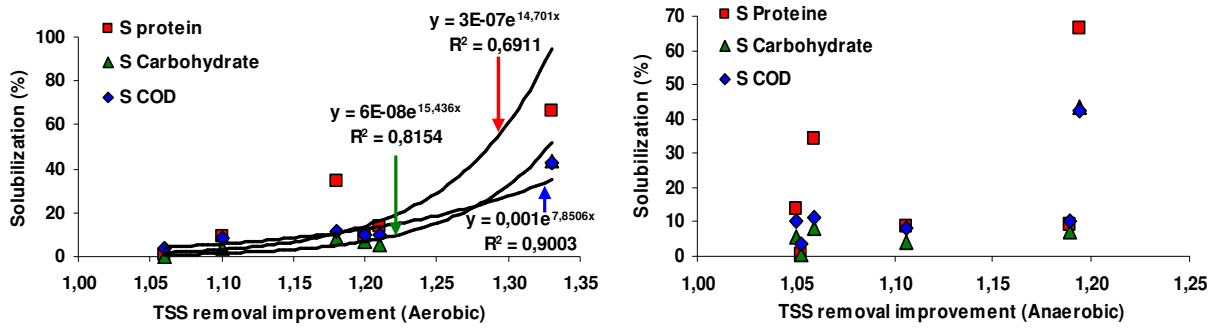

Figure 3-100: Protein, carbohydrate and COD solubilizations as a function of TSS removal improvement under aerobic and anaerobic conditions.

The existence of exponential correlation under aerobic conditions and the lack of this correlation under anaerobic conditions may be due to different sludge elimination mechanism under aerobic and anaerobic conditions.

To obtain a better understanding of sludge reduction improvement, correlations between TSS removal improvement and solubilization parameter (e.g. COD, protein and carbohydrate) and degree of disintegration after pretreatment were investigated under aerobic and anaerobic conditions.

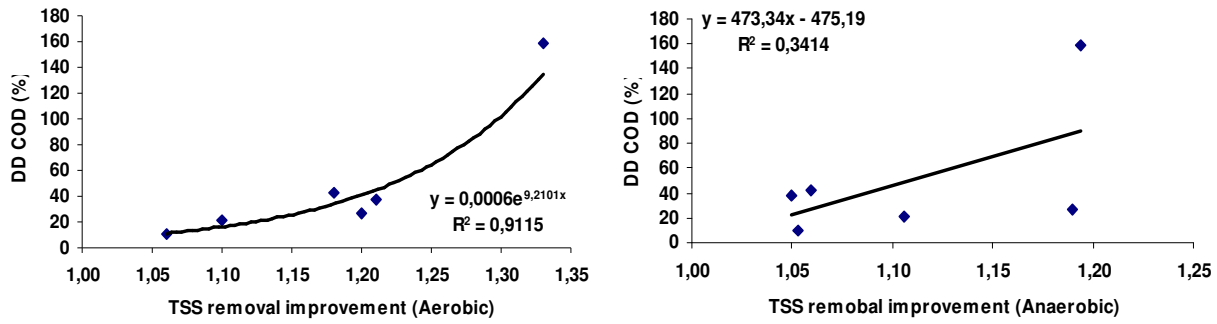

Figure 3-101: Disintegration degree of COD as a function of TSS removal improvement in aerobic and anaerobic digestion.

Under aerobic condition, an exponential correlations with a correlation factor R^2 = 0.91 between DD_{COD} and TSS removal improvement may be established. On the contrary under anaerobic conditions no clear correlation between DD_{COD} and TSS removal improvement may be established (see Figure 3-101).

7.3 Conclusion

Production of sludge and its reduction in WWTPs is a quite complex phenomenon, implying several mechanisms.

All three techniques (ultrasound, ozone and thermal treatment) led to solids solubilization and to aerobic and anaerobic biodegradability enhancement.

The comparison of aerobic and anaerobic digestion in terms of biodegradability improvement led to the following conclusions:

- Soluble COD, phosphorus, nitrogen and carbohydrates removal yields under anaerobic conditions are always higher than or equal to the same values under aerobic conditions; on the contrary, soluble proteins removal efficiencies are lower under anaerobic conditions.

- Nevertheless, the removal improvements due to pre-treatment are more important under aerobic conditions than under anaerobic conditions.

- TSS removal efficiencies and thus sludge reduction are always higher under anaerobic conditions: the best removal efficiency is attributed to ultrasonic pre-treatment (86.11%). Ultrasound and ozone led the best removal efficiency improvements.

Table 3-58: Improvement of removal yield in anaerobic reactors compared to aerobic reactors.

	Control-1	Ultrasonic	Ozonation	Autoclave	Control-2	Thermal (90°C)	Thermal (60°C)	Thermal (40°C)
COD	-12.99	13.38	22.95	34.34	34.38	13.44	29.33	30.59
TSS	34.74	41.94	25.86	22.22	17.07	26.86	22.86	18.67
VSS	46.84	59.54	28.61	32.29	20.48	43.95	26.24	21.95
Protein	18.02	4.54	22.33	1,31	18.20	-9.45	28,87	14.30
Carbohydrate	21.20	-7.17	18.40	32.30	25.33	18.34	19.69	9.71
Nitrogen	19.48	18.64	11.76	9.86	12.07	9.09	5.66	11.29
Phosphorus	7.69	13.04	4.62	8.13	6.54	9.68	4.41	4.17

The investigation of relationship of solubilization parameters with specific energy input and biodegradability with sludge reduction improvement led to some interesting results. It is necessary to mention that it is difficult to put on the same level solubilization parameters resulting from completely different mechanisms. At the end of the study the following general tendencies can be drawn:

- Clear correlations between removal improvement of the different parameters and specific energy input cannot be established but the general evolution is comparable from one parameter to another (except in the case of proteins which behavior is completely different).
- It was possible to establish a linear correlation between soluble COD removal improvement and BOD_5/COD_S ratio either under aerobic and anaerobic conditions.
- Soluble phosphorus and nitrogen removal improvement can be linearly correlated with their corresponding solubilization parameters under aerobic conditions.
- Under aerobic conditions, TSS removal improvement increased exponentially with increasing solubilization of proteins, carbohydrates and COD and disintegration degree.
- It was more difficult to find correlation under anaerobic conditions than under aerobic conditions.

8. Economic evaluation

The use of disintegration in order to enhance the digestion process is the best-researched full-scale application today. Economic-efficiency and energy-balance calculations are important tools for performing the cost-benefit analysis of a disintegration process.

An economic evaluation of sludge reduction costs was achieved for each pre-treatment. A vast variety of parameters interfere with economic efficiency. Some examples may be investment costs, personnel costs, costs for unite servicing, energy costs of disintegration process, operating and maintenance costs, dewatering, disposal and etc. Thus, the results obtained from reactors can not determine all of the characteristics related to economic calculations and are not sufficient.

Unfortunately, most of the above mentioned parameters were not considered in this study. The economic evaluation in this work emphasizes on the pilot scaled result. Of course the economic evaluation presented here may not be exact or sufficient; however it does provide a realistic estimation of the real full scale implementation. The investment costs are neglected. The total sludge elimination cost per ton of removed TSS was calculated for different methods. The calculations were based on the total energy requirement of each method and the TSS removal yield achieved by that method.

The rate of total specific energy (kJ/kg-$TSS_{Removal}$) was calculated for each pre-treatment method (solubilization if applicable and digestion) under aerobic and anaerobic condition. Total energy ($E_T = E_S + E_A$) for aerobic reactor is the sum of applied energy during pretreatment step (E_S) and the energy applied by air diffuser (E_A).

Table 3-59: Energetic balance of the different methods of sludge treatment.

	Control 1	Ultrasonic	Thermal (90°C)	Autoclave	Control 2	Ozonation	Thermal (40°C)	Thermal (60°C)
$E_{Solubilization}$ (kJ)	0.0	230	324	5400	0.0	648	144	216
	Aerobic							
Total energy (kJ) ($E_T = E_S+E_A$)	489888	490118	490212	495288	606528	607176	606672	606744
E_S/ E_T (%)	-	0.05	0.066	1.09	-	0.11	0.024	0.035
Sludge removal yield respect to control (%) in TSS_f	-	43.98	24.50	27.71	-	29.27	8.54	14.63
	Anaerobic							
Total energy (kJ) ($E_T = E_S+E_{Ag}+ E_H -E_{CH4}$)	493409	493606	493657	498760	610771	611323	610912	610928
E_S/ E_T (%)	-	0.05	0.065	1.08	-	0.11	0.024	0.035
Sludge removal yield respect to control (%) in TSS_f	-	50.15	15.38	13.85	-	36.76	10.29	20.59

Total energy (E_T) for anaerobic reactor ($E_T = E_S + E_{Ag} + E_H - E_{CH4}$) is the specific energy of solubilization plus the energy consumption of the agitator and heater (used to maintain the temperature of anaerobic reactors between 35°C – 37°C) minus the energy provided by methane release during the process.

By investigating the results it can be seen that the energy consumed during the solubilization step (E_S) is negligible compared to total applied energy (E_T). According to Table 3-59, under aerobic conditions, the minimum E_S/E_T ratio is 0.05% for ultrasonic reactor and the maximum ratio is 1.09% for autoclave. Under anaerobic conditions, the minimum ratio is 0.05% for ultrasonic reactor and the maximum is 1.08% for autoclave. Despite the low amount of energy used during pretreatment steps, they can strongly influence the final removal yield. The highest sludge (TSS) removal yield after solubilization and biological digestion corresponds to ultrasonic (50.15% for anaerobic reactor and 43.91% for aerobic reactor more than control sample). After ultrasonic reactor, the highest elimination efficiency of TSS belongs to ozone reactor (36.76% and 29.27% more than control sample for anaerobic and aerobic reactors respectively). For thermal treatment at 90°C and autoclave the rate of removal yield under aerobic treatment is higher than anaerobic reactors.

Table 3-60: Economic balance calculation of different methods under aerobic and anaerobic conditions.

	Control 1	Ultrasonic	Thermal (90°C)	Autoclave	Control 2	Ozonation	Thermal (40°C)	Thermal (60°C)
	Aerobic							
Total specific energy (kJ/kg-TSS $_{removal}$)	29334611	22102277	24968506	24580050	20560271	17103549	19454976	18728862
SE total (kWh/kg-TSS $_{removal}$)	8.15	6.14	6.94	6.83	5.71	4.75	5.40	5.20
Cost (€/ton-TSS $_{removal}$)	900	680	760	750	630	520	590	570
Cost reduction %	-	24.5	15.6	16.7	-	17.5	6.3	9.5
	Anaerobic							
Total specific energy (kJ/kg-TSS $_{removal}$)	23461710	19665564	22292851	22517397	18508217	15575110	17617505	16791001
SE total (kWh/kg-TSS $_{removal}$)	6.52	5.46	6.19	6.26	5.14	4.33	4.89	4.66
Cost (€/ton-TSS $_{removal}$)	720	600	680	690	570	480	540	510
Cost reduction %	-	16.7	5.6	4.2	-	15.8	5.3	10.5

The next step is to convert applied specific energy from kJ/kg-$TSS_{Removal}$ to kWh and to apply the price of electricity, which is 0.11€ per kWh for France in 2008, in order to obtain the total

cost of consumed energy during solubilization and biological digestion steps for different pre-treatment methods and control sample (only biological digestion). The results are compared with each other in Table 3-60.

Under aerobic conditions, the cost of energy consumption for control sample (considering its sludge removal rate during digestion process) was 900 €/ton-$TSS_{Removal}$ while for the sample that was sonicated prior to biological digestion, total cost is calculated to be 680 €/ton-$TSS_{Removal}$ (24.5% cost reduction). The cost reduction due to different methods can be classified as follows:

ultrasonic > ozonation > autoclave > thermal(90°C) > thermal(60°C) > thermal(40°C)

The sludge elimination cost under anaerobic conditions is about 25% less than aerobic conditions (see Table 3-60). In this study, the cost of sludge removal without prior pretreatment was 720 €/ton-$TSS_{Removal}$ while for ultrasonic reactor (solubilization + digestion) this cost was 600 €/ton- $TSS_{Removal}$ (17% cost reduction compared to control sample). The costs of anaerobic reactors may be classified as follows:

ultrasonic > ozonation > thermal(60 °C) > thermal(9 0°C) > thermal(4 0°C) > autoclave

As a consequence, the best combination in terms of sludge reduction and cost saving is an ultrasonic (200000 kJ/kgTSS and 50W) and ozonation (0.101gO_3/g-TSS) pre-treatment prior to anaerobic digestion.

Chapter 4

Conclusion and perspective

Chapter 4: Conclusion and perspective

Conclusion

The treatment and disposal of excess sludge represents a bottleneck of wastewater treatment plants all over the world, due to environmental, economic, social and legal factors. There is therefore a growing interest in developing technologies to reduce the wastewater sludge generation. Several strategies are currently being developed for minimisation of sludge production on biological wastewater treatment plants.

In this study, three kinds of pre-treatment were considered in the aim of improving aerobic and anaerobic sludge digestion performances: mechanical (US), thermal (Bain-marie and Autoclave), and Oxidative (O_3);

The objectives of this work are:

1) The choice of pre-treatment conditions in regard to solubilization and biodegradability improvement of organic matter

2) A comparative study of aerobic and anaerobic digestion of the above pre-treated sludge in terms of biodegradability enhancement (kinetics and stoechiometrics parameters) and in terms of sludge reduction improvement.

3) An economic evaluation of the global processes.

The final objective was to validate the association of a specific sludge pretreatment (ultrasonic, ozonation, and thermal treatment) and a biological treatment (aerobic or anaerobic digestion) in terms of both sludge reduction and economic and energetic savings.

1) Choice of the more effective conditions for the different pre-treatment of activated sludge

Pre-treatment showed immense potential in municipal wastewater residual pretreatment and its application in sludge disintegration may significantly improve the overall biodegradability of biological sludge during aerobic and anaerobic digestion. In the solubilization step, the optimum parameters for each treatment technique were determined using bench scale studies.

The aim of these treatments was to solubilize and/or reduce the size of organic compounds, especially refractory compounds, in order to make them more easily biodegradable.

The effects of different sludge reduction processes like ultrasonic treatment (specific energy ranging from 0 to 200000 kJ.kg-TSS^{-1} with three different input powers : 50, 100 and 200 W), ozone treatment (0 to 0.15 gO_3.g-TSS^{-1}), thermal treatment (sludge was heated at three different temperatures ,40°C, 60°C, and 90°C, during different contact times ,10, 20, 40, 60, 120, and 480 minutes) and autoclave (at 121°C, 15 minutes and 1.5 bar) on solubilization were investigated. Sludge was concentrated up to 13-15 g.L^{-1} of TS.

- **Sonication**

The effects of specific energy and input power on solubilization parameters and biodegradability were investigated.

The impact of specific energy on COD solubilization was also studied. The highest solubilization rate can be observed at specific energy of 200000 kJ.kgTSS^{-1}. It attains from 3-4% for 5000 kJ.kgTSS^{-1} to 12-13% for 200000 kJ.kgTSS^{-1}. For a given input power, the specific energy seriously affects COD solubilization. And also, the COD solubilization for intensities of 50, 100, and 200 Watts are nearly the same (11.97%, 12.48%, and 12.66% respectively). Thus for a specific energy of 200000 kJ.kgTSS^{-1}, the power input does not significantly change the COD solubilization rate. Thus, this work recommends using high specific energies (200000 kJ.kgTSS^{-1}) and low input powers (50 Watt).

The COD_S/COD_T ratios after ultrasonic pre- treatment were greatly improved (from 1.51% to 18.93%), suggesting that a large amount of insoluble organics of sludge flocs were transferred into soluble organics. In fact COD_S/COD_T increases with specific energy. This increase is all the same for three intensities (50, 100, and 200 W). It means that the highest COD solubilization occurred at SE = 200000 kJ.kgTSS^{-1}. This increase is slightly more significant when the applied power is 50 W (18.93, 18.08, and 17.28 for 50, 100, and 200 Watts of power respectively and energy of 200000 kJ.kgTSS^{-1}).

The COD degree of disintegration, for high (200000 kJ.kgTSS^{-1}) and low (5000 kJ.kgTSS^{-1}) SE, increasing input power intensity does not significantly affect DD_{COD} rate. For instance, at 200000 kJ.kgTSS^{-1}, increasing power from 50W to 200W leads to a slight 2% increase in DD_{COD}. The impact of specific energy on DD_{COD} was also investigated. The highest

disintegration rate corresponds to SE of 200000 kJ.kgTSS^{-1} (35.85% for 50W, 37.37% for 100W, and 37.92% for 200W of power).

BOD_5 increases with specific energy and power density. The input power is the determining parameter of BOD_5 solubilization. Biodegradability (BOD_5/COD_S) does not increase due to specific energy augmentation. On the other hand, by increasing input power for a given specific energy biodegradability increases, and the highest biodegradability occurs at 200W of input power. We can conclude that the biodegradability does not increase with specific energy but does increase with power.

TSS solubilization rate increases with specific energy. This raise is much more significant for the case of 50 Watts of power and 80 minutes of applying time (achieving 72.80%) than those of 100 W (during 40 minutes) and 200 W (during 20 minutes). This study confirms that using low power intensities (50W) and high specific energies (200000 kJ.kgTSS^{-1}) leads to higher solubilization rates. Experiments showed that the highest TSS and VSS solubilization rates occur at the energy of 200000 kJ.kgTSS^{-1} and input power of 50W (72.8% and 78.85% respectively).

TSS/TS ratio was 88.83% for untreated sludge. This ratio is strongly reduced in the case of treated sludge (24.16%) with SE = 200000 kJ.kgTSS^{-1} and power of 50 W. In fact, solids content in particulate fraction decreased with increasing supplied specific energy. Also VSS/TSS ratio decreases from 78.88% for raw sludge to 61.33% for sludge sample sonicated with SE = 200000 kJ.kgTSS^{-1} and intensity of 50W.

The ultrasonic treatment chosen is (200000 kJ.kg-TSS^{-1}) and low input powers (50 Watt)

- **Ozonation**

The different solubilization parameters were optimal for an ozone dose of 0.1 gO_3.g-TSS^{-1}, above this value the different parameter were decreasing. The values for COD solubilization (S_{COD}) and degree of disintegration (DD_{COD}), COD_S/COD_T and BOD_5 solubilization were respectively equal to 10.39%, 24.56, 9.56%, and 7.02%. The decrease of the concentration of soluble organic matter in the sample can be explained by the raise of mineralization of soluble organic matter. In this study the highest COD and BOD solubilization and COD degree of disintegration occurred for the ozone concentration of 0.1 gO_3.g-TSS^{-1} (i.e. ozonation during 60

minutes). By increasing ozone dosage further more, solubilization did not improve and even decreased slightly.

The maximum TSS solubilization is obtained with an ozone dosage of 0.14 $gO_3.g\text{-}TSS^{-1}$ (16.67%), and TSS solubilization decreases with further increase in the ozone concentration. At the same time, the VSS solubilization is observed at the ozone dosage of 0.1 $gO_3.g\text{-}TSS^{-1}$ (24.38%), and VSS solubilization is not affected by further increases in ozone concentration.

A significant decrease in suspended solids concentrations was observed: the initial TSS/TS ratio was 98.95% (for untreated sludge) and the minimal TSS/TS ratio, obtained for an ozone dose of 0.139 $gO_3.g\text{-}TSS^{-1}$, was 82.36%. A logarithmic relation was established between the TSS/TS ratio and the ozone dose ($R^2 = 0.8345$).

The organic matters content (VSS/TSS) was decreased after 60 minutes of ozonation with 0.1 $gO_3.g\text{-}TSS^{-1}$ concentration (63.28%) and then increased. It can be concluded that there existed a threshold beyond which the sludge flocs could be sufficiently disintegrated. In fact increasing ozone dose (prolonging ozonation time) does not lead to an increase in the sludge solubilization.

The ozonation treatment chosen was of $0.1gO_3.g\text{-}TSS^{-1}$

- **Thermal treatment**

During thermal treatment both temperature and duration of exposition were investigated. This study revealed that for thermal COD solubilization and degree of disintegration are not remarkably affected by prolonging treatment duration above 60 minutes. At the same time, by increasing temperature from 40°C to 90°C, these ratios were remarkably increased. It can be concluded that increasing temperature is more effective than prolonging contact time, and the main parameter for increasing solubilization and biodegradability is temperature.

The highest S_{COD} and DD_{COD} corresponded to autoclave (121°C and 15 minutes) and Bain-Marie treatment with 90°C during 60 minutes (16.87% and 27.51% for S_{COD} and DD_{COD} respectively). Also, the highest solubilization ratio (COD_S/COD_T) happened at 90°C of temperature and 60 minutes of heating time (17.2%).

Concerning BOD_5 also, the highest solubilization is observed with Bain-Marie at 90°C. (20.11% after 60 minutes) and autoclave (23.7%). The highest biodegradability (BOD_5/COD_T)

ratio corresponds to autoclave treatment (10.65%) and Bain-Marie at 90°C during 60 minutes (8.52%).

TSS and VSS concentrations meet their minimum values at 90°C and 60 minutes. For example TSS decreases from 12.68 $g.L^{-1}$ to 7.85 $g.L^{-1}$ (38.09% reduction) for Bain-Marie at 90°C and 60 minutes and from 12.68 $g.L^{-1}$ to 9.43 $g.L^{-1}$ (26.63% reduction) for autoclave treatment.

TSS/TS ratio as well as VSS/TSS ratio decreased with the increase of treatment temperature. TSS/TS ratio confirms that highest solubilization rate happens at 90°C of temperature and 60 minutes of heating time from 97.54% for control sample to 60.38% for 90°C of temperature and 60 minutes of contact time, and to 78.45% for autoclave.

TSS/TS ratio as well as VSS/TSS ratio decreased with the increase of treatment temperature. TSS/TS ratio confirms that highest solubilization rate happens at 90°C of temperature and 60 minutes of heating time from 97.54% for control sample to 60.38% for 90°C of temperature and 60 minutes of contact time, and to 78.45% for autoclave (solubilization rate increased 38.09% and 19.57% for Bain-Marie and autoclave respectively). At the same time VSS/TSS ratio indicates organic matters solubilization and sludge reduction. The lowest ratio of VSS/TSS corresponds to 90°C of Bain-Marie during 60 minutes and autoclave treatment (67.90% and 67.66%).

Thermal treatment at 40°C, TSS^{-1}, and 90°C with duration of 60 minutes of contact time and autoclave treatment were the chosen pre-treatment.

❁ Comparison of the chosen pre-treatment

The rate of specific energy applied to each sample of sonication, ozonation and thermal treatment can be summarized as follows:

$$\underset{\text{kj/kg-TSS}}{SE} \rangle \underset{661600}{\text{autoclave}} > \underset{555700}{\text{thermal}(90°C)} > \underset{216000}{\text{thermal}(60°C)} > \underset{205800}{\text{ultrasonic}} > \underset{144000}{\text{thermal}(40°C)} > \underset{46300}{\text{ozonation}} > \underset{0.0}{\text{control}}$$

- The highest DD_{COD} corresponds to ultrasonic and autoclave treatment and can be classified as follows :

US (35.85%) > Autoclave (33.15%) > 90°C (27.51%) > O_3 (24.56%) > 60°C (17.13%) > 40°C (0.75%)

- The highest rate of soluble COD solubilization corresponds to thermal treatment (autoclave and thermal at 90°C).

Autoclave (20.69%) > 90°C (16.87%) > US (11.97%) > 60°C (10.50%) > O_3 (10.39%) > 40°C (0.46%)

- With regard to TSS and VSS, the highest solubilization rate belonged to US and the lowest corresponded to autoclave. At this study, in thermal treatment with increased temperature, the rate of solubilization of TSS and VSS increased (however obtained results from autoclave appeared weird). The results of TSS solubilization can be reported as follows:

US (72.80%) > 90°C (38.09%) > 60°C (23.19%) > 40°C (14.27%) > O_3 (13.82%) > Autoclave (11.37%)

2) Aerobic and anaerobic digestion of the pre-treated sludge

In this part, the performances and dynamics of aerobic and anaerobic digestion of sludge submitted to different processes of sludge reduction production were assessed in regard to sludge reduction and biodegradability improvement and further choose the most cost effective pre-treatment leading to the highest sludge elimination efficiency. Digestion of the above pre-treated sludge was carried out in aerobic and anaerobic batch reactors and the results were compared to non treated sludge.

Aerobic sludge digestion

Aerobic digestion after pre-treatment is rarely investigated while it can be of interest for small collectivities. The biodegradability was assessed by chemical and biochemical parameters removal yields and sludge reduction across TSS and VSS removal. Pre-treatment revealed to improve sludge biodegradability rather than sludge reduction.

a) Biodegradability improvement

Concerning sludge aerobic digestion processes, the highest removal yield of total COD corresponded to ultrasonic treatment (81.89%) and then ozonation (73.82%) and thermal treatment (< 73%). But the highest removal efficiency improvement corresponded to ozonation (1.26 times more than control sample). In aerobic reactors, specific energy did not seriously affect the removal yield of COD_T. The classification of total COD removal yield improvement was:

$$COD_T \rangle ozonation > ultrasonic \geq thermal$$

Concerning soluble COD, the highest removal efficiency improvement corresponded to ozonation (1.41 times more than control sample). However, the highest rate of solubilization corresponded to ultrasonic (42.62%). Thus, it can be said that in this series of analysis, there were no clear correlation between solubilization and COD_S removal yield. But, the highest instantaneous specific rates (q_{COD}) corresponded to ultrasonic treatment (134 $mgCOD_S.gVSS^{-1}.d^{-1}$). Thus ultrasound led to the highest removal yield of COD in the shortest time.

Ultrasonic treatment that led to highly biodegradable soluble organic matters (BOD_5/COD_S ratio values were 68% after solubilization and 44% after solubilization + digestion more than control sample), had also a high solubilization rate (61.49%). It means that the enhancement of sludge biodegradability depended upon the kind of pretreatment and the rate of solubilization.

$$\frac{BOD_5}{COD_S}\Big\rangle \text{ultrasonic} > \text{thermal} > \text{ozonation}$$

Concerning total proteins, sonication pre-treatment led to an improvement in degradation. The removal yield improvement in ultrasound pretreated was higher than other samples in both pilots (1.70 times more than control sample). The classification of total proteins removal yield improvement was:

$$Protein_T \rangle \text{ultrasonic} > \text{thermal} > \text{ozonation}$$

With regard to total carbohydrates, By comparing the two series of experiments (both pilot), it can be observed that however ozone did not lead to a high solubilization rate during pre-treatment steps (7.14%), its removal yield improvement during digestion processes is rather high (11 percent more than control sample). The classification of total carbohydrates removal yield improvement was:

$$Carbohydrate_T \rangle \text{ozonation} > \text{ultrasonic} \approx \text{thermal}$$

b) Improvement of sludge reduction production

Pretreatment is effective for the removal yield of TSS and VSS. Total suspended solids (TSS) removal yield was improved by the pre-treatment under aerobic condition. The improvement for ultrasonic, ozonation and thermal treatment (90°C) is about 1.33, 1.20 and 1.18 times more than control sample, respectively. Besides, autoclave and thermal (60°C) treatments have a negligible impact on TSS removal.

Regarding the process of ultrasonic and ozonation, there is a linear correlation between VSS removal yield improvement and solubilization. However, there is no such relation between autoclave and thermal treatment, and solubilization. This is probably due to the discrepancy in the different mechanisms studied.

$$\text{TSS and VSS} \rangle \text{ ultrasonic} > \text{ozonation} > \text{thermal}$$

Anaerobic sludge digestion

Anaerobic degradation was improved by sludge disintegration and it was found that digestion time could be reduced. Researches showed that anaerobic digestion in combination with disintegration of sludge resulted in the highest degree of degradation. Sludge reduction and biodegradability enhancement due to pre-treatment was confirmed in this study.

c) Biodegradability improvement

The highest total COD removal yield corresponds to sonicated sample (84.31% = 1.26 times more than control sample) and the lowest elimination efficiency is attained on the thermal (40°C) sample (74.84% = 1.03 times more than control sample). An exponential relation with correlation factor of 0.72 may be established between COD solubilization and total COD removal yield improvement. It means that by increasing solubilization, the rate of removal efficiency improvement also increases is a semi-linear manner. The classification in terms of total COD removal yield was:

$$COD_T \rangle \text{ultrasonic} > \text{thermal} > \text{ozonation}$$

The highest rate of soluble COD removal efficiency was 93.42% for ultrasonic treatment in the first series of experiments (20% more than control sample) and was 89.34% for ozonation in the second series of experiments (22% more than control sample). The highest instantaneous specific rates (q_{COD}) rate occurs on the ultrasonic sample (112.80 mg COD.g-VSS^{-1}.d^{-1}) which decreases strongly during the first week and reaches 36.77 mg COD.g-VSS^{-1}.d^{-1}. We can conclude that high solubilization rate (e.g. ultrasound) led to a rise in the soluble phase and decreases the particulate phase and consequently shortens the digestion time and biodegradability.

The highest biodegradability ratio (BOD_5/COD_S) corresponds to ultrasound pretreatment in first series of experiments (84.79%) and ozonation in pilot 2 (96.73%). Despite the high

specific energy (kJ.kg-TSS^{-1}) required to perform a thermal pretreatment, this treatment does not show a high COD solubilization and biodegradability efficiency compared to sonication and ozonation. The ratio enhancement for total biodegradability was 15, 14 and 11 percent more than control sample respectively for ozonation, ultrasonic and thermal treatment at 60°C.

$$\frac{BOD_5}{COD_S}\Big\rangle \text{ozonation} \geq \text{ultrasonic} > \text{thermal}$$

The highest value of removal enhancement of total protein belongs to ultrasonic (1.43 times more than control sample) and then autoclave, thermal treatment (90°C) and ozonation (respectively 1.28, 1.22 and 1.12 more than control sample). The classification in terms of total protein removal enhancement was:

$$\text{Protein}_T \rangle \text{ultrasonic} > \text{thermal} > \text{ozonation}$$

The removal yields of total carbohydrate at the end of digestion were nearly the same for control sample and other reactors. Compared to control sample, the removal improvements of 7% for Ozonation, 5% for autoclave and thermal (60°C), 2% for ultrasonic and 1% for thermal (40°C) were obtained. The classification in terms of total carbohydrate removal improvement was:

$$\text{Carbohydrate}_T \rangle \text{ozonation} > \text{thermal} > \text{ultrasonic}$$

d) Improvement of sludge reduction production

Sonication which had the highest solubilization rate had also the highest biogas production (1.7 times more than control sample). The enhancement in biogas production obtained by autoclave, ozone, and thermal treatment at 90°C and 60°C was respectively 1.45, 1.38, 1.30, and 1.24 times control sample. In this study, biogas production at 40°C was approximately the same as control sample (only 1.01 times control sample). The classification for Biogas production enhancement was:

$$\text{Biogas} \rangle \text{ultrasonic} > \text{autoclave} > \text{ozonation} > \text{thermal}$$

The total values range of TSS removal yield is increased from 66% to 86.11% under anaerobic condition. Ultrasonic and then ozonation lead to the highest TSS elimination efficiency (19 percent more than control sample) while thermal treatments were not very successful in TSS

removal. TSS removal yield for thermal treatments (40°C, 90°C and autoclave) did not led to significant improvement of sludge removal (TSS degradation improvement for 40°C = 5%, 90°C = 6%, and 121°C (autoclave) = 5%). For thermal treatment (60°C) the rate of removal yield was 11% higher than control sample.

$$\text{TSS} \rangle \text{ ultrasonic} = \text{ozonation} > \text{thermal}$$

the pretreated sample with the highest VSS solubilization rate (ultrasonic with 54.98%), had the highest VSS degradation (92.5%). 90°C thermal treatment and ozonation were solubilized at mostly equal rates (21% and 19%), thus they have a nearly equal biodegradability rate (86.60% and 84.71%). Also 40°C and 60°C thermal treatment, which led to lowest solubilization rates (11.47% and 6.45%), had the lowest biodegradation rates (79.87% and 75.68%). In this study, the removal yield of ozonation was 17% and ultrasound 13% more than control sample. The rate of elimination efficiency of thermal treatment was approximately the same as the control sample.

Comparison between different pretreatments under aerobic and anaerobic conditions

The comparison between batch aerobic and anaerobic digestion tests carried out with untreated and treated sludge showed a beneficial effect of the pre-treatment by ultrasound, ozonation and thermal treatment on hydrolysis kinetics and biogas.

- ***Effect of ultrasonic pre-treatment***

Ultrasonic pre-treatment is an effective method of sludge elimination and reduction of produced sludge. Ultrasound leads to a high sludge solubilization, thus a great amount of non biodegradable or slow biodegradable matter will be easily degraded and quickly digested during biological digestion step. This process leads to a reduced biological digestion time and increased sludge biodegradability. In this work the optimum specific energy was (200000 kJ.kg-TSS^{-1}). The results showed that using high specific energy along with low input power led to higher elimination efficiency compared to other configurations. By comparing the aerobic and anaerobic digestion of sonicated sludge, it can be concluded that although sonication led to a considerable increase in aerobic elimination efficiency, anaerobic elimination efficiency is much higher than aerobic elimination efficiency.

❁ ***Effect of ozonation pre-treatment***

Ozonation is of special interest among other chemical pretreatments because it does not increase final volume of sludge due to additional chemical substances applied to sludge. In fact, ozonation leads to partial oxidation and hydrolysis of organic matters of sludge. Ozonation pre-treatment not only solubilizes solids, may also result in solid mineralization. Ozone optimum dose was $0.101 gr O_3.gr\text{-}TSS^{-1}$. Further increasing of ozone dose and ozonation time does not improve solubilization and sludge biological elimination efficiency. For ozonated samples, in all cases, anaerobic digesters are more successful than aerobic digesters. The difference between aerobic and anaerobic digesters is very remarkable for some parameters.

❁ ***Effect of thermal pre-treatment***

Thermal treatment is an easy, less expensive method for breaking flocs and destroying cell walls compared to ozonation and sonication. In this study low temperature thermal treatments (40°C, 60°C) and high temperature thermal treatments (90°C and autoclave) were used. This study showed that thermal treatment at temperatures less than 100°C also may lead in increased sludge solubilization and biodegradability. However thermal treatment led to lower TSS removal yields compared to ozonation and sonication. For most thermal treated samples, we can see that anaerobic digesters had a higher elimination efficiency compared to aerobic digester. The optimum configuration of thermal treatment in this study was 90°C during 60 minutes.

The results of the three above mentioned methods can be summarized as follows:

- Ultrasonic pretreatment is more successful in sludge solubilization compared to ozonation and thermal treatment.
- Ultrasonic pretreatment is more successful in sludge biological elimination and TSS reduction compared to ozonation and thermal treatment.
- Ultrasonic leads to higher biogas production during anaerobic digestion.
- Anaerobic digestion is more successful than aerobic digestion in sludge removal.

The comparison between aerobic and anaerobic conditions showed that the biodegradability increased linearly with soluble COD removal improvement. This correlation was very clearer under aerobic and anaerobic conditions. Nevertheless it was not possible to establish a clear

correlation between soluble COD removal and solubilization parameters (COD, protein and carbohydrate) under aerobic and anaerobic conditions.

Under aerobic condition, an exponential correlation with a correlation factor $R^2 = 0.91$ between DD_{COD} and TSS removal improvement may be established. On the contrary, under anaerobic conditions no clear correlation between DD_{COD} and TSS removal improvement may be established.

Ozone and ultrasonic treatments before anaerobic digestion led to the best improvement of TSS removal. Ultrasonic treatment is energetically costly but the digestion time can be reduced. Ozone treatment is less costly but the length of the digestion largely contributes to sludge reduction.

It is difficult to establish systematic correlations between solubilization and/or specific energy and biodegradability or sludge reduction improvement. The possible reason is the big discrepancy between the mechanisms involved in the different pre-treatment.

3) Economic evaluation

In this study, the sludge elimination cost under anaerobic conditions is about 25% less than aerobic conditions. Under aerobic conditions, the cost of energy consumption for control sample was 900 €/ton-$TSS_{Removal}$ while for the sample that was sonicated prior to biological digestion, total cost is calculated to be 680 €/ton-$TSS_{Removal}$ (24.5% cost reduction). Under anaerobic conditions, the cost of sludge removal without prior pretreatment was 720 €/ton-$TSS_{Removal}$ while for ultrasonic reactor (solubilization + digestion) this cost was 600 €/ton-$TSS_{Removal}$ (17% cost reduction compared to control sample). The cost reduction due to different methods can be classified as follows:

ultrasonic> ozonation> thermal

The best combination in term of sludge reduction and cost saving is an ultrasonic (200000 kJ.kg-TSS^{-1}) and ozonation (0.101gO_3/g-TSS) pre-treatment prior to anaerobic digestion.

Perspectives

Future research should be focused on reduction and minimization of excess sludge production, optimization of specific energy applied in solubilization processes, dosing mode (continuous or intermittent), and reactor configuration.

- In an ultrasonic phenomenon, the temperature of the sludge under treatment uncouthly increases. The temperature of sludge increases with more ultrasonic radiation power. As a result the test parameters are under the influence of ultrasonic radiation as well as the increased temperature. To better understand the effect of ultrasonic radiation itself, the effect of temperature should be eliminated. In our study, the temperature has been under control during the sonication. But in an industrial scale, increase of temperature due to ultrasonic radiation may be helpful toward a better yield. Thus the differentiation of thermal and physical effects should be carried out.

- In ozonation process there are always interaction between free radicals and organic matters. An accurate understanding of this phenomenon is crucial to prediction of total efficiency.

- Using higher temperatures, i.e. over 100°C, followed by a consistent compression between high and low temperature treatments seems to be helpful.

- It would be interesting to have an accurate understanding of chemical and physical properties of pre-treated sludge and investigate their potential impact on xenobiotics and toxic metals retention and their accumulation properties.

- Obtaining a higher insight on the impact of heavy metals on aerobic and anaerobic digestion of pretreated sludge and their impact on kinetics parameters and population evolution may be an essential research field.

- Qualitative study the physical properties of the resulting sludge such as dewater-ability, density, size, settleability, specific resistance to filtration, etc, should be carried out. These results compared to those obtained after biodegradation of non pretreated sludge may lighten the effects of sludge pretreatment on sludge physical characteristics.

- Investigation of environmental and clinical impacts of different pretreatment methods such as ultrasonic and ozonation in an industrial scale wastewater treatment plant may prove some pretreatments to be more environment-friendly than others.
- A study of the impact of the pre-treatment on cell membrane integrity and microbiological parameters would be helpful.
- Developing cost and energetic balance study and life cycle analysis would provide engineers with valuable help in their choice of pretreatment.

Therefore, the current legal constraints, the rising costs and public sensitivity of sewage sludge disposal necessitate the development strategies for reduction and minimization of excess sludge production. Pre-treatment techniques coupled with sludge biological digestion processes promisse one of the most successful and one of the most practical methods for sludge production reduction and for the removal of major operating problems in municipal and industrial waste water treatment nowadays, in so far as the costs of the used techniques are controlled and the real impacts on environment are evaluated.

References

References

Adewuyi, Y.G. (2001) Sonochemistry: Environmental science and engineering application, *Ind. Eng. Chem. Res*., **40,** (22), PP. 4681–4715.

Ahn, K.H., Park, K.Y., Maeng, S.K., Hwang, J.H., Lee, J.W., Song, K.G. and Choi, S. (2002) Ozonation of wastewater and ozonation for recycling, *Water Science and Technology,* **46,** (10), PP. 71–77.

Akin, B., Khanal, S. K., Sung, S., Grewelland D. and Leeuwen, J.V. (2006) Ultrasound pre-treatment of waste activated sludge, *Water Science & Technology: Water Supply*, **6,** (6), PP. 35–42.

American Public Health Association, American Water Works Association, Water Pollution Control Federation, (1992) Standard methods for the examination of water and wastewater, *In: L.S. Clesceri, A.E. Greenberg, R.R. Trussel (Eds.), 18th ed., APHA*.

Anderson, N. J., Dixon, D. R., Harbour, P. J. and Scales, P. J. (2002) Complete characterisation of thermally treated sludges, *Water Science and Technology,* **46,** (10), PP. 51-54.

Anon (2000) Working document on Sludge, *Third Draft*. *European Union Commission, Brussels*, 27 April, 2000.

ATV. (2000) Verfahren und Anwendungsgebiete der mechanischen Klärschlamm desintegration, *Work report ATV-working group AK-3.1.6 Klärschlamm desintegration, part 1, Korrespondenz Abwasser*, **47,** (4), PP. 570–576.

ATV. (2001) Verfahrensvergleich und Ergebnisse der mechanischen Klärschlamm desintegration, *work report ATV-DVWK-working group AK-1.6 Klärschlamm desintegration, part 2, Korrespondenz Abwasser*, **48,** (3), PP. 393–400.

ATV (2003) Müller, J., Tiehm, A., Böcker, K., Eder, B., Kopp, J., Kunz, P., Neis, U., Oles, J., Otte-Witte, R., Schmelz, K.G.and Seiler, K. (2003) Thermische, chemische und biochemische Desintegrationsverfahren, Report of ATV/DVWK – Specialist group "Sewage Sludge Disintegration". *Korrespondenz Abwasser*, **50,** (6).

Baier, U. and Schmidheiny, P. (1997) Enhanced anaerobic degradation of mechanically disintegrated bio-solids, *IAQW International Conference on waste water sludge, Cestochowa, Poland,* Part 1, PP. 106–112.

Barjenbruch, M., Hoffmann, H. and Tränker, J. (1999) Minimizing of foaming in digesters by pre-treatment of the surplus sludge, *Water Science and Technology,* **42,** (9), 235–242.

Barjenbruch, M. and Kopplow, O. (2003) Enzymatic, mechanical and thermal pre-treatment of surplus sludge, *Advances in Environmental Research,* **7,** PP. 715-720.

Barlindhaug, J. and Odegaard, H. (1996) Thermal hydrolysis for the production of carbon source for de-nitrification, *Water Science & Technology,* **34,** (1-2), PP.371-378.

Battimelli, A., Millet, C., Delgenès, J.P. and Molleta, R.R. (2003) Anaerobic digestion of waste activated sludge combined with ozone post-treatment and recycling, *Water Science and Technology,* **48,** (4), PP. 61–68.

Bernal-Martinez, A. (2005) Elimination des hydrocarbures aromatiques polycycliques présents dans les boues d'épuration par couplage ozonation – digestion anaérobie, *Ph.D thesis, Génie des Procédés Ecole Doctorale : Science et Procédé Biologiques et Industriels, ontpellier II, France.*

Bernal-Martinez, A. Carrère, H., Patureau, D. and Delgenès, J.P. (2007) Ozone pre-treatment as improver of PAH removal during anaerobic digestion of urban sludge, *Chemosphere,* **68,** PP. 1013–1019.

Bien, J. and Wolny, L. (1997) Changes of some sewage sludge parameters prepared with an ultrasonic field, *Water Science and Technology,* **36,** (11), PP. 101-106.

Bien, J. B., Malina, G., Bien, J. D. and Wolny, L. (2004) Enhancing anaerobic fermentation of sewage sludge for increasing biogas generation, *Journal of Environmental Science and Health Part a-Toxic/Hazardous Substances & Environmental Engineering,* **39,** (4), PP. 939-949.

Bitton, G. (2005) Wastewater microbiology, *Third edition, New York, Willey-Liss pub.*

Böhler, M. and Siegrist, H. (2004) Partial ozonation of activated sludge to reduce excess sludge, improve denitrification and control scumming and bulking, *Water Science and Technology,* **49,** (10), PP. 41–49.

Bougrier, C. (2003) Optimisation of anaerobic digestion using a physicochemical co-treatment: application to biogas production from wastewater sludge, PhD Thesis, Génie des procédés, Université Montpellier II, 258 p. (in French).

Bougrier, C. (2005) Optimisation du procédé de méthanisation par mise en place d'un co-traitement physico-chimique: Application au gisement de biogaz représenté par les boues d'épuration des eaux usées, *Ph.D thesis, Inst Natl des Science Applied (INSA), Toulouse, France.*

Bougrier, C. Carrère, H. and Delgenès J.P. (2005) Solubilization of waste-activated sludge by ultrasonic treatment, *Chemical Engineering Journal,* **106**, PP.163–169.

Bougrier, C., Albasi, C., Delgenès, J.P. and Carrère, H. (2006) Effect of ultrasonic, thermal and ozone pre-treatments on waste activated sludge Solubilization and anaerobic biodegradability, *Journal of Chemical Engineering and processing,* **45**, (8), PP. 711-718.

Bougrier, C., Delgenès, J.P. and Carrère, H. (2007) Impacts of thermal pre-treatments on the semi-continuous anaerobic digestion of waste activated sludge, *Biochemical Engineering Journal*, **34,** PP. 20–27.

Bougrier, C., Delgenès, J.P. and Carrère, H. (2008) Effects of thermal treatments on five different waste activated sludge samples Solubilization, physical properties and anaerobic digestion, *Journal of Chemical Engineering and processing,* **139**, PP. 236-244.

Braguglia, C.M., Mininni, G., Tomei, M.C. and Rolle, E. (2006) Effect of feed/inoculum ratio on anaerobic digestion of sonicated sludge, *Water Science & Technology,* **54,** (5), PP. 77–84.

Brooks, R.B. (1970) Heat treatment of sewage sludge, *Water Pollution Control,* **69,** (2), PP. 221–231.

Brown, J. P., Clark, P., and Hogan, F., (2003) Ultrasonic sludge treatment for enhanced anaerobic digestion at Orange County Sanitation District, *In: WEFTEC 2003 Conference Proceedings, Los Angeles, California. Water Environment Federation, Alexandria, Virginia.*

Cacho Rivero, J. A. (2005) Anaerobic digestion of excess municipal sludge, optimization for increased solid destruction, *Ph.D thesis, department of Civil and Environmental Engineering of the University of Cincinnati ,USA.*

Camacho, P. (2001) Excess sludge process reduction by physical, chemical or biological coupling, *Ph.D. thesis*, *Institut National des Sciences Appliquées, Toulouse, France.*

Camacho, P., Déléris, S., Geaugey, V., Paul, E. and Ginestet, P. (2002) A comparative study between mechanical, thermal and oxidative disintegration techniques of wasted activated sludge, *Water Science and Technology,* **46,**(10), PP. 79–87.

Camacho, P., Ginestet, P. and Audic, J.-M. (2003) Pilot plant demonstration of reduction technology during activated sludge treatment of wastewater. *WEFTEC'03, October 11–15, Los Angeles, USA.*

Camacho, P., Ginestet, P. and Audic, J.-M. (2005) Understanding the mechanisms of thermal disintegrating treatment in the reduction of sludge production, *Water Science & Technology* **52,** (10–11), PP. 235–245, *Q* IWA Publishing.

Canales, A., Pareilleux, A., Rols, J.L., Goma, G. and Huyard, A. (1994) Decreased sludge production strategy for domestic wastewater treatment, *Journal of Water Science and Technology*, **30,** (8), PP. 97–106.

Carballa, M., Manterola, G., Larrea, L., Ternes, T., Omil, F. and Lema, J.M. (2007) Influence of ozone pre-treatment on sludge anaerobic digestion: Removal of pharmaceutical and personal care products, *Chemosphere,* **67,** PP. 1444–1452.

Carballa, M., Omil, F. and Lema, M. (2004) Improvement of anaerobic digestion operation and digested sludge characteristics using a chemical and thermal pre-treatment. *Proceedings, 10th World Congress Montréal, Canada.*

Casellas, M., Dagot, C. and Baudu, M. (2006) Set up and assessment of a control strategy in a SBR in order to enhance nitrogen and phosphorus removal, *Process Biochemistry*, **41,** PP. 1994-2001.

Ceccaroni, L. (2001) Ontowedss-an ontology-based environmental decision- support system for the management of waste water treatment plant, *Ph.D thesis, University of Polytechnic of Catalonia Barcelona, Spain.*

Cesbron, D., Déléris, S., Debellefontaine, H., Roustan, M. and Paul, E. (2003) Study of competition for ozone between soluble and particulate matter during activated sludge ozonation, *Trans IChemE* 81, (Part A), PP. 1165–1170.

Chang, J., Chudoba, P., and Capdeville, B. (1993) Determination of the maintenance requirement of activated sludge, *Journal of Water Science & Technology,* **28,** PP. 139–142.

Chauzy, J., Cretenot, D., Fernandes, and Patria, L. (2002) Bio Thelys: a new process for sludge minimization and sanitization, *6th European Bio-solids and Organic Residuals Conference.*

Chauzy, J., Cretenot, D., Patria, L., Fernandes, P., Sauvegrain, P. and Levasseur, J. P. (2003) Bio Thelys: a new sludge reduction process, *Bio-solids 2003: Water Sludge as a Resource, Trondheim (Norway),* 23-25 June 2003.

Chauzy, J., Graja, S., Gerardin, F., Cre´tenot, D., Patria, L. and Fernandes, P. (2004) Minimisation of excess sludge production in a WWTP by coupling thermal hydrolysis and rapid anaerobic digestion, *In Proc, of the 4th IWA World Water Congress and Exhibition Programme, 19–24 September 2004, Marrakech, Morocco.*

Chitra, S., Paramasivan, K., Sinha, K.P. and Lal, B.K. (2004). Ultrasonic treatment of liquid waste containing EDTA, *J. Clean. Prod*. **12,** PP. 429-435.

Chiu, Y.C., Chang, C.N., Lin, L.G. and Huang, S.J. (1997) Alkaline and ultrasonic pre-treatment of sludge before anaerobic digestion, *Water Science & Technology,* **36**, (11), PP. 155–162.

Choi, H.B., Hwang, K.Y. and Shin, E. B. (1997) Effects on anaerobic digestion of sewage sludge pre-treatment, *Water Science & Technology*, **35,** (10), PP. 07–211.

Chu, C.P., Feng, W.H., Chang, B.W., Chou, C.H. and Lee, D.J. (1999) Reduction in microbial density level through freezing and thawing, *Journal of water research,* **33,** PP. 3532–3535.

Chu, C. P., Chang, B. V., Liao, G. S., Jean, D. S. and Lee, D. J. (2001) Observations on changes in ultrasonically treated waste-activated sludge, *Journal of Water Research,* **35,** (4), PP. 1038-1046.

Chu, C. P., Lee, D. J., Bea-Ven Chang, C. S. Y., and Tay, J. H. (2002)"Weak" ultrasonic pre-treatment on anaerobic digestion of flocculated activated bio-solids, *Water Research,* **36,** PP. 2681–2688.

Chu, L.B., Yan, S.T., Xing, X.H., Yu, A.F., Sun, X.L. and Jurcik, B. (2008) Enhanced sludge solubilization by microbubble ozonation, *Chemosphere,* **72,** PP. 205–212.

Clark, P. (1998) Ultrasound in sludge processing: *The technology of the future? Innovations 200 Conference, Cambridge.*

Clark, P.B. and Nujjoo, I. (2000) Ultrasonic sludge pre-treatment for enhanced sludge digestion, *Water Environmental Management,* **14,** (1), PP. 66–71.

Climent, M., Ferrer, I., Mar-Baeza, M., Artola, A., Vàzquez, F. and Font, X. (2007) Effects of thermal and mechanical pre-treatments of secondary sludge on biogas production under thermophilic conditions, *Chemical Engineering Journal,* **133,** PP. 335–342.

Collignon, A., Martin, G., Martin, N, and Laplanche, A. (1994) Bulking reduced by with the use of ozone, *Ozone: Science & Engineering,* **16,** (5), PP. 385-402.

Cui, R. and Jahng, D. (2004) Nitrogen control in AO process with recirculation of solubilized excess sludge, *Water Research,* **38,** PP. 1159–1172.

Cui, R. and Jahng, D. (2006) Enhanced methane production from anaerobic digestion of disintegrated and deproteinized excess sludge, *Biotechnology Letters,* **28**, PP. 531–538.

Davis, E.M. (1988) Protein assay: a review of common techniques, *Am. Biotechnol,* Lab. (6), PP. 28-37.

De Silva, V. and Nickel, K. (2004) Application of ultrasound technology for anaerobic digestion, Proceedings, *10 th World Congress Montréal, Canada*.

Degrémont. (1989) Water Technical Memorandum, *9em Edition, Tome 1 et 2, Editions Lavoisier, Paris.*

Déléris, S., Paul, E., Debellefontaine, H. and Geaugey, V. (1999) Sludge reduction in wastewater treatment plants. Mass balances for assessing the efficiency of combined treatment system: activated sludge and ozonation, *2nd European Congress of Chemical Engineering, Montpellier (France),* 5-7 October 1999.

Déléris, S., Paul, E., Audic, J.M., Roustan, M. and Debellefontaine, H. (2000) Effect of ozonation on activated sludge solubilization and mineralization, *Ozone Science Engineering,* **22,** (5), PP. 473–487.

Déléris, S., Geaugey, V., Camacho, P., Debellefontaine, H. and Paul, E. (2002) Minimization of sludge production in biological processes: an alternative solution for the problem of sludge disposal, *Water Science & Technology*, **46,** (10), PP. 63–70.

Delgenès, J. P., Penaud, V. and Moletta, R. (2003) Pre-treatments for enhancement of anaerobic digestion of solid waste, *Biomethanization of the Organic Fraction of Municipal Solid Wastes, J. Mata-Alvarez Editor*. Chapter 8, IWA Publishing, P. 201.

Dewil, R., Baeyens, J. and Goutvrind, R. (2006) Ultrasonic treatment of waste activated sludge, *Published online in Wiley Inter Science (www.interscience.wiley.com),* DOI 10.1002/ep, 10130.

Dignac, M.F., Derenne, S., Ginestet, P., Bruchet, A., Knicker, H. and Largeau, C. (2000) Determination of structure and origin of refractory organic matter in bio-epurated wastewater

via spectroscopic methods: comparison of conventional and ozonation treatments, *Environmental Science Technology,* **34,** PP. 3389–3394.

Ding, W.CH., Li, D.X., Zeng, X.L. and Long, T.R. (2006) Enhancing excess sludge aerobic digestion with lov intensity ultrasound, Journal of Cent. South univ. technology, 13, (4), PP. 408-411.

Dohányos, M., Zábranská, J., Jeníc̆ek, P., S̆tĕpová, J., Kutil, V. and Horejs̆, J. (2000) The intensification of sludge digestion by the disintegration of activated sludge and the thermal conditioning of digested sludge, *Wat. Sci. Tech.*, **42,** (9), PP. 57–64.

Doré, M. (1989) Chimie des oxydants et traitement des eaux*, Technique et documentation – Editions Lavoisier, Paris.*

Drier, D.E. and Obma, C.A. (1963) Aerobic digestion of solids, *Walker Process Equipment Co. Bulletin,* **33-S-18194,** Aurora, IL.

Dziurla, M.A., Salhi, M., Leroy, P., Paul, E., Ginestet, Ph. and Block, J.C. (2005) Variations of respiratory activity and glutathione in activated sludges exposed to low ozone doses, *Water Research,* **39,** (2005), PP. 2591–2598.

Eastman, J.A. and Ferguson, J.F. (1981) Solubilization of particulate organic carbon during the acid phase of anaerobic digestion, *Journal of WPCF*, **53,** (3), PP. 352–366.

Edeline, F. (1997) L'épuration biologique des eaux. Théorie & technologie des réacteurs, CEDEBOC Editeur, Paris.

Egemen, E., Corpening, J., Padilla, J., Brennan, R. and Nirmalakhandan, N. (1999) Evaluation of ozonation and cryptic growth for bio-solids management in wastewater treatment, *Water Science and Technology,* **39,** PP. 155–158.

Egemen, E., Corpening, J. and Nirmalakhandan, N. (2001) Evaluation of an ozonation system for reduced waste sludge generation, *Water Science and Technology,* **44,** (2–3), PP. 445–452.

Elbing, G. and Dünnebil, A. (1999) Thermal cell decomposition with subsequent digestion, *I. Laboratory tests, Korrespondenz Abwasser,* Germany, **46,** (4), PP. 538–547.

Elissalde, N. (1994) Les germes pathogènes dans les boues résiduaires des stations d'épurations urbaines*, Contrats ADEME n° 2750010 et 2750009, 90p.*

Evans, G. (2001) Bio-waste and biological waste treatment, *published by Earthscan.*

Fischer, H.B., List, E.J., Koh, R.C.Y., Imberger, J. and Brooks, N.H. (1979) Mixing in Inland and Coastal waters, *Academic press, N.Y.*

Fisher, R.A. and Swanwick, S.J. (1971) High temperature treatment of sewage sludge, *Water Pollution Control,* **71,** (3), PP. 255–370.

Fjordside, C. (2001) An operating tale from Naestved Sewage Treatment Plant, *Municipal Wastewater Treatment Nordic Conference, Copenhagen, 17-19 January 2001.*

Frolund, B., Palmgren, R.n Keinding, K. and Nielsen, **P.H (1996)** Extraction of extracellular polymers from activated sludge using a cation exchange resin, *Water Research,* **30**, PP. 1749-1758.

Gavala, H.N., Yenal, U., Skiadas, I.V., Westermann, P. and Ahring, B.K. (2003) Mesophilic, thermophilic anaerobic digestion of primary and secondary sludge. Effect of pre-treatment at elevated temperature, Water Reserch, **37,** PP. 4561–4572.

Gary R. Krieger, and John Burke Sullivan. (2001) Clinical environmental health and toxic exposures, *Published by Lippincott Williams and Wilkins.*

Gaudy AF & Gaudy ET (1980) Microbiology for Environmental Scientists and Engineers, *McGraw-Hill, New York.*

Giovanni B. De Franchi (2005) Effect of Acid and Base Pre-treatment on the Anaerobic Digestion of Excess Municipal Sludge, Master of Science, *department of Civil and Environmental Engineering of the University of Cincinnati, USA.*

Goel, R., Tokutomi, T. and Yasui, H. (2003) Anaerobic digestion of excess activated sludge with ozone pre-treatment, *Water Science and Technology,* **47,** (12), PP. 207–214.

Gomez Palacios, J. M., Ruiz de Apodaca, A., Rebello, C. and Azcarate, J. (2002) European policy on biodegradable waste: a management perspective, *Water Science and Technology,* **46,** (10), pp. 311-318.

Gonze, E., Gonthier, Y., Boldo, P. et Bernis, A. (1997) Etude de l'oxydation du pentachlorophenol dans différentes géométries de réacteurs à ultrasons de haute fréquence, *Canadian Journal of Chemical Engineering,* **75,** PP. 245-255.

Gonze, E., Fourel, L., Gonthier, Y., Boldo, P. and Bernis, A. (1999) Wastewater pre-treatment with ultrasonic irradiation to reduce toxicity, *Chemical Engineering Journal,* **73,** PP. 93-100.

Gonze, E. (2000) Design and characterization of high frequency ultrasonic reactors for wastewater treatment, *Recent Development Chemical Engineering,* **4,** PP. 137-160.

Gonze, E., Pillot, S., Valette, E., Gonthier, Y. and Bernis, A. (2003) Ultrasonic treatment of an aerobic activated sludge in a batch reactor, *Journal of Chemical Engineering and Processing,* **42,** (12), PP. 965-975.

Grady, C. P. L., Daigger, G. T., and Lim, H.C. (1998) Biological Wastewater Treatment, *2nd Ed., Marcel Dekker, Inc. New York, N.Y.*

Graja, S., Chauzy, J., Fernandes, P., Patria, L.and Cretenot, D. (2005) Reduction of sludge production from WWTP using thermal pre-treatment and enhanced anaerobic methanisation, *Water Science & Technology,* **52,** (1-2), PP. 267–273.

Grönroos, A., Kyllönen, H., Korpijärvi, K., Pirkonen, P., Paavola, T., Jokela, J., and Rintala, J., (2005) Ultrasound assisted method to increase soluble chemical oxygen demand (COD_S) of sewage sludge for digestion, *Ultrasonic Sonochemistry,* **12,** PP. 115–120.

Guellil, A., Boualam, M., Quiquampoix, H., Ginestet, P., Audic, JM. and Block, JC. (2001) Hydrolysis of wastewater colloidal organic matter by extra-cellular enzymes extracted from activated sludge flocs, *Water Science Technology,* **43,** (6), PP. 33–40.

Guibelin, E. (2002) Sustainability of thermal oxidation processes: Strengths for the new millennium, *Water Science & Technology*, **46**, (10), PP. 259–267.

Gunten, U.V. (2003) Ozonation of drinking water, Part I & II. Oxidation kinetics and product formation, *Water Reseurce, in press*.

Harrison, S.T.L. (1991) Bacterial cell disruption: a key unit operation in the recovery of intracellular products, *Biotechnol. Adv*., **9,** PP. 217–240.

Haug, R.T. (1977) Sludge processing to optimize digestibility and energy production, *Journal of Water Pollution Control Federation,* **49,** PP.1713–1721.

Haug, R.T., LeBrun, T.J. and Tortorici, L.D. (1983) Thermal pre-treatment of sludge-a field demonstration, *Journal Water Pollution Control Federation,* **55,** (1), PP. 23–34.

Haug, R.T., Stuckey, D.C., Gossett, J.M. and McCarty, P.L. (1978) Effect of thermal pre-treatment on digestibility an dewater-ability of organic sludge *Journal of Water Pollution Control Federation,* **50,** PP. 73–85.

He, S-B., Xue, G, and Wang, B-Z (2006) Activated sludge ozonation to reduce sludge production in membrane bioreactor (MBR), *Journal of Hazardous Materials,* **B.135**, PP. 406–411.

Henze, M. and Harremoës, P. (1990) Chemical-biological nutrient removal-The Hypro Concept, *In Chemical Water and Wastewater Treatment, Hahn, H.H. and Klute, R. (eds), Springer-Verlag, Berlin,* PP. 449–510.

Herbert, D., Elsworth, R. and Telling, R.C. (1956) The continuous culture of bacteria: a theoretical and experimental study, *J. Gen. Microbiol,* PP. 114- 601.

Hiraoka, M., Takeda, N., Sakai, S. and Tasuda, A. (1984) Highly efficient anaerobic digestion with thermal pre-treatment, *Water Science & Technology*, **17,** PP. 529–539.

Hoffmann, M. R., Hua, I. et Höchemer, R. (1996) Application of ultrasonic irradiation for the degradation of chemical contaminants in water, *Ultrasonics Sonochemistry,* **3,** PP. S163-S172.

Hogan, F.M., Mormede, S., Clark, P.B. and Crane, M.J. (2004) Ultrasonic sludge treatment for Enhanced anaerobic digestion, *Water Science. Technology*, **50,** (9), PP. 25–32.

Horan, N.J. (1990) Biological Wastewater Treatment Systems, *Chichester, UK: Wiley publication.*

Hua, I., and Hoffmann, M. R. (1997) Optimization of ultrasonic irradiation as an advanced oxidation technology, *Environmental Science Technology,* **31,** PP, 2237-2243.

Huysmans, A., Weemaes, M., Fonseca, P. A. and Verstraete, W. (2001) Ozonation of activated sludge in the recycle stream, *Journal of Chemical Technology and Biotechnology,* **76,** (3), PP. 321-324.

Jeongsik, K., Chulhwan, P., Tak-Hyun, K., Myunggu, L., Sangyong, K., Seung-Wook, K. and Jinwon, L. (2003) Effects of various pre-treatment for enhanced anaerobic digestion with waste activated sludge". *Journal of Bioscience and Bioengineering,* **95,** (3), 271-75.

John, T. Novak., Mary, E., Mary, E. Sadler., and Sudhir, N. Murthy. (2003) Mechanisms of floc destruction during anaerobic and aerobic digestion and the effect on conditioning and dewatering of biosalids, *Journal of water research,* **37**, PP.3136-3144.

Kamma, R., Thorkild, H-J. and Per. Halkjre ,N. (1994) Measurement of pools of protein, carbohydrate and lipid in domestic wastewater, *Water Research*, ***28,*** *(2)*, *PP. 251-262.*

Kamiya, T. and Hirotsuji, J. (1998) New combined system of biological process and intermittent ozonation for advanced wastewater treatment, *Water Science and Technology,* **38,** PP. 145–153.

Kayser, R. and Nellenschulte, T. (1992) Untersuchungen über die enzymatische Klärschlammstabilisierung (ESS) (Investigations on the enzymatic sewage-sludge-stabilization), *Research paper*, Institute of Sanitary Engineering, Technical University of Braunschweig.

Khanal, S.K., Isik, H., Sung, S., and van Leeuwen, J. (2006) Ultrasound pre-treatment of waste activated sludge: evaluation of sludge disintegration and aerobic digestibility. *In Proceedings of IWA World Water Congress and Exhibition*, *September 10–14, 2006, Beijing, China*.

Khanal, S. K., Grewell, D., Sung, S. and van Leeuwen, J. (Hans). (2007) Ultrasound Applications in Wastewater Sludge Pre-treatment, *Critical Reviews in Environmental Science and Technology*

Karnik, B.S., Davies, S.H.R., Chen, K.C., Jaglowski, D.R., Baumann, M.J. and Masten, S.J. (2005) Effects of ozonation on the permeate flux of nanocrystalline ceramic membranes, *Water Research,* **39,** PP. 728–734.

Kepp, U., Machenbach, I., Weisz, N. and Solheim, O.E. (2000) Enhanced stabilization of sewage sludge through thermal Hydrolysis, 3 years of experience with full-scale plant, *Water Science and Technology,* **42,** (9), 89–96.

Kepp, U. and Solheim, O.E. (2001) Meeting increased demands on sludge quality–experience with full scale plant for thermal disintegration, *Proceedings. 9th World Congress, Anaerobic Conversion for Sustainability*.

Kim, J., Park, C., Kim, T. H., Lee, M., Kim, S., Kim, S. W. et Lee, J. (2003) Effects of various pre-treatments for enhanced anaerobic digestion with waste activated sludge, *Journal of Bioscience and Bioengineering,* **95,** (3), PP. 271-275.

Kopp, J., Müller, J.A., Dichtl, N. and Schwedes, J. (1997) Anaerobic digestion and dewatering characteristics of mechanically disintegrated excess sludge, *Water Science and Technology,* **36,** (11), PP. 129-136.

Kristensen, G.H., Jörgensen, P.E., Strube, R. and Henze, M. (1992) Combined pre-precipitation, biological sludge hydrolysis and nitrogen reduction – a pilot demonstration of integrated nutrient removal. *Water Science and Technology*, **26,** (5–6), PP. 1057–1066.

Kunz, P. and Wagner, S. (1994) Ergebnisse und Perspektiven aus Untersuchungen zur Klärschlammdesintegration, *awt Abwassertechnik,* **44,** (2), PP. 33–40.

Lafitte-Trouqué, S. and Forster, C. F. (2002) The use of ultrasound and g-irradiation as pre-treatments for the anaerobic digestion of waste activated sludge at mesophilic and thermophilic temperatures, *Bioresource Technology,* **84,** PP. 113-118.

Lee, J.W., Cha, H.Y., Park, K.Y., Song, K.G. and Ahn, **K.H. (2005)** Operational strategies for an activated sludge process in conjunction with ozone oxidation for zero excess sludge production during winter season, *Water Research,* 39, PP. 1199–1204.

Lehne, G., Müller, j.A. and Schwedes, J. (2001) Mechanical disintegration of sewage sludge, *Journal of Water Science & Technology,* **43,** (1), PP. 19-26.

Li, Hui. (1994) Mechanisms of enhancing liquid-solid mass transfer with ultrasound [J]. *Journal of Shenyang Institute of Chemical Technology,* 8, (3), PP. 175 - 181. (in Chinese)

Li, Y.Y. and Noike, T. (1992) Upgrading of anaerobic digestion of waste activated sludge by thermal pre-treatment, *Journal of Water Science and Technology*, **26**, (3-4), PP. 857–866.

Liu, J.C., Lee, C.H., Lai, J.Y., Wang, K.C., Hsu, Y.C. and Chang, B.V. (2001) Extra-cellular polymers of ozonized waste activated sludge, *Water Science & Technology,* **44,** (10), PP. 137–142.

Liu, Y. (2000) Effect of chemical un-coupler on the observed growth yield in batch culture of activated sludge, *Water Research,* **34,** PP. 2025–2030.

Liu, Y. (2003) Chemically reduced excess sludge production in the activated sludge process, *Chemosphere,* **50,** (1), PP.1-7.

Liu, Y. and Fang, H.H.P. (2003) Influences of extra-cellular polymeric substances (EPS) on flocculation, settling, and dewatering of activated sludge, Crit. Reviews in Environmental Science Technology, **33,** (3), PP. 237–273.

Liu, Y. and Tay, J. H. (2001) Strategy for minimization of excess sludge production from the activated sludge process, *Research review paper, Biotechnology Advances,* **19,** (2), PP. 97-107.

Ma, Y.S. and Lin, J.G. (1998) Effect of pre-sonication on removal of organic matters resulting from chlorinated humic acids, *Water Science and Technology,* **38,** (6), PP. 253–260.

Mace, S., Costa, J. and Mata-Alvarez, J. (2001) Sewage sludge pre-treatments for enhancing its anaerobic biodegradability, *Bioprocessing of solid waste & sludge,* **1,** (3), PP. 3.

Martinage, V. and Paul, E. (2000) Effect of environmental parameters on autotrophic decay rate, *journal of Environmental Technology,* **2,** PP. 31–41.

Mason, C.A., Hamer, G. and Bryers, D. (1986) The death and lysis of micro-organisms in environmental processes, *FEMS Microbiology, Rev,* **39,** PP. 373–401.

Mason C. A. and Hamer G. (1987) Cryptic growth in Klebsiella pneumoniae, *Applied Microbiology and Biotechnology,* **25,** PP. 577-584.

Mayhew, M. and Stephenson, T. (1998) Biomass yield reduction: Is biochemical manipulation possible without affecting activated sludge process efficiency? *Journal of Water Science Technology,* **38,** (8–9), PP. 137-144.

Mesas, J.A. (2003) Efecto de los ultrasonidos en el tratamiento de lodos de depuradora de aguas residuales. *Tecnologïa del agua, 232, Enero, 2003*.

Metcalf and Eddy. (1991) Wastewater engineering: treatment, disposal and reuse, George Tchobanoglous and Franklin L. Burton, *Third Edition, McGraw-Hill, Inc., New York.*

Müller, J.A. (1996) Mechanischer Klärschlammaufschlb, *Ph.D thesis, Technical University of Braunschweig, ISBN 3–82–2053.*

Müller, J. A., Lehne, G., Schwedes, J., Battenberg, S., Naveke, R., Kopp J., Dicht, N., Scheminski, A., Krull, R. and Hempel, D. C. (1998) Disintegration of sewage sludges and influence on anaerobic digestion, *Water Science and Technology,* **38,** (8-9), PP. 425-433.

Müller, J.A. and Pelletier, L. (1998) L'eau, l'industrie, *les nuisances*, **217,** PP. 61–66.

Müller, J.A. (2000-a) Disientegration as a key-step in sewage sludge treatment, *Water Science & Technology*, **41,** (8), PP. 123–130.

Müller, J. A. (2000-b) "Pre-treatment processes for the recycling and reuse of sewage sludge", *Water Science and Technology,* **42,** (9), PP. 167-174.

Müller, J.A. (2001) Prospects and problems of sludge pre-treatment processes, *Water Science & Technology,* **44,** (10), PP. 121–128.

Müller, J.A. (2002) Sludge Pre-treatment Processes – Results and Applications. *IWA World Water Congress 2002 Melbourne*. Paper nr. e21094a.

Müller, J.A., Winter, A. and Strünkmann, G. (2004) Investigation and assessment of sludge pre-treatment processes, *Water Science & Technology,* **49,** (10), PP. 97–104.

Mustranta, A. and Viikai, L. (1993) Dewatering of activated sludge by an oxidative treatment, *Water Science & Technology*, **28,** (1), PP. 213–221.

Nah, I. W., Kang, Y. W., Hwang, K. Y. and Song, W. K. (2000) Mechanical pre-treatment of waste activated sludge for anaerobic digestion process, *Water Research,* **34,** (8), PP. 2362-2368.

Neis, U., Nickel, K. and Tiehm, A. (2000) Enhancement of anaerobic sludge digestion by ultrasonic disintegration, *Water Science and Technology,* **42,** (9), PP. 73–80 © IWA Publishing 2000.

Neyens, E., Baeyens, J., Weemaes, M. and De Heyder, B. (2002) Advanced bio-solids treatment using H_2O_2 oxidation, *Environmental Engineering sience,* **19,** (1), 27–35.

Neyens, E. and Baeyens, J. (2003) A review of thermal sludge pre-treatment processes to improve dewater-ability, *Journal of Hazardous Materials,* **B98,** PP. 51–67.

Neyens, E., Baeyens, J., Weemaes, M and De-heyder, B. (2003) Hot acid hydrolysis as a potential treatment of thickened sewage sludge, *Journal of Hazardous Materials*, **98**, (1-3), PP. 275–93.

Neyens, E., Baeyens, J., Dewill, R. et De Heyder, B. (2004) Advanced sludge treatment affects extracellular polymeric substances to improve activated sludge dewatering, *Journal of Hazardous Materials,* **106B,** PP. 83-92.

Nickel, K. and Neis, U. (2007) Ultrasonic disintegration of biosolids for improved biodegradation, *Ultrasonics Sonochemistry*, **14,** PP. 450–455.

Nielsen, H.B., Mladenovska, Z., Westermann, P. and Ahring, B.K. (2004) Comparison of two-stage thermophilic (68°C/55°C) anaerobic digestion with one-stage thermophilic (55°C) digestion of cattle manure, *Journal of Biotechnology & Bioengineering,* **86,** PP. 291–300.

Nishijima, W., Fahmi, Mukaidani, T. and Okada, M. (2003) COD removal bymulti-stage ozonation-biological treatment, *Water Research,* **37,** PP. 150–154.

Nishimura, F., Katoh, G. and Fujiwara, T. (2001) Improvement and reduction of activated sludge by ozonation and its application to wastewater treatment, *Proceedings of 15th Ozone World Congress,* vol. I, London.

Odegaard, H., Paulsrud, B. and Karlson. I. (2002) Wastewater sludge as a resource – sludge disposal strategies and corresponding treatment technologies aimed at sustainable handling of wastewater sludge, *Journal of Water Science and Technology*, **46,** (10), PP. 295–303.

Odegaard, H. (2004) Sludge minimization technologies – an overview, *Journal of Water Science & Technology*, **49**, (10), PP. 31–40.

Onyeche, T.I., Schlaefer, O., Schroeder, C., Bormann, H and Sievers, M. (2001) Ultrasonic cell disruption of stabilised sludge with subsequent anaerobic digestion, *Proceedings. 9th World Congress, Anaerobic Conversion for Sustainability*.

OTV. (1997) Treat and to valorise sludge (in french), *Ouvrage collectif n°2*, *Editions Lavoisier, Cachan*.

Pelczar, M.J.Jr., Chan, E.C.S. and Krieg, N.R. (1993) Microbiology: Concept and Application, *McGraw-Hill, Inc.* (International Edition).

Park, K.Y., Ahn, K.H., Maeng, S.K., Hwang, J.H. and Kwon, J.H. (2003) Feasibility of Sludge Ozonation for Stabilization and Conditioning, *Ozone: Science & Engineering,* **25,** (1), PP. 73-80.

Park, C. and Novak, J.T. (2007) Characterization of activated sludge exocellular polymers using several cation-associated ectraction methods, *Jornal of water research*, **41,** PP. 1679-1688.

Paul, E., Rols, J. L. and Debellefontaine, H. (1999) Perspectives de recherche et d'innovation pour une réduction de la production des boues urbaines, *Journée technique : station d'épuration comment maîtriser à la source la qualité et la quantité des boues, INSA, Toulouse (France),* 29 avril 1999.

Paul, E. and Buffière, P. (2001) Procédé d'épuration biologique des eaux résiduaires en cultures mixtes, *Brevet Institut National de la propriété industrielle, France.*

Paul, E. and Salhi, M. (2003) Reduction of excess sludge production: an evaluation of combined processes, *Proc. IWA Leading Edge Conference Series*, Noordwijk, The Netherlands, 26–28 May 2003.

Paul, E., Camacho, P., Spérandio, M. et Ginestet, P. (2005) Technical and economical evaluation of a thermal, and two oxidative techniques for the reduction of excess sludge production, *1st International Conference on Engineering for Waste Treatment*, *Albi (France),* 17 - 19 May 2005.

Paul, E. Camacho, P. Lefebvre, D. and Ginestet, P. (2006) Organic matter release in low temperature thermal treatment of biological sludge for reduction of excess sludge production, *Water Science & Technology, IWA Publishing*, **54,** (5), PP. 59–68.

Pérez-Elvira, S. I., Nieto Diez P. and Fdz-Polanco F. (2006) Sludge minimisation technologies, *Reviews in Environmental Science and Bio-Technology,* **5,** PP. 375–398.

Petrier, C., Jiang, Y. and Lamy, M. (1998) Ultrasound and environment: sonochemical destruction of chloromatic derivatives, *Journal of Environmental Science Technology,* **32,** PP.1316–1318.

Pinnekamp, J. (1989) Effects of thermal pre-treatment of sewage sludge on anaerobic digestion, *Water Science & Technology*, **21**, (4–5), PP. 97–108.

Pirt, S.J. (1965) The maintenance energy of bacteria in growing cultures, *Proc. R. Soc. London,* B 163, PP. 224–231.

Prechtl, S., Scheneider, R., Bischof, F. and Faulstich, M. (2001) Digestion of waste water after pre-treatment by the process of thermal pressure hydrolysis, *Proceedings, 9th World Congress, Anaerobic Conversion for Sustainability*.

Rai, C.L., Struenkmann, G., Mueller, J., and Rao, P.G. (2004) Influence of ultrasonic disintegration on sludge growth and its estimation by respirometry, *Envron. Sci. Technol*. 38, PP. 5779–5785.

Rajan, R.V., Lin, J.G. and Ray, B.T. (1989) Low-level chemical pre-treatment for enhanced sludge solubilization, *Journal Water Pollution Control Federation,* **61,** (11-12), PP. 1678–1683.

Ray, B.T., Lin, J. and Rajan, R.V. (1990) Low-Level Alkaline Solubilization for Enhanced Anaerobic Digestion, *Journal Water Pollution Control Federation,* **62,** PP. 81-87.

Ried, A., Stapel, H., Koll, R., Schettlinger, M., Wemhöner, F., Hamann-Steinmeier, A., Miethe, M. and Brombach, A. (2002) Optimierungsmöglichkeiten beim Betrieb von biologischen Kläranlagen durch den Einsatz von Ozon, *Korrespondenz Abwasser*, **49,** (5), PP. 648–661.

Rivard, C.J. and Nagle, N.J. (1996) Pre-treatment technology for the beneficial biological reuse of municipal sewage sludges. *Applied Biochemistry and Biotechnology*, **57-58**, PP. 983–991.

Rocher, M., Goma, G., Begue, A.P., Louvel, L. and Rols, J.L. (1999) Towards a reduction in excess sludge production in activated sludge processes: biomass physicochemical treatment and biodegradation, *Applied Microbiology and Biotechnology,* **51**, PP. 883–890.

Rooksby, F. (2001) Ultrasound for enhancement of sludge digestion, *In: Proceedings of the joint CIWEM and Aqua Environmental Technology Transfer, 6th European Bio-solids and Organic Residuals Conference. Wakefield, UK,* **34,** (6).

Roxburgh, R., Sieger, R., Johnson, B., Rabinowitz, B., Goodwin, S., Crawford, G. and Daigger, G. (2006) Sludge minimization technologies – Doing more to get less, *Copyright © 2006 Water Environment Foundation. All Rights Reserved – Canada.*

Sakai, Y., Fukase, T., Yasui, H. and Shibata, M. (1997) An activated sludge process without excess sludge production, *Water Science and Technology,* **36, (**11**),** PP. 163–170.

Saktaywin, W., Tsuno, H., Nagare, H., Soyama, T. and Weerapak, J. (2005) Advanced sewage treatment process with excess sludge reduction and phosphorus recovery. *Water Research*, **39,** (5), PP. 902–910.

Salhi, M. (2003) Combined process (activated/ozonation) for the reduction of excess sludge production: mechanisms of ozone action and process integration in the water treatment chain, *PhD Thesis*, *Génie des procédés de l'environnement, Institut National des Sciences Appliquées de Toulouse*, *France*, 360 p.

Salhi, M., Déléris, D., Debellefontaine, H., Ginestet, P. and Paul, E. (2003) More insights into the understanding of reduction of excess sludge production by ozone, *In Proc. of the IWA*

International Conference on BIOSOLIDS, Wastewater Sludge as a Resource, 23–25 June, Trondheim, Norway.

Saroj, D.P., Kumar, A., Bose, P., Tare, V. and Dhopavkar, Y. (2005) Mineralization of some natural refractory organic compounds by biodegradation and ozonation, *Water Research,* **39,** PP. 1921–1933.

Salsabil, M. R., Prorot, A., Casellas, M. and Dagot, c. (2008) Pre-treatment of activated sludges: effect of sonication on aerobic and anaerobic digestibility, *Chemical Engineering Journal, in press.*

Sawyer. Clair. N., McCarty. Perry. L. and Parkin. Gene. F. (2002) Chemistry for environmental engineering and science, *Published by McGraw-Hill professional, fifth edition.*

Scheminski, A., Krull, R. and Hempel, D.C. (1999) Oxidative treatment of digested sewage sludge with ozone, *IAQW specialised conference on disposal and utilisation of sewage sludge: Treatment methods and application modalities, Athens, Greece,* PP. 241–248.

Scheminski, A., Krull, R. and Hempel, D. C. (2000) Oxidative treatment of digested sewage sludge with ozone, *Water Science & Technology*, **42,** (9), PP. 151-158.

Schmitz, U., Berger, C.R. and Orth, H. (2000) Protein analysis as a simple method for the quantitative assessment of sewage sludge disintegration, *Water Research,* **34**, PP. 3682–3685.

Schneider, D., Nickel, K., Tiehm, A. and Neis, U. (1998) Klärschlammreduzierung mittels Ultraschall, *ATV-Schriftenreihe Abwasser, Abfall, Gewässerschutz*, **12**, PP. 541–556.

Sievers, M. and Schaefer, S. (2007) The impact of sequential ozonation – aerobic treatment on the enhancement of sludge dewaterability, *Water Science & Technology,* **55,** (12), PP. 201–205 *Q* IWA Publishing.

Skiadas, I.V., Gavala, H.N., Lu, J. and Ahring, B.K. (2004) Thermal pre-treatment of primary and secondary sludge at 70°C prior to anaerobic digestion*, in: Proceedings of the 10th World Congress, vol. 2, Anaerobic Digestion 2004: Anaerobic Bioconversion,. Answer for Sustainability, Montreal, Canada.*

Spellman Frank. R. (1996) Wastewater bio-solids to compost, *Published by CRC press.*

Spellman, Frank. R. (2000) Spelman's standard handbook for wastewater operators, *Published by CRC press, advanced level, volume III.*

Spinosa, L. (2001) Evolution of sewage sludge regulations in Europe, *Water Science and Technology,* **44,** (10), PP.1-8.

Stephenson, R.J. and Dhaliwal, H. (2000) Method of liquefying micro-organisms derived from wastewater treatment processes, *US Patent* No 6.013.183.

Stephenson, R.J., Laliberte, S. and Elson, P. (2004) Use of a high-pressure homogenizer to pre-treat municipal bio-solids: introducing the Micro-Sludge TM process, *Proceedings, 10th World Congress Montréal, Canada.*

Stuckey, D.C. and Mc Carty, P.L. (1979) Thermo-chemical pre-treatment of nitrogenous materials to increase methane yield, *Biotechnol. Bioeng. Symp*, **8**, PP. 219–233.

Stuckey, D.C. and Mc Carty, P.L. (1984) The Effect of Thermal Pre-treatment on the Anaerobic Biodegradability and Toxicity of waste Activated Sludge, *water Research,* **18,** PP. 1343-1353.

Tanaka, S., Kobayashi, T., Kamiyama, K.I. and Bildan, L.N.S. (1997) Effects of thermo-chemical pre-treatment on the anaerobic digestion of waste activated sludge, *Water Science & Technology*, **35,** (8), PP. 209–215.

Theodore, Onyeche and Sven Schäfer (2003) Sludge homogenisation as a means to reduce sludge volume and increase energy production, *Ejeafche* ISSN: 1579–4377, Volume **2,** (Issue 2).

Thomas, A.H. (1950) Graphical determination of BOD curve constants. *Water Sewage Works*, **97**, PP. 123–124.

Thomas, L., Jungschaffer, G. and Sprössler, B. (1993) Improved sludge dewatering by enzymatic treatment, *Water Science & Technology*, **28,** (1), PP. 189–192.

Tiehm, A. (2001) Combination of ultrasonic and biological pollutant degradation, In: Mason, T.J. and Tiehm A. (eds) *Ultrasound in Environmental Protection*, *advances in sonochemistry,* JAI press – Elsevier Sci., **vol. 6**, PP. 25-58. In Press Inc.

Tiehm, A., Kohnagel, I. and Neis, U. (2001-a) Removal of chlorinated pollutants by a combination of ultrasound and biodegradation, *Journal of Water Science and Technology,* **43,** (2), PP. 297-303.

Trably, E. (2002) Etude et optimisation de la biodégradation d'Hydrocarbures Aromatiques Polycycliques (HAPs) et de Polychlorobiphényls (PCBs) au cours de la digestion anaérobie et aérobie de boues urbaines contaminées, *Génie des procédés, Université Montpellier II,* Montpellier, 280 p.

Tsai, S.P. and Lee, Y.H. (1990) A model for energy sufficient culture growth, *Journal of Biotechnology & Bioengineering,* **35,** PP.138–145.

Tsukamoto, I., Constantinoiu, E., Furuta, M., Nishimura, R. and Maeda, Y. (2004) Inactivation effect of sonication and chlorination on Saccharomyces cerevisiae. Calorimetric Analysis, *Ultrasonics Sonochemistry,* **11,** (3-4), PP. 167-172.

Turovskiy, Izrail, S. and Mathai, P.K. (2006) Wastewater sludge processing, *Published by John Wiley and Sons*, *Inc.*

Valo, A., Carrère, H. and Delgenès, J.P. (2004) Thermal, chemical and thermo-chemical pre-treatment of waste activated sludge for anaerobic digestion, *Journal of Chemical Technology and Biotechnology,* 79, PP. 1197–1203.

Van Leeuwen, J. (1992) A review of the potential application non-specific activated sludge bulking control, *Water SA,* **18,** PP. 101-105.

Van Lier, J. B., Tilche, A., Ahring, B. K., Macarie, H., Moletta, R., Dohanyos, M., Hulshoff Pol, L. W., Lens, P. and Verstraete, W. (2001) New perspectives in anaerobic digestion, *Water Science and Technology,* **43,** (1), PP. 1-18.

Vesilind, P. Aarne. (2003) Wastewater treatment plant design, *IWA publishing, by Water Environment Federation.*

Wang, W., Hiraoka, M., Takeda, N., Sakai, S., Goto, N. and Okajima, S. (1988) Solubilization of sludge solids in thermal pre-treatment for anaerobic digestion. *Proc. of environmental, and Sanience. Engineering Research,* **24,** PP. 41–54.

Wang, W., Noguchi, C., Hara, Y., Sharon, C., Kakimoto, K. and Kato, Y. (1997) Studies on anaerobic digestion mechanism: Influence of pre-treatment temperature on biodegradation of waste activated sludge, *Environmental Technology,* **18,** PP. 999–1008.

Wang, J., Huang, C.P., Allen, H.E., Poesponegoro, I., Poesponegoro, H., Takiyama, L.R. (1999) Effects of dissolved organic matter and ph on heavy metal uptake by sludge particulates exemplified by copper (ii) and nickel (ii): three-variable model, *Water Environment Research,* **71** (2), PP. 139-147.

Wang, F., Wang, Y. and Ji, M. (2005) Mechanisms and kinetics models for ultrasonic waste activated sludge disintegration, *Journal of Hazardous Materials*, **B123,** and PP. 145–150.

Wang, X., Wang, L., Liu, Y. and Duan, W. (2007) Ozonation pre-treatment for ultra-filtration of the secondary effluent, *Journal of Membrane Science,* 287, PP. 187–191.

Weemaes, M.P.J. and Verstraete, W.H. (1998) Evaluation of current wet sludge disintegration techniques, *Journal of Chemical Technology and Biotechnology,* **73**, (8), PP. 83-92.

Weemaes, M., Grootaerd, H., Simoens, F. and Verstraete, W. (2000) Anaerobic digestion of ozonized bio-solids, *Water Research,* **34,** (8), PP. 2330-2336.

Wei, Y., Van. Houten, R.T., Borger, A.R., Eikelboom, D.H. and Fan, Y. (2003) Minimization of excess sludge production for biological wastewater treatment, *Journal of Water Research*, **37**, (18), PP. 4453–4467.

Weisz, N., Kepp, U., Norli, M., Panter, K. and Solheim, O.E. (2000) Sludge disintegration with thermal hydrolysis–cases from Norway, Denmark and United Kingdom, *1'st IWA World Congress, Paris 3–7 July. Pre-prints,* Book 4: 288–295.

Winter, A. (2002) Minimisation of costs by using disintegration at a full-scale anaerobic digestion plant, *Water Science & Technology,* **46,** (4–5), PP. 405–412.

Winter, A. and Müller, J. A. (2002) Comparison of disintegration methods at a full-scale anaerobic digestion plant, *VII Latin American workshop and symposium on anaerobic digestion,* Merida, Yucatan (Mexico), October 2002.

Yasui, H. and Shibata, M. (1994) An innovative approach to reduce excess sludge production in the activated sludge process, *Water Science and Technology,* **30,** PP. 11–20.

Yasui, H., Nakamura, K., Sakuma, S., Iwasaki, M. and Sakai, Y. (1996) A full-scale operation of a novel activated sludge process without excess sludge production, *Water Science and Technology,* **34,** (3–4), PP. 395–404.

Yavich, A.A., Lee, K.H., Chen, K.C., Pape, L. and Masten, S.J. (2004) Evaluation of biodegradability of NOM after ozonation, *Water Research,* **38,** PP. 2839–2846.

Yeom, I.T., Lee, K.R., Lee, Y.H., Ahn, K.H. and Lee, S.H. (2002) Effects of ozone treatment on the biodegradability of sludge from municipal wastewater treatment plants, *Water Science and Technology,* **46,** (4-5), PP. 421–425.

Yin, X., Han, P., Lu, X. and Wang, Y. (2004) A review on the dewater-ability of bio-sludge and ultrasound pre-treatment. *Ultrasonic Sonochemistry,* **11,** PP. 337–348.

Yoon, S., Kimb, H. and Lee, S. (2004) Incorporation of ultrasonic cell disintegration into a membrane bioreactor for zero sludge production, Process Biochemistry, **39,** PP. 1923–1929.

Yu, G.H., He, P.J., Shao, L.M. and Zhu, Y.S. (2008) Extra-cellular proteins, polysaccharides and enzymes impact on sludge aerobic digestion after ultrasonic pre-treatment, *Journal of water research,* **42,** (8-9), PP. 1925-1934.

Zhang, P., Zhang, G. and Wang, W. (2007-a) Ultrasonic treatment of biological sludge: Floc disintegration, cell lysis and inactivation, *Bioresource Technology,* **98,** PP. 207-210.

Zhang G., Zhang P., Yang J. and Chena Y. (2007-b) Ultrasonic reduction of excess sludge from the activated sludge system, *Journal of Hazardous Materials,* **145,** PP. 515–519.

Zhao, Q.L. and Kugel, G. (1997) Thermophilic/mesophilic digestion of sewage sludge and organic waste, *Journal of the Environmental Science Health,* **31**, PP. 2211-2231.

Zhao, Y.X., Yin, J., Yu, H.L., Han, N. and Tian, F.J. (2007) Observations on ozone treatment of excess sludge, *Water Science & Technology,* **56,** (9), PP. 167–175.

Appendix

1) List of publications

Salsabil, M.R., Prorot, A., Casellas, M. and Dagot, C. (2008). Pre-treatment of activated sludges: effect of sonication on aerobic and anaerobic digestibility, *Chemical Engineering Journal, In Press, Accepted Manuscript*, Available online 11 September 2008.

Salsabil, M.R., Casellas, M., Dagot, C. and Baudu, M. (2007). Effect of ultrasonic and thermal treatment on sludge solubilization by biological digestion methods, *7th International Congress of GRUTTEE on Behavior of Pollutions and Water Treatments*, 29 - 31 October 2007, Pau, France.

Salsabil, M.R., Prorot, A., Casellas, M., Dagot, C. and Baudu, M. (2007). Effect of ultrasonic on sludge solubilization by biological digestion methods and flow cytometry, *Recent progress in process engineering journal,* Number 96, 2007, SFGP (French Society of Process Engineering), Paris, France.

Salsabil, M.R., Dagot, C. and Baudu, M. (2006). Effect of ultrasonic on sludge solubilization by biological digestion methods, *the 9th national congress on environmental health,* 7-9 November 2006, Isfahan, Iran.

Dagot, C., Prorot, A., Salsabil, M.R. and Loprat, P. (2006). Characterization of the microbial activity within the framework of the minimiozation of excess sludge production. *Fondation de l'eau de Gdansk: disintegration of municipal sludge,* Gdansk, Pologne.

2) List of Equations

Rate of change of biodegradable volatile solids = $\frac{dM}{dt} = -k_d M$ *Eq.1*

Specific energy = SE = $\frac{P_{(W)} \times t_{(Sec)}}{C_{(g/l)} \times V_{(L)}}$ (kJ.kg^{-1}-TSS) *Eq.2*

Mass of ozone = $M_{O3} = \frac{N \times (V_2 - V_1) \times X}{V_S \times C}$ (gO_3/g-TSS) *Eq.3*

Degree of Disintegration = $DD_{COD} = \frac{COD_S - COD_{S0}}{COD_{S-NaOH} - COD_{S0}} \times 100$ (%) *Eq.4*

Solubilization of X = $S_X = \frac{X_S - X_{S0}}{X_{P0}} \times 100$ (%) *Eq.5*

Solubilization of TSS = $S_{TSS} = \frac{TSS_0 - TSS}{TSS_0}$ (%) *Eq.6*

VS solubilization = $S_{VS} = \frac{VS_0 - VS}{VS_0}$ (%) *Eq.7*

Removal efficiency = (Re) = $\frac{C_{t_0} - C_{t_f}}{C_{t_0}} \times 100$ (%) *Eq.8*

COD uptake rate = $r_{COD} = \frac{\Delta COD_{t_1 t_2}}{t_2 - t_1}$ (mg O_2.L^{-1}.d^{-1}) *Eq.9*

Biogas production rate = $r_{Biogas} = \frac{\Delta V\ biogas_{t_1 t_2}}{t_2 - t_1}$ (mL BG.d^{-1}) *Eq.10*

Specific soluble COD uptake rate = $q_{COD} = \frac{r_{COD}}{\frac{VSS_{t_1} + VSS_{t_2}}{2}}$ (mg COD_S.g-VSS^{-1}.d^{-1}) *Eq.11*

Specific Biogas production rate = $q_{biogas} = \frac{r_{Biogas}}{\frac{VSS_{t_1} + VSS_{t_2}}{2}}$ (mL BG.g-VSS^{-1}.d^{-1}) *Eq.12*

Yields of biogas = $Y = \frac{V\ Biogas}{(COD_{S\ t_0} - COD_{S\ t_f}) \times V_{reactor}}$ (mL BG.g-COD_S^{-1}) *Eq.13*

Rate of apparatus energy = $E_S = p_{(W)} \times t_{(sec)}$ (kJ) *Eq.14*

Total energy of aerobic digestion = $E_T = E_S + E_A$ (kJ) *Eq.15*

Total energy of anaerobic digestion = $E_T = E_S + E_{Ag} + E_H - E_{CH\,4}$ (kJ) *Eq.16*

Total solids = TS = $\frac{(W_2 - W_1) \times 1000}{V_{sample}}$ (g-TS.L^{-1}) *Eq.17*

Volatile solids = VS = $\frac{(W_2 - W_3) \times 1000}{V_{sample}}$ (g-VS.L^{-1}) *Eq.18*