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Optimisation d'un réacteur biologique séquentiel à lit fluidisé pour le traitment des eaux

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List of abbreviations

A2O: Anaerobic-Anoxic-Oxidation process
ANAMMOX: ANaerobic AMMonium OXidation
AO: Anaerobic-Oxidation process
AOB: Ammonia Oxidizing Bacteria.
ASBR: Anaerobic Sequence Batch Reactor
BASE: Biofilm Airlift Suspension-Extension
BOD5: 5 days Biochemical Oxygen Demand
BSBR: memBrane SBR
C/N: Carbon Nitrogen ratio
C/P: Carbon Phosphorus ration
CANON: Completely Autotrophic Nitrogen removal Over Nitrite.
CASS (-CAST -CASP): Cyclic Activated Sludge System or -Technology or -Process
CFBB: Circulating Fluidized Bed Bioreactor
COD: Chemical Oxygen Demand
CSTR: Continuous Stirred Tank Reactor.
DATIAT: Demand Aeration Tank and Intermittent Aeration Tank,
DHS: Down-flow Hanging Sponge
DO: Dissolved Oxygen
DPB: Denitrifying Phosphorus removing Bacteria
EBPR: Enhanced Biological Phosphorus Removal.
EFBBR: Extra-loop Fluidized Bed BioReactor,
EPA: American Environmental Protection bureau,
EPS: ExoPolySaccharides
FA: Free Ammonia
FBBNR and FBBDR: Fluidized-Bed Biofilm Nitritation and Denitritation Reactors
FBBR: Fluidized Bed BioReactor
FBR: Fluidized Bed Reactor
GAC: Granular Activated Carbon
GAC-BFB: Granular Activated Carbon Biological Fluidized Bed
HRT: Hydraulic Resident Time
ICEAS: Intermittent Cycle Extended aeration System
IDEA: Intermittent Decanted Extended Aeration
MLE: Modified Ludzack-Ettinger
MLVSS: Mixed Liquor Volatile Suspended Solids
MSBR: Modified Sequencing Batch Reactor
MLSS: Mixed Liquor Suspended Solids
NH_4-N: Ammonia
NO_2-N: Nitrite
NO_3-N: Nitrate
NOB: Nitrite Oxidizing Bacteria
NOx-N: Nitrite + Nitrate
OLAND: Oxygen-Limited Autotrophic Nitrification and Denitrification system
OLR: Organic Loading Rate
ORP: Oxidation-Reduction Potential
OUR: Oxygen Uptake Rate
P: Phosphorus
PAC: Powder Activated Carbon
PAOs: Phosphate Accumulating Organisms
PE: PolyEthylene
PFR: Plug Flow Reactor
PHA: Poly-β-HydroxyAlkanoate
PHB: PolyHydroxyButyrate
PHV: PolyHydroxyValerate
PN: ProteiNs
PP: PolyPropylene
PO_4-P: Phosphate
PS: PolyStyrene
PVC: PolyVinylChloride
RBC: Rotating Biological Contractor
SBR: Sequencing Batch Reactor
SCOD: Soluble Chemical Oxygen Demand
SHARON: Single reactor for High Ammonium Removal Over Nitrite
SND: Simultaneous Nitrification and Denitrification
SS-SBR: Soil Sludge SBR
TBC/TBA: Turbulent Bed Contactor/Absorber.
TKN: Total Kjeldahl Nitrogen
TN: Total Nitrogen
TOC: Total Organic Carbon
TP: Total Phosphorus
UCT: University of Cape Town
UNITANK: alternative biological treatment (UNited TANK)
WWTPs: WasteWater Treatment Plants

Nomenclature

$\frac{D}{UL}$: discrete number
A: biofilm surface area, m^2
C:* dimensionless concentration
C: concentration (such as oxygen, reactor, etc…)
C_0: original concentration of the reactor (V)
C_n: concentration of the n^{th} reactor (V)
Cs: saturation concentration of DO (mg/L)
D: diffusion coefficient
D: dilution coefficient, D=F/V, h^{-1}
D_f: diffusion coefficient, m^2/h
d_{intc}: interieur diametre of particle support (m)
dS/dt: consume rate of the substrate, mg/L h
d_s: diameter of the solid (m)
Ds: diffusivity of substance S in biofilm (m^2/h)
dX_a/dt: consume rate of the suspended microorganism, mg/L h
dX_b/dt: consume rate of the cohered microorganism, mg/L h
F: flow velocity, m^3/h
G(W): decreasing function of carrier surface occupancy percentage
g: acceleration of gravity (m^2/s)
h: hauteur of particle support (m)
K: maximum rate of substance (kg of S kg VSS.h)
K_0: coefficient of Monod for oxygen (kg/m^3)
k_a: decay rate of the suspended microorganism, h^{-1}
k_A: rate coefficient with the area, m/d
K_b: ammonia dissociation constant
k_b: decay rate of the cohered microorganism, h^{-1}
K_i: coefficient of inhibition (kg/m^3)
K_{La}: transfer coefficient (s^{-1}).
k_s: coefficient of liquid transfer solid (m/s)
K_s: coefficient of Monod (kg/m^3)
k_{sa}: saturation coefficient of the suspended microorganism, mg/L
k_{sb}: saturation coefficient of the cohered microorganism, mg/L
k_{vf}: first-order reaction constant, h^{-1}
K_w: water ionization constant
L: length element, m
M_c: mass of particles in reactor (kg)
N: number of particles in reactor
n: serial number
Q_c: Circulation flow (m^3/s)
Q_g: inspratory capacity (gas) (L/h)
R: radial distance since the center of bioparticle (m)
r: reaction rate
r_A: reaction rate per unit time and unit biofilm area, g/m^2 h;
Re: Reynolds number according to the theory of the turbulence of Kolmogorov (used for the columns of transfer)
r_p: radii of bioparticule (m)
r_s: radii of particle support (m)
S: concentration of substance
$S=S_a+S_b$: relation to the concentration of the activated sludge and biofilm, mg/L
S_0: concentration of substance S in solution ($kg\ COD/m^3$)
S_1,: area of the circle pipe, (m^2)
S_2: Area of Venturi aero-ejector pipe
S_c: Schmidt number
Sh: Sherwood number
t: average mixing time (s)
U: average velocity of the flow (m/s)
u_1: liquid velocity in the circle pipe (m/s)
u_g: speed of gas (m/s)
u_t: terminal velocity of the particles
V: reactor volume, m^3
v: viscosity of the liquid (m^2/s)
V_0: approach velocity
V_B: volume of bed particles per unit of cross-section, m
V_{bio}: volume of biofilm (m^3)
Vc: volume of particle support (m^3)
V_{om}: minimum fluidization velocity
Vr: volume of reactor (m^3)
W: cohered microorganism occupancy percentage on carrier
X: concentration of fixed biomass (kg/m^3 reactor)
X_a: suspended microorganism concentration in reactor, mg/L
X_b: cohered microorganism concentration on carrier, mg/dm^3
X_{bm}: maximum cohered microorganism concentration on carrier, mg/dm^3
X_s: concentration of bacteria using S ($kg\ MLVSS/m^3$)
Y: fraction of fixed biomass (mg biofilm/ g PVC)
Y_a: yield coefficient of the suspended microorganism
Y_b: yield coefficient of the cohered microorganism
$Y_{xs/s}$: output of use of substrate for the bacteria using S (kg MLVSS/kg COD)
Z:* dimensionless length
ΔP: pressure drop of the Venturi aero-ejector (pa)
ΔP: unrecoverable pressure-loss, N/m^2
ΔP_B: unrecoverable pressure-loss across entire bed, N/m^2

Greek letter

α: adhere rate of the suspended microorganism, h^{-1}
β: fall off rate of the cohered microorganism, h^{-1}
φ : random variable
σ_φ^2 : random variance
θ: residence time of each reactor (s)
δ: biofilm thickness (m)
ρ_c: mass volume of particle support (kg/m^3)
μ_{ma}: maximum specific consume rate of the suspended microorganism, h^{-1}
μ_{mb}: maximum specific consume rate of the cohered microorganism, h^{-1}
$\mu_{S.max}$: maximum growth rate of bacterium using S
ε: void fraction
ε_G: fraction voluminal of gas in reactor
ρ: liquid density (kg/m^3)
ρ: density dries of biofilm (kg/m^3)
ρ_f: fluid density, kg/m^3
ρ_p: particle density, kg/m^3

Contents

Introduction générale

Depuis de très nombreuses années, le traitement biologique des eaux usées, c'est-à-dire la réduction de la pollution carbonée contenue dans les eaux, par le procédé à "boues activées" constitue l'approche la plus répandue en France et dans de nombreux pays. Bien que cette typologie de procédés permette avec quelques aménagements, de transformer également l'azote par nitrification, ils ont pour conséquence d'entraîner des niveaux de rejet importants en nitrates ou nitrites. Les taux d'élimination du phosphore par voie biologique sont également faibles. Ces rejets chargés en éléments nutritifs peuvent engendrer des problèmes d'eutrophisation du milieu récepteur. Il apparaît donc nécessaire de développer des équipements compacts pour le traitement avancé des eaux résiduaires mais également d'améliorer le parc existant afin de traiter la pollution azotée et phosphorée.

Parmi les techniques biologiques disponibles, réacteurs à membrane, lits filtrants, biodisques, le bioréacteur à lit fluidisé (FBBR) apparaît comme un procédé intéressant au regard de son hydrodynamique et du transfert de masse; la fluidification est préconisée en biotechnologie pour améliorer le contact entre phases et de plus en plus de procédés utilisent cette technologie.

Le mode de conduite est également un paramètre important pour l'amélioration des performances épuratoires des stations de traitement. Avec le développement de la régulation et du contrôle automatique des procédés, les procédés séquentiels discontinus (SBR) sont plus largement utilisés en traitement des eaux, notamment pour des rejets en faible quantité ou sporadiques. Les avantages du SBR sont de plus en plus pris en considération. Ainsi les FBBR combinent alimentation séquentielle et fluidisation.

Dans les FBBR, les avantages des boues activées sont combinés à ceux des biofilms et chacune des biomasses peut jouer son propre rôle. Par exemple, la biomasse libre peut traiter le phophore par déphosphatation biologique tandis que la partie biofilm peut intervenir dans la dénitrification. Ainsi dans un même réacteur, déphosphatation et dénitrification peuvent être simultanées

La présente étude a pour objet le développement d'un bioréacteur séquentiel à lit fluidisé travaillant en boucle (EFBBR). Le réacteur est composé d'une part d'un réacteur de 38 litres tubulaire constitué d'une zone ascendante de fluidisation et d'une zone de décantation, la circulation du fluide étant assurée, par une conduite de mise en circulation.

Un travail d'optimisation sur le fonctionnement du réacteur est présenté de manière à éliminer le carbone, l'azote et le phosphore. L'étude est réalisée sur des eaux synthétiques puis des eaux usées prétraitées.

La première partie du manuscrit est consacrée à une revue bibliographique sur les 4 aspects essentiels du procédé que nous avons développé :

- La mise en œuvre de lits fluidisés dans les réacteurs biologiques
- Les réacteurs à fonctionnement discontinu séquentiels (SBR)
- Les biofilms dans les réacteurs biologiques
- Les conditions biologiques à mettre en œuvre pour l'élimination de l'azote et du phosphore

Le second chapitre se propose de rapporter les résultats dans 5 parties. Les 4 premières sont construites sous la forme de publications à soumettre et la dernière présente quelques éléments sur la modélisation de nos résultats sur les phases aérobie et anoxie.

De nos jours, la conception des réacteurs peut être ajustée du point de vue mécanique pour un meilleur mélange et une conception optimisée. De nouvelles configurations de réacteurs sont proposées sur des bases d'analyses de l'hydrodynamique de flux biphasiques ou triphasiques comme la vitesse de circulation du liquide ou le transfert gazeux dans le réacteur. Le temps de mélange est un paramètre particulièrement important pour la conception, la modélisation et l'exploitation. Le transfert d'oxygène est

un des paramètres les plus importants dans le fonctionnement de nombreux réacteurs biologiques. Ainsi, la première partie du travail proposé consiste a évaluer les effets des différentes phases sur l'hydrodynamique du réacteur avec en particulier l'influence de la nature du garnissage (pouzzolane, tube PVC), la vitesse du fluide et les effets du transfert de l'air par un système d'aéro-éjecteur du type venturi. Le transfert d'oxygène fait également l'objet d'une modélisation selon les conditions de fonctionnement.

Dans une seconde partie, les performances épuratoires du bioréacteur séquentiel à lit fluidisé (EFBBR) sont évaluées en fonction des conditions de fonctionnement : charge en entrée de réacteur, rapports C/N et C/P, température... Un garnissage constitué d'anneaux de PVC a été choisi et les résultats concernant l'élimination du carbone, de l'azote et du phosphore sont discutés. Les réactions de nitrification et dénitrification seront évaluées à partir de paramètres comme le concentration en ammoniaque, la température, le rapport C/N et le suivi des concentrations en NO_3-N et NO_2-N. La variation des rapports C/N, C/P et les effets de la température sur l'élimination du phosphore sont discutés.

Le bioréacteur étudié (EFBBR) est une combinaison de biomasse libre et de biofilm. La formation et le développement du biofilm sont des facteurs important pour la validation d'un réacteur à lit fluidisé. De nombreuses études relèvent des paramètres clés sur le développement du biofilm comme les caractéristiques et les concentrations dans l'effluent, le type de média, l'hydrodynamique du milieu, les conditions d'apport en nutriments,….Dans cette troisième partie la formation du biofilm pour des conditions opératoires variables est observée. Des méthodes simples sont utilisées pour la caractérisation du biofilm (épaisseur, production d'exopolyméres) et des corrélations avec les paramètres de fonctionnement sont recherchées.

L'accumulation de nitrites a parfois été observée dans les bioréacteurs séquentiels à lit fluidisé. Le phénomène est complexe et quelques facteurs peuvent influencer cette production comme le pH, la température, le taux d'oxygène dissous, la concentration en ammoniaque. Cette partie à pour objet d'approcher ce phénomène dans le cas de notre réacteur avec l'observation de l'influence des principaux paramètres et notamment l'influence de l'alternance de concentrations forte puis faible en oxygène dissous.

Il existe de nombreux travaux sur le fonctionnement et les mécanismes mis en jeux dans les réacteurs séquentiels discontinus. Cependant l'élaboration de modèle complet pour décrire les SBR reste un enjeu important de la recherche sur ce type de réacteur. Des modèles spécifiques aux cultures libres ou au biofilm sont très largement utilisés, la combinaison des deux types de biomasses dans un modèle est rarement proposée. Ainsi, dans une dernière partie nous avons cherché à adapter un modèle mathématique au fonctionnement de notre réacteur.

La synthèse des principaux résultats est proposée en conclusion générale.

Chapter I. Literature review

I.1 Preface

Nowadays organics (COD), nitrogen (such as ammonium NH_4-N) and phosphorus (P) removal are playing the more important role in wastewater treatment. Generally, the removal of COD and NH_4-N are treated by bio-oxidation and nitrification/denitrification, and phosphorus can be removed by the bacterial bio-enrichment or chemical precipitation. But the traditional process has some drawbacks include(Hao X.D. and van Loosdrecht M.C.M.,2003): energy consumption, COD requirement for denitrification and biological phosphorus removal, sludge production, no recovery of nutrients and emissions of CO_2 into the atmosphere.

Because the effluent standards have been tightened increasingly, COD become routinely and eutrophication is coped with widely as the goal. Nitrogen, phosphorus removal has become the various countries' main target. Without a doubt, deals with strictly the effluent standard, the traditional process can not be competent because of the above malpractices (van Loosdrecht M.C.M, et al., 1997).

The literature review was concerned to give a progress report on four necessary fields for the development and optimization of the process. The plan of this chapter follows the logic which enabled us to finalize the purification process (Figure 1.) and to establish the methodology study.

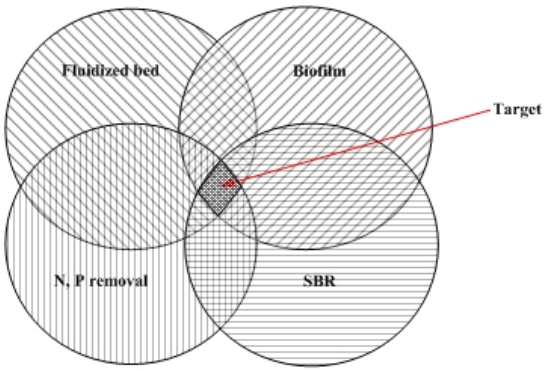


Figure 1. General diagram of literature review.

- Equipment:
  - fluidization principle,
  - developments of fluidized bed,
  - applications.
- Process:
  - performance characteristics of SBR,
  - developments,
  - applications.
- Microorganisms state:
  - biofilm formation,
  - mass transfer,
  - reactors developments.
  - applications.
- Factors:
  - principle of N, P removal,
  - conventional and novel process,
  - applications

I.2 The Principle and Application of Fluidized Bed

I.2.1 General Description

The fluidized bed reactor is one kind of reactor which carries on the mass transfer or heat transfer operation using the fluidization concept. The fluidized bed reactor has a history of several dozens of years. At first it was mainly used in the chemical synthesis and the petrochemistry industry, afterwards because this kind of reactor displayed in many aspects the unique superiority, caused its application scope enlarged gradually to metal smelting, the air purification and other many fields (Fan, L.S., 1989).

Since 1970's (Beer C.,1974), people have successfully applied the fluidization technology to the wastewater biochemical process field. The solid particle fluidization technology is a industrialization technology which developed since 20th century 40's, it can improve the contact between the solid particle and fluid, in reactor the heat transfer and mass transfer accelerated greatly. Due to the strenuous perturbation of air bubbles, the biological particle (biofilm on carrier), fluid (wastewater), gas (air in aerobic fluidized bed) three-phase can contact sufficiently in reactor. The particles provide the great accrete place for the microorganisms and the biomass enriched. Compared the pollutants removal efficiency it can be found that the biological fluidized bed is more significant than the conventional processing (Lu Y. S., 2001).

In 1980 the international academic conference whose subject of the application on the wastewater treatment using the fluidization technology was held in Manchester (Owens R. W.,1980), it is symbolized that the biological fluidized bed technology was obtained on people's universal approval. In USA'S Ann Arbor, Sutton P. M. (1990) and General Motors Company organized the international academic conference whose subject was the wastewater treatment using the fluidization technology. At this conference people considered identically that the granular activated carbon (GAC) as carrier in biological fluidized bed technology for wastewater contains the complex organics treatment was extremely effective. At present the massive research works in theories and practices of biological fluidized bed were launched.

I.2.2 Principle of Fluidization

1. Phenomenon of Fluidization

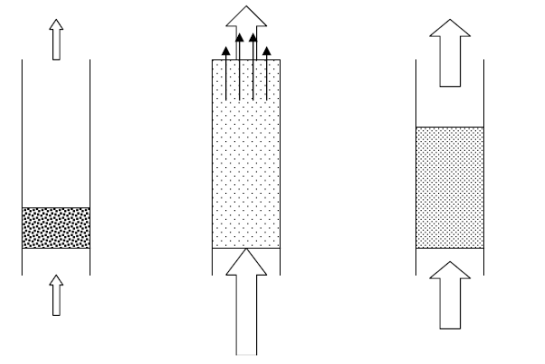
When a fluid is pumped upward through a bed of fine solid particles at a very low flow rate the fluid percolates through the void spaces (pores) without disturbing the bed. This is a fixed bed process.

If the upward flow rate is very large the bed mobilizes pneumatically and may be swept out of the process vessel. At an intermediate flow rate the bed expands and is in what we call an *expanded* state. In the fixed bed the particles are in direct contact with each other, supporting each other's weight. In the expanded bed the particles have a mean free distance between particles and the particles are supported by the drag force of the fluid. The expanded bed has some of the properties of a fluid and is also called a *fluidized* bed.

As shown in Figure 2., the velocity of the fluid through the bed opposite to the direction of gravity determines whether the bed is fixed, expanded, or is swept out. There is a minimum fluidization velocity V_{om}, at which the bed just begins to fluidize. When the approach velocity V_0 (otherwise known as the empty tank velocity, given by the fluid volumetric flow rate divided by the cross-sectional area of the vessel), is greater than or equal to the minimum fluidization velocity *and* it is less than the terminal velocity of the particles $V_{om} \leqslant V_o < u_t$ then the bed forms a fluidized bed. When $V_o < V_{om}$ then the bed remains as a fixed bed. At the other extreme, when $V_o \geqslant u_t$, the bed mobilizes.(http://chemical.uakron.edu/fclty/chase/Solids/solids.html)

2. Geldart Classification of Particles

Geldart (1973) observed the nature of particles fluidizing and categorized his observations by particle diameter versus the relative density difference between the fluid phase and the solid particles. He identified four regions in which the fluidization character can be distinctly defined. (see Figure 3.)



(a) Slow Flow Rate, Fixed Bed, $V_{Om} > V_O$

(b) High Flow Rate, Mobilized Bed, $u_t < V_O$

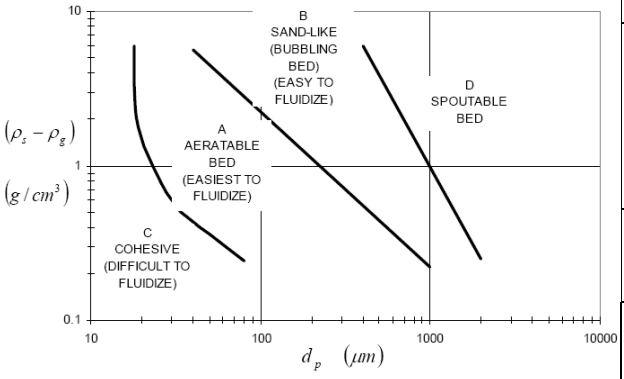
(c) Intermediate Flow Rate, Fixed Bed, $V_{Om} < V_O < u_t$

The fixed bed (a) occurs when the approach velocity, V_0, is much smaller than the minimized fluidization velocity, V_{om}.

The pneumatically mobilized bed (b) occurs when the approach velocity is much greater than the particle terminal velocity, u_t .

The expanded bed (c) occurs when the approach velocity is intermediate between the minimum fluidization velocity and the terminal velocity.

Figure 2. Fixed, mobilized and expanded beds



Group A particles are characterized by
- Bubbling bed fluidization,
- The bed expands considerably before bubbling occurs,
  - ◊ Gas bubbles rise more rapidly than the rest of the gas,
  - ◊ Bubbles spit and coalesce frequently through the bed,
  - ◊ Maximum bubble size is less than 10 cm,
  - ◊ Internal flow deflectors do not improve fluidization,
- Gross circulation of solids occurs.

Group B particle beds are the most common. These beds
- Are made of coarser particles than group A particles and more dense,
- Form bubbles as soon as the gas velocity exceeds V_{0m}
- Form small bubbles at the distributor which grow in size throughout the bed,
- Have bubble sizes independent of the particle size, and
- Have gross circulation.

Group C particles
- Are difficult to fluidize and tend to rise as a slug of solids,
- Form channels in large beds with no fluidization, and
- Tend to be cohesive.

Group D particles
- Are very large, dense particles,
- Form bubbles which coalesce rapidly and grow large,
- Form bubbles which rise slower than the rest of the gas phase,
- Form beds whose dense phase surrounding the bubbles has low voidage,
- Cause slugs to form in beds when the bubble size approaches the bed diameter, and
- Spout from the top of the bed easily.

Figure 3. Geldart classification of fluidized beds.

Particle properties are related to the type of fluidized beds. (Geldart, 1973).

3. The steady-state balance of forces for a fluidized suspension

Consider a control volume of unit cross-sectional area and height L in a fluidized bed (Gibilaro L.G., 2001). The only surfaces consider in the axial direction are provided at the two horizontal boundary across-sections by the fluid pressure; the net effect of these surface forces is to support the total weight of particles and fluid in the control volume:

$$\Delta P = P(z) - P(z+L) = (\varepsilon\rho_f + (1-\varepsilon)\rho_p)Lg \qquad (1)$$

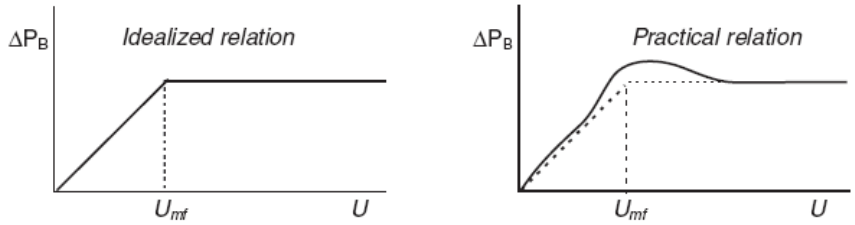


Figure 4. Unrecoverable pressure loss in a fluidized bed

The unrecoverable pressure loss, an indelible consequence of maintaining the particles in suspension, is thus:

$$\Delta p = \Delta p - \rho_f Lg = (\rho_p - \rho_f)(1-\varepsilon)Lg \qquad (2)$$

An important property of fluidized beds follows immediately from this simple relation. If we apply it to the whole bed, of height L_B, rather than just a fixed slice of height L, then the product $(1-\varepsilon)L_B$ represents the total volume VB of particles per unit cross-section, which remains unchanged as the bed expands: as the fluid flux is increased, L_B increases and (1-ε) decreases so as to maintain their product at a constant value. Thus the unrecoverable pressure loss ΔP_B for the whole bed becomes:

$$\Delta P_B = (\rho_p - \rho_f)V_B g = a \ \ constant \qquad (3)$$

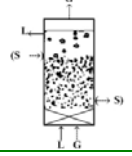
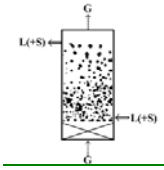
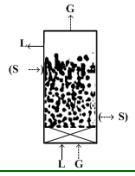
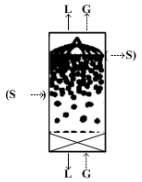
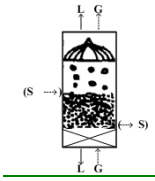
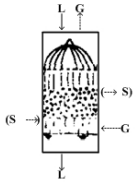
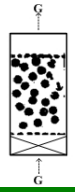
This well-known relation is illustrated in Figure 4.In practice, the transition between the fixed and fluidized states involves some particle rearrangement, with the breakdown of bridging structures, which are inherent in the initial packing and subsequent defluidization operations; rather than an abrupt change in slope at the minimum fluidization velocity, a more gradual approach to the constant ΔP_B is observed in practice, often with some overshoot in the transition region.

I.2.3 Equipment-description and Classification of Reactors

Three-phase fluidized bed bioreactors contain solid, liquid and gas phases. Either the gas or the liquid phase is continuous, sometimes with recycle of either phase. The purpose of the fluidized solid phase is to form a spontaneous support for oxidizing bacteria. Fan L. S. (1989) has defined various operational modes by use of a letter and numbering system. This provides clarity when discussing reactor configurations. The

broad classification system is presented in Table 1.

Table 1. Modes of gas/liquid/solid fluidization, expanded bed regimes (summarized from Fan L. S. 1989).

Mode designation	Continuous phase	Flow direction	Description
E-I-a-1 	liquid	cocurrent upflow	Solid charging and discharging is independent of the liquid flow (u_t>0.05 m/s). Particles usually uniformly distributed.
E-I-a-2 	liquid	cocurrent upflow	Solid charge and discharge usually liquid flowrate dependent (u_t<0.05 m/s). High particle concentration at bed base, gradually increasing with axial distance up the bed.
E-I-b 	gas	cocurrent upflow	Particle bed is supported by gas phase, and solid charge/discharge is gas flow independent.
E-II-a-1 	liquid	countercurrent flow	Inverse fluidized bed. Particle density is less than liquid density. Solid charge/discharge independent of either phase.
E-II-a-2 	liquid	countercurrent flow	If the solid density is greater than the liquid density then the bed is supported by upflowing gas bubbles. Solid charge/discharge independent of either phase. (can sometimes behave like TBC -see below)
E-II-b 	gas	countercurrent flow	Liquid density %-solid density, then gas phase supports solid phase, with trickling liquid. Sometimes known as turbulent bed contactor/absorber (TBC/TBA).
E-III-b 	liquid	gas upflow, liquid batch	Particle density >liquid density, bed is gas phase supported. Solid concentration is uniform at high velocity, and drops off exponentially with decreasing gas velocity.
E-III-a 	gas	gas upflow, liquid batch	Gas phase supported particles with a mist-like or liquid film. Solid concentration is uniform at high velocity, and drops off exponentially with decreasing gas velocity.

I.2.4 Characteristics of Biological Fluidized Bed Processes

The biological fluidized bed reactor uses the biofilm which covered on carrier surface and bring into play its function. Among these available different processes (such as: activated sludge process, trickling filters, biodisc, etc.) to create efficient contacts between phases, fluidized bed bioreactor (FBBR) seems to be the best one and present many advantages relating to hydrodynamics and mass transfer phenomena. The use of fluidization as a contact technique in biotechnology field gained considerable importance.

In biological fluidized bed, the small size particle provided the surface area where the microorganism can adhere, roost and grow greatly, and in reactor keeps high microorganism density, thus enhanced the reactor loading. Table 2. is given the spective surface areas of several kinds biofilm process (Wei C. H.. 1991).

Table 2. Relative surface area of the several biofilm area

process	Relative surface area (m^2/m^3)
Fluidized bed	3000~5000
Biofilter	40~120
Biodisc	120~180
Contacted oxidation	130~1000

The fluidization operating mode create the effective mass transfer condition in reactor, according to oxygen or mass transmission speed enhances obviously, the oxygen utilization is efficient as well. High biomass and significant mass transfer condition enable the biological fluidized bed to be possible to maintenance effect and reduce the reactor volume, consequently save the plant investment. Compared the activated sludge process, the biological fluidized bed has the strong anti-impact load capability, has does not the sludge expanded. Wei C. H. (1989) considered that the fluidized bed was with the great cubage loading (α) and sludge loading (β) which showed as Table 3. Obviously, its α is 13 times of conventional activated sludge system, 10 times of stage-aeration and 38 times of Biofilter.

Table 3. Values of α and β in different processes (Wei C. H. *et al*., 1998)

Process	α （$KgBOD_5/m^3.d$）	β （$kgBOD_5/Kg.vssd$）
Conventional activated sludge system	0.264~0.72	0.216-0.456
Stage-aeration system	0.36~1.272	0.192-0.36
Biofilter	0.090~0.36	
Three-phase fluidized bed	3.635~91.92	0.204-4.32

In order to prevent the carrier escape, generally in reactor supposes the buffer zone, and the biofilm which falls off may separate in buffer zone. When the loading is weak and the discharge standard of suspended solid density is not special, second settling pond should be omitted, and the process is simplified. As a result of the gas perturbation in three-phase fluidized bed, the biofilm renews quickly with high activeness, and the membrane escape equipment need not be installed as possibility.

So far, the biological fluidized bed was employed in organic wastewater treatment had approximately 30 years histories, and the varied structures were innovated. However, the numerous researchers are inconsistent to the classification of the biological fluidized bed. Several typical kinds are described as following:

1. Conventional Biological Fluidized Bed

A. Two-phase biological fluidized bed (Lu Y. S., 2001)

The typical two-phase fluidized beds are shown in Figure 5a,b, the fluidization power originates from the extra circulating pump, in fluidized bed the carrier pellets expand and the fluidization under the hydrodynamic function. Among them, Figure 5a is anaerobic fluidized bed, Figure 5b is aerobic fluidized bed, the aerobic process needs the wastewater which aerated outside, then feeds in fluidized bed. The merits of two-phase biological fluidized bed including: high handling capability, no jamming problem, strong anti-impact load capability, compact structure, etc.. But the disadvantages still existed: control difficultly for the expansion and biofilm thickness; in aerobic stage the high capability aerator is absolutely necessarily.

B. Three-phase biological fluidized bed (Lu Y. S., 2001)

The traditional three-phase biological fluidized bed can solve two-phase fluidized bed pre-aeration difficultly, reduce the energy consumption. Through the air

bubble perturbation, further strengthened between the liquid-solid mass transfer effect, and may control the biofilm thickness to a certain extent by hydrodynamic shearing force (see Figure 5c.)

2. Nevel Biological Fluidized Bed Reactor

Along with the wastewater process technology unceasing development, highly effective, the low consumption and treat to the organics waste water which degrade difficultly is one biological fluidized bed development direction. Introduces several kinds in the last few years appear new biological fluidized bed reactor as follow:

A. Circulation biological half fluidized bed

The Beijing chemical industry institute developed a novel half fluidized bed (see Figure 5d). The circulation biological half fluidized bed realized the fluidized bed and the fixed bed series operation, it not only had the good circulation characteristics, moreover overcame the difficulty of the low removal efficiency for degrade difficultly organics in mixing reaction. Treated with the starch wastewater, the hydraulic resident time (HRT) is shorter than 4h, COD load is 4.2kg/m^3d, the least liquid/gas rate is 37:1.

B. Oxygenation internal recycling three-phase compound biological fluidized bed

Based on the compound biological fluidized bed, the North China engineering institute chemical industry innovated the structure which is made up of three-phase fluidized bed at bottom, at top has safety filters and padding, the effluent through the oxygenation system, then enter the contacted oxygenation bed with further reaction. Composed concurrently with the fluidized bed and filter bed, the pilot is provided with small energy consumption, great compatibility, low liquid/gas rate, the application prospect will be widely.(see Figure 5e)

C. BASE three-phase biological fluidized bed reactor

Van Loosdrocht M.C.M. et al., (2000) displayed a new integrated airlift biological fluidized bed reactor BASE (Biofilm Airlift Suspension-Extension) (see Figure 5f). This kind of reactor was increased one catheter (anoxia area) in original BAS, obtained the enough resident time and created the anoxia condition, NH3-N

removal could be achieve effectively. Adjusted the barometric pressure of aerobic area and minor loop hole of aerobic-anoxic sector at the base which can be controlled the liquid and biofilm circulation in two sectors, therefore does not need add the pump and the circulate pipeline.

D. The new Circox airlift three-phase fluidized bed reactor

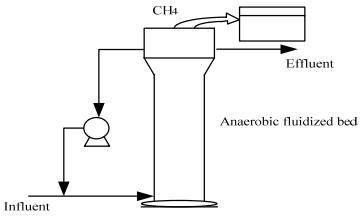
Frijters (2000) presented a Circox airlift fluidized bed reactor (see Figure 5g). This kind of fluidized bed was added one anaerobic area in traditional fluidized bed, the denitrifying ability was enhanced. Due to the reactor has the aeration and anaerobic area, the mixing uniformity and higher liquid speed can be obtained. The Circox airlift fluidized bed was used in potato wastewater anaerobic pretreatment, and COD removal rate was high, its volume loading may meet 4-10kg/ m^3d, the denitrify rate up to 90%, the biomass in bed achieved as high as 30g/L, the surplus sludge rate only has 2%-10%.

E. Internal-loop fluidized bed

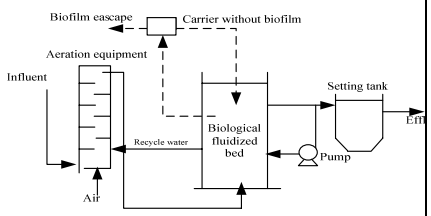
The reactor consists of a three-phase (biofilm particles, water and air) internal-loop airlift reactor (see Figure 5h) for nitrification, which is extended with a two-phase (biofilm particles and water) external concentric downflowing bed, the extension for denitrification. As a result of the special design of reactor, the liquid velocity in extension can be manipulated by the overpressure in the headspace of aerobic compartment, thus controlling the liquid recirculation ratio between the aerobic compartment and extension. (Nicolella C.,2000).

F. Triplet loop fluidized bed (Wei C.H. et al.,1999)

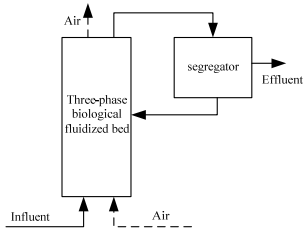
Hydrodynamics and mass transfer of triplet loop biological fluidized bed reactors (see Figure 5i) were studied in terms of gas holdup，liquid circulation velocity and volumetric mass transfer coefficient． It was bound from experiments that the main factor affecting hydrodynamics and mass transfer is gas holdup. Liquid circulation velocity decreases with increase in the gas holdup，whereas volumetric mass transfer coefficient increases with it，Compared with performance in conventional loop reactor，the gas holdup in triplet loop reactor increases by ten to fifteen percent, and volumetric mass transfer coefficient in triplet loop reactor Increases by over ten percent.



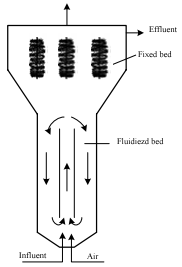
(a) Traditional anaerobic FBR
(Lu Y. S., 2001)



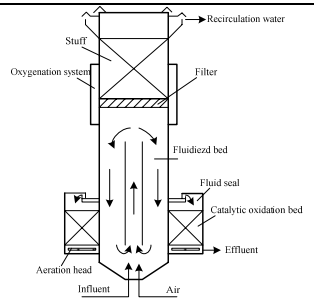
(b) Traditional aerobic FBR
(Lu Y. S., 2001)



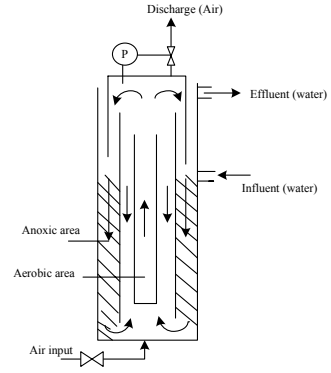
(c) Traditional three-phase FBR
(Lu Y. S., 2001)



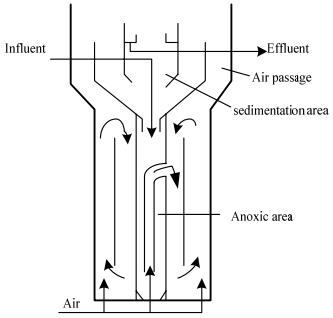
(d) circulation biological half FBR
(Li C.H,2002)



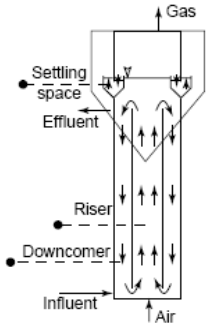
(e) Oxygenation internal recycling three-phase compound FBBR
(Li C.H,2002)



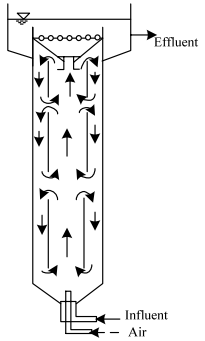
(f) BASE three-phase FBR
(Van Loosdrocht M.C.M. et al., 2000)



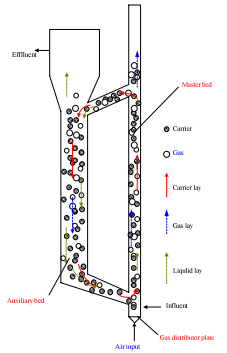
(g) Circox airlift three-phase FB
(Frijters,2000)



(h) internal-loop three-phase FBR
(Nicolella C.,2000)



(i) triplet loop FBR
(Wei C.H. et al.,1999)



(j) Extra-loop three-phase FBR
(Hua Bin, et al.,2002)

Figure 5. sketches of biological fluidized bed development

G. the extra-circulation three-phase biological fluidized bed

The fluidized bed is made of Plexiglass and shown schematically in Figure 5j, which consists of a main bed and an auxiliary bed. The inside diameter and height of the main bed are 100 mm and 970 mm, while that of the auxiliary bed are 200 mm and 770 mm. The total volume of the fluidized bed is 38 L. Granular activated carbon (40~60mech, 1160kg/m^3) is chosen as the microorganism carrier. The transformation between aerobic and anoxic state in reactor is facilitated by an automatic control box. Hua B., et al.(2002) demonstrated that COD removal efficiency kept 80% as HRT longer than 4 h in reactor.

The use of fluidized particles as a support matrix for the active bacteria offers several advantages over purely suspended bacteria. Phillip C.W. and Judy A. R.(1996) summarized the advantages in Table 4.

Table 4. Advantages of fluidized bed bioreactors.

- the immobilized bacteria are more resistant to toxic shocks and feed fluctuations
- the reactor has a higher biomass load and density, and reaction rates are often faster due to the higher cell density
- the bacteria have higher attachment and enrichment properties,
- the reactor has a large liquid-solid contact area
- fluidized beds do not clog
- the use of immobilisation over free suspension also decouples the inter dependence of the reactor phase dilution rates and the cell growth rate
- separation of cells from the fermentation broth is easier and it is not necessary for inoculation and batch wise cultivation of microorganisms
- compact design, with no moving parts within the reactor
- all operation can occur in one unit (alleviating the need for additional separation and agitation), and designs are relatively simple (allowing for simpler modification or troubleshooting)
- inexpensive carrier materials can be used (with designed surface and pore characteristics)
- they have higher mass transport characteristics
- relatively low energy input, especially compared to CSTRs

I.2.5 Applications using Biological Fluidize dBed

Nowadays, the fluidization technology was used in wastewater treatment, and the fluidized bed was applied in many fields, such as: A solid-liquid-gas, multiphase, fluidized bed bioreactor with low density particles was used to treat the high organic content starch industry wastewater. Textile wastewater was treated by means of a fluidized-bed loop reactor and immobilized anaerobic bacteria. A fluidized-bed reactor (FBR) was employed to treat copper-containing wastewater by mean of copper precipitation on the surface of sand grains. The conditions for optimum copper removal efficiency were also investigated (Lee C., et al., 2004). Riekkola -Vanhanen et al., (2003) studied the sulphate-reducing biofilm and suspension processes for treatment of synthetic wastewater containing sulphate, zinc and iron. González G. et al., (2001) compared the stirred tank and fluidized-bed bioreactors and found that the FBB showed better performance than the suspended-culture bioreactor, and the phenol degradation efficiencies was higher than 90%. A laboratory-scale study was conducted to evaluate the efficiency of a fluidized bed reactor operated under anaerobic condition with bioaugmentation to treat the cephalexin containing pharmaceutical factory effluent. A down-flow anaerobic fluidized bed treating red wine distillery wastewater during 1.5 years (laboratory scale). The granular activated carbon biological fluidized bed (GAC-BFB) process was used to treat landfill leachate containing organic material with typical COD values in the range 800 to 2,700 mg/l, but with high concentrations of ammonia in the range 220 to 800 mg/l. N.J. Horan, H. Gohar and B. Hill (1997) found that the GAC-BFB system offers a highly effective option for the biological removal of ammonia from high ammonia leachates, with the additional advantage of a good COD removal. The experimentation studies and applications using fluidized bed are showed in Table 5.

Table 5. Experimentation studies and applications using the fluidized bed

	wastewater	carrier	HRT	Organic loading rate (OLR)	Removal efficiency	Remark	Authors
1	organic wastewater	perlite	2 to 0.19 d	35 kg COD/m^3/d.	COD 84%	anaerobic	Sowmeyan R. and Swaminathan G.,(2008)
2	Brewery wastewater	triturated polyethylene		up to 10 g COD/L d	COD > 90%.	anaerobic	Alvarado-Lassman A., et al., (2008)
3	industrial cluster wastewater		6.0 h	2.08 kg COD/m^3 d	COD 94%	anaerobic	Kumar A., et al., (2008)
4	synthetic municipal wastewater	lava rock	0.44 h.	5.3 kg C /m^3 d 0.54 kg N/m^3 d	P 30% NH_4^+-N 90%	anoxic aerobic	Chowdhury N., et al., (2008)
5	textile industry effluents	small PVC cylinders			COD 80 and 72% (stabilization) 60 and 28% (holding) 74% (neutralization)	aerobic	de Souza A.A.U., et al. (2008)
6	cutting-oil wastewater	porous support medium	11 h	13 kg COD/m^3 d	COD67.1% (TOC71.3%)	anaerobic	Perez M., et al., (2007)
7	starch wastewater	low density biomass	24 h		COD 93.8%	aerobic	Rajasimman M. and Karthikeyan C. (2007)
8	phenol	glass			phenol 80%		José L. et al., (2007)
9	fluoride wastewater	granular calcite			CaF_2>97%, SiO_2<1% be recycled		R. Aldaco, et al.,(2007)
10	starch wastewater	GAC		85.44 kg COD/(m^3·d).	COD 92%	anaerobic	Rangasamy P. et al. (2007)
11	municipal wastewater	lava rock	SRT 45–50d	sludge yield of 0.12–0.135 g VSS/ g COD.	Without particles: (C), (N) ,(P) 94%, 80% ,65% with bioparticles (C), (N) ,(P) 91%, 78%, 85%	anoxic /aerobic	Patel A. et al.,(2006)
12	textile wastewater	Special porous beads (Siran®)	6 h		Full decoloration	anaerobic/ aerobic	Georgiou D. and Aivasidis A. (2006)

Table5 continue:

13	cephalexin drug-based pharmaceutical effluent	bioaugmentation	3-12 h.		COD 88.5%	anaerobic	Saravanane R., et al., (2001)
14	wine distillery wastewater	ground perlite an expanded volcanic rock	0.35 days.	17 kg TOC/m^3 d	75 and 95% TOC removal	anaerobic	García-Bernet D.,et al., (1998)
15	pentachlorophenol	GAC	18.6 to 2.3 h		COD 34 g/L*d to less than 1.36 g/L*d.	anaerobic /aerobic	Gregory J.et al.,(1998)
16	ethylene an d propylene glycols	porous media particles	1.7 h	TOC 0.88 g/L-d	TOC >96%	aerobic	Wen K. et al.,(1998)
17	photographic processing wastewater	1. sponge cubic media; 2. crushed cement 3. biological activated carbon (BAC).			BOD 5,700 g/m^3 to < 600 g/m^3	Anaerobic /aerobic	Hirata A. et al.,(1997)
18	groundwater	GAC		3 and 6 kg-COD/m^3d	BTX 90% benzene, toluene and xylene =BTX	anaerobic /aerobic	Thomas C. et al.,(1992)
19	synthetic municipal wastewater	lava rock		5.3 kg C/m^3 d 0.54 kg N/m^3 d	SBOD≤10 mg/L TN < 10 mg/L P 30%	anoxic /aerobic	Chowdhury N. et al., (2008)
20	polychlorinated biphenyls	modified cement particles			PCB 95 ± 2.01% in 5 days		Borja J.Q., et al.,(2006)
21	NH_4-N	spherical, pseudocubic and elliptical granules		1.5 kg-N/m^3 d		aerobic	Tsuneda S., et al.,(2003)
22	phenolic industrial wastewater	cells of Pseudomonas putida ATCC 17484		0.5 g phenol/L d	phenol 90%	aerobic	González G., et al.,(2001)

I.3 Sequencing Batch Reactor (SBR)

Sequencing Batch Reactor (SBR) is as early as in 1914 invented by English scholar Ardern and Locket for the water treatment process. At the beginning of 70's, Irvine R. used the laboratory scale conducts the system using SBR process, and in 1980 under the subsidization of American environmental protection bureau (EPA), the first SBR sewage treatment plant was rebuild in Culwer city. At present there are some production installments which are operating (Mace S. and Mata-Alvarez. J., 2002).

I.3.1 Common SBR Characteristics

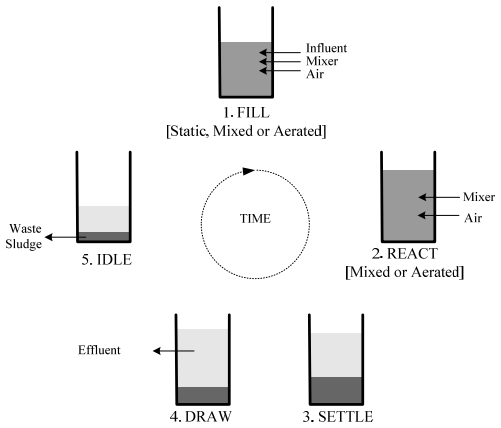


Figure 6. The stages of SBR

The SBR process operated according to the time succession, one operating process is divided five stages (Figure 6.): Feed, Reaction, Settle, Draw, and Ideal.

General: SBRs are a variation of the activated-sludge process. They differ from activated-sludge plants because they combine all of the treatment steps and processes into a single basin, or tank, whereas conventional facilities rely on multiple basins. According to a 1999 U.S. EPA report (Wastewater Technology Fact Sheet, 1999), an SBR is no more than an activated sludge plant that operates in time rather than space.

Basic treatment process: In its most basic form, the SBR system is a set of tanks that operate on a fill-and draw basis. Each tank in the SBR system is filled during a discrete period of time and then operated as a batch reactor. After desired treatment, the mixed liquor is allowed to settle and the clarified supernatant is then drawn from the tank.

Central to SBR design is the use of a single tank for multiple aspects of wastewater treatment. A detailed discussion of each period of the SBR is provided in

the following subsections, along with a description of typical process equipment and hardware associated with each.

Fill: The influent to the tank may be either raw wastewater (screened and degritted) or primary effluent. It may be either pumped in or allowed to flow in by gravity. The feed volume is determined based on a number of factors including desired loading and detention time and expected settling characteristics of the organisms. The time of Fill depends upon the volume of each tank, the number of parallel tanks in operation, and the extent of diurnal variations in the wastewater flow rate. Virtually any aeration system (e.g., diffused, floating mechanical, or jet) can be used. The ideal aeration system, however, must be able to provide both a range of mixing intensities, from zero to complete agitation, and the flexibility of mixing without aeration. Level sensing devices, or timers, or in-tank probes (e.g., for the measurement of either dissolved oxygen or ammonia nitrogen) can be used to switch the aerators and/or mixers on and off as desired.

React: Biological reactions, which were initiated during Fill, are completed during React. As in Fill, alternating conditions of low dissolved oxygen concentrations (e.g., Mixed React) and high dissolved oxygen concentrations (e.g. Aerated React) may be required. While Fig. 1 suggests that the liquid level remains at the maximum throughout react, sludge wasting can take place during this period as a simple means for controlling the sludge age. By wasting during React, sludge is removed from the reactor as a means of maintaining or decreasing the volume of sludge in the reactor and decreases the solids volume. Time dedicated to react can be as high as 50% or more of total cycle time. The end of React may be dictated by a time specification or a level controller in an adjacent tank.

Settle: In the SBR, solids separation takes place under quiescent conditions (i.e., without inflow or outflow) in a tank, which may have a volume more than ten times that of the secondary clarifier used for conventional continuous-flow activated sludge plant. This major advantage in the clarification process results from the fact that the entire aeration tank serves as the clarifier during the period when no flow enters the tank. Because all of the biomass remains in the tank until some fraction must be wasted, there is no need for underflow hardware normally found in conventional clarifiers. By way of contrast, mixed liquor is continuously removed from a

continuous-flow activated-sludge aeration tank and passed through the clarifiers only to have a major portion of the sludge returned to the aeration tank.

Draw (Decant): The withdrawal mechanism may take one of several forms, including a pipe fixed at some predetermined level with the flow regulated by an automatic valve or a pump, or an adjustable or floating weir at or just beneath the liquid surface. In any case, the withdrawal mechanism should be designed and operated in a manner that prevents floating matter from being discharged. The time dedicated to Draw can range from 5 to more than 30% of the total cycle time. The time in Draw, however, should not be overly extended because of possible problems with rising sludge.

Idle: The period between Draw and Fill is termed Idle. Despite its name, this "idle" time can be used effectively to waste settled sludge. While sludge wasting can be as infrequent as once every 2 to 3 months, more frequent sludge wasting programs are recommended to maintain process efficiency and sludge settling.

Because during SBR operation process, in various stages running time, the intermixture volume of the reactor change as well as the running status all may act according to the character of the sewage, the quality of the effluent and the request of movement function and so on which change nimbly. For the SBR reactor, only is the time sequential control, does not have the barrier of the space control. Therefore it can be controlled nimbly. Thus, the SBR process developed extremely quick, and derived from permits the many kinds of new SBR processing.

I.3.2 Processes Developments

Conventional or classics SBR process has the certain limitation for using in the projects. For example, if the influent capacity is great; it has to adjust reaction system, so the investment will be increased. And to demand the special target to the water quality, denitrifying or dephosphorus, then also must make the suitable improvement to the process. Thus in the application practices, the tradition SBR process can develop gradually other several kinds of new development as follows.

1. ICEAS

ICEAS (Intermittent Cycle Extended aeration System) emerged to the beginning of 1980's in Australia, is a innovational SBR process (Ouyang., 1995).

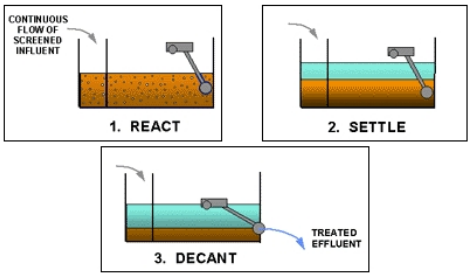


Figure 7. the process of ICEAS

Compared with conventional SBR, ICEAS which showed as Figure 7., it can be found that the major characteristic is: the end of influent area in reactor increased one pre-reaction zone, the operation for continuously the influent (at reaction and draining time still maintain water level), intermittent draining water, the reaction and ideal stage are not obvious. This system which treats the municipal sewage and industrial wastewater, the management in processing is more convenient and the cost is more economic than the conventional SBR system. But because the water passes through to entire operational cycle each stage, at the settle stage the influents can create the hydraulic turbulence in reaction zone and affect the spate separation, thus the influent volume may be received limit at a certain extent. The usual hydraulic resident time is longer.

2. CASS(CAST,CASP)

CASS (Cyclic Activated Sludge System) or CAST (-Technology) or CASP (-Process) process is one kind of the circulation activated sludge methods. The predecessor of process is ICEAS, obtained the patent in USA and Canada by Goronszy (Slater N J, Goronszy M C.,1994.).

Compared ICEAS process, its volume of pre-reaction ponds is smaller. CASS (see Figure 8.) is the optimized reasonable biological reactor.

The craft will advocate that the partial surplus sludge in reaction zone will be back to selector, during deposition stage has not the influent, the effluent will be stabilized. CASS is suitable for the more industrial wastewater and the request of denitrifying dephosphorus processing.

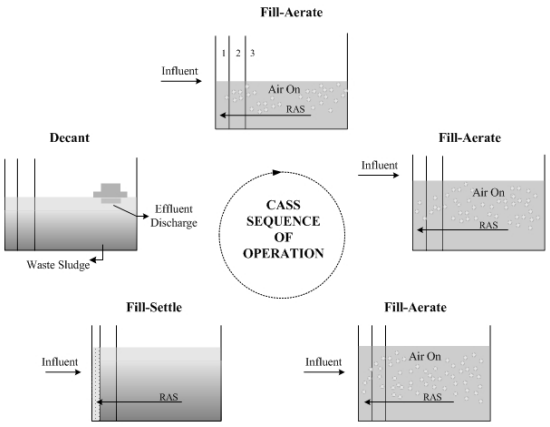


Figure 8. CASS™ (Cyclic Activated Sludge System)

3. IDEA

The intermittent decanted extended aeration (IDEA) basically maintained the merits of CAST, the operation process used the continuously influent, sequencing aeration, cyclical draining. Compared CAST, the pre-reaction zone (biology selector) changed to the separately premix pond with the SBR main body construction, the partial surplus sludge returned to premix pond, and at middle reactor the influent was be used. The premix pond establishment may enable to the sewage which has a longer resident time under high loading, guarantee the high flocculation bacterium choice. (Robert W.C., et al.,1999).

4. DAT-IAT

This process is a new process which used the sole SBR pond for continuously operation. It is situated between the conventional activated sludge method and SBR model, has both the effectiveness of the afore continuity and flexibility of the latter, is suitable to treat the high water quality and water volume. DAT-IAT main construction is made up of the Demand Aeration Tank (DAT) and Intermittent Aeration Tank (IAT), under common condition in DAT the influent continuously and aeration continuously as well, its effluent enters to IAT where the aeration, deposition, discharge of the water and the surplus sludge are completed.

5. UNITANK

The UNITANK system, its main structure is made up of three standards ponds which connected, each pond is equipped with aeration system which may use the blast or the mechanical surface aeration, and with matches stirring, two flank suppose have

the water lashers and the sludge discharges, two pond are used as aeration and sedimentation in turn, the sewage may enter any of the three (Feng. 1999).

Within one cycle, the original water unceasingly enters into reactor, through the time and spatial control, forms the aerobic, anaerobic and anoxic condition. Besides maintenance original automatic control, UNITANK system also has the simple pool and discharge structure, the stable water quality, need not backflow sludge. And by controlled the change of influent drop, the backflow and denitrify and dephosphorus may be achieved.

6. ASBR

Dague (1992) utilized SBR in anaerobic processing, and developed a ASBR (Anaerobic Sequence Batch Reactor). ASBR also has the merits of SBR, such as the craft is simple, the operation is flexible, the propelling force of biochemical reaction is big and bears the impact loading, etc.. ASBR may obtain the lower effluent density by sequencing feeding, simultaneously use sequencing draining water, discharge unceasingly sludge which subsidence performance is worse, and optimize the granule sludge further.

7. SS-SBR (SOIL SLUDGE SBR)

Irvine R.L. et al.,(1993.) used the soil as the reactor to treat the organics which was degraded difficultly. He used the air osmotic membrane which was buried in the underground for aeration and as carrier for biology growth, so it was enable to biofilm fixed. Thus maintain the microorganisms with worse subsidence which is easy to suspension flush and slow-growing, then eliminated the ordinary SBR stuff stage lengthen the reaction time (indirectly reduces response cycle). The new concept proposed not only provide the new mentality and the method for local soil pollution processing, simultaneously for wastewater treatment using the artificial wetland.

8. PAC-SBR

Chen and Wei (1995) treated the high concentrated organic wastewater with powder activated carbon which named PAC-SBR process whose operation cycle is 18h including the influent 0.5h (limit aeration), aeration 15h, precipitation 2h, effluent and sludge discharge 0.5h. The experiment results showed that: The PAC surface is the highly concentrated sewage, oxygen and sludge three-phase coexistence, the

condition of the biochemical reaction is surpassed than SBR. Between PAC and sludge had the mutual control action which increased the use rate, lengthened the sludge age, enhanced the revolution loading, improved the effluent quality, and obtained the biochemical effect better than SBR.

9. Membrane SBR

Unified SBR and the contact method may develop the new membrane method SBR called BSBR. BSBR has a lot of advantages such as the rapid starts-up, high efficiency quickly, simple management. The experiment indicated: BSBR processing effect is good to the conventional SBR due to the BSBR unified the merits of the biological contact oxidation and SBR (Helness, H. and Odegaard, H., 2001; Lim, J.et al.,20 04)

10. MSBR

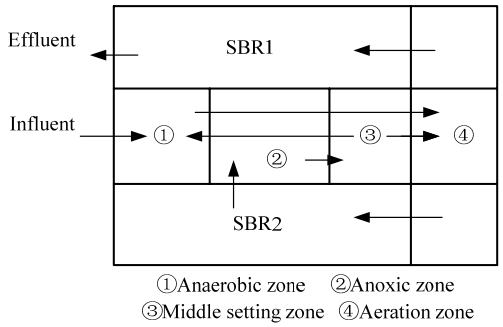


Figure 9. Typical dephosphorus and/or denitrogenation MSBR installment

MSBR (Modified Sequencing Batch Reactor) is the improved SBR reactor, and combines the conditional activated sludge technology, and develops more ideal wastewater processing (Wang et al., 2003). The most obvious difference was MSBR can keep the stable liquid level, the influent and discharge continuously, this can improve the utilization of SBR pond volume completely, thus can be possible to use in large-scale sewage treatment. The change is benefited from the middle reaction zone introduction; the wastewater does not enter directly to SBR pond, but enter the middle reaction zone advanced.

In conventional SBR, the period of influent has to control in short time and keep the enough reaction time for pollutant degeneration. But in MSBR, two SBR ponds are used in reaction or clarifying in turn, when serves as the settling pond, because the wastewater already has the enough reaction time, and the pollutant is degraded completely, could not influence to the discharge, thus might keep the water level stably all the time under the influent and discharge continuously.

On based of process design, the conventional SBR needs the large capacity pond,

thus increase construction investments or add the number of the SBR ponds. In these two aspects, MSBR has the great superiorities. The establishment of MSBR middle reaction zone is agile, its size and the condition can change according to the water treatment request: If merely removes the organic matter, the middle reaction zone only needs the complete aeration; If has eliminates the phosphorus and/or denitrogenation, the intermediate needs to carry on the separation again. Figure 9. is one of the typical dephosphorus and/or denitrogenation MSBR installment.

I.3.3 Applications using SBR

Presently according to the SBR technology development, it can apply in a lot of fields of wastewater treatment. Table 6. listed the partial kinds of wastewater which used SBR process for water quality purification. Table 7. Presented the partial of urban sewage treatment using SBR.

Table 6. Partial kinds of wastewater using SBR process

	Removal efficiency	Authors
highly toxic industrial effluent	COD85%, thiocyanate98%, phenols 99%	Marañón et al., (2008)
pulp and paper mill effluents	COD 86–90%, color 96–99%,	Akmehmet I. et al.,(2007)
Cu^{2+} and Zn^{2+}	Zn^{2+}92.61±0.28%, Cu^{2+}83.77±0.93%, $BOD_5$98±0%, COD92±0%, TKN78.1±0.1%	Sirianuntapiboon S, Thadchai H,(2007)
tannery soak liquor	COD 78% at an OLR of 0.5kg $CODm^{-3}d^{-1}$	Lefebvre O., et al.,(2006)
synthetic wastewater	COD76%, NH_4-N72%, PO_4-P26%, 4-CP34%	Kargi F., et al., (2005)
slaughterhouse wastewater	COD99%, N-NH_4 85%and P-PO_4 99%	Merzouki M., et al.,(2005)
milk industry wastewater	COD97.9±0.0%, $BOD_5$97.9±0.1%, TKN 79.3 ±1.0%, oil & grease 94.8±0.5%	Sirianuntapiboon S, et al (2005)
indigested piggery wastewater	N99.8%, P97.8%	Obaja D., et al.,(2005)
azo dye acid red 151 (AR151)	14% to 16% of the decoloration	Buitrón G.(2004)
2,4-dichlorophenol	successfully cope with 2,4-DCP at 166 mg/l	Quan X.C., et al.,(2003)
municipal sewage wastewater	meet the agricultural irrigation standards	Lin S. H. and Cheng K. W. (2001)
saline wastewater	with NaCl at 0.03% to 0.2%.	Intrasungkha N, et al.,(1999)
coupling municipal wastewater	$BOD_5$98%, TSS90%, NH_3-N89%	Umble A.K. et al.,(1997)
Winery wastewater	COD_T93%; COD_S95%; $BOD_5$97.5%	Torrijos M. and Moletta R. (1997)

Table 7. Urban wastewater treatment using SBR

wastewater	targets	removal efficiency	Authors
domestic wastewater (3 stations at USA)	C,N,P	63%, 65%, 82% TKN 33%, 55%, 92% P 93%,94%,98% BOD_5	Melcer et al. (1987)
domestic wastewater	C,N,P	66 - 81% N inorganic	Cuevas-Rodriguez et al. (1998)
Urban wastewater	C,N,P	89% COD 75% PO_4^{3-} 98 % NH_4-N 87% NO_3-N	Garzon-Zunigz et Gonzales-Martinez (1996)
Urban wastewater	C N P	83% NGL 86% Ptotal	Bernades et al. (1996) a)
little alectivite wastewater	CNP	85.6% MLSS 76.9% Ptotal 94.5% BOD_5	Rim et al. (1997)
wastewater	CNP	90% MLSSS 89% NH_4-N 98% BOD_5	Umble et Ketchum, (1997)
tannery wastewater	CNP	95% MLSSS 91% COD 89% P 96 % BOD_5	Banas et al. (1999) Kabcinski et al. (1998)
urban wastewater	CNP	CNP>90%	Keller et al. (2001)

At present the wastewater treatment system which using SBR process were focused on C, N, P, and the activated sludge and biofilm can treat the C,N,P at same time, but biofilm SBR can not remove P easily (Table8., 9.). (Casellas M.2002)

Table 8. Studies on nitrification and denitrification rate using SBR

Auteurs	Nitrification (mg NH_4-N /g MLSSS .h)	Denitrification exogenesis (mg NO_3-N.g/MLSSS.h)	Denitrification endogenesis (mg NO_3-N.g/MLSSS.h)
Choi et al. (1997)	0.83 - 1.08 (nitrition) 2.75 - 3 (nitration)	10.05 (C easy biodegradable) 1.33 (C hard biodegradable)	0.12
Rodrigues et al. (2001) Effluent brasserie	5.3 - 7.3 (no anoxic) 1.83 - 2.38 (with anoxic)	1.58	
Rim et al. (1997) petite alectivite	1 – 2.1 0.5 (<10°C)	3.3 - 7	
Banas et al. (1999) urbane, effluent tanneries	1.6	5.4 - 8.7	
Oleszkiewicz and Berquist (1988) effluent urban and industrial	0.33 (2°C)	0.875 (- 15°C) 0.125 (- 2°C)	
Yang et al. (1999)	1.6		4.8
Delgenes et al. (1998)	0.11		
Kim et al. (2001) (Furumai et al. (1999) ; Chang and Hao, (1996)) (Furumai et al. (1999) ; Artan et al. (1998))	4.2 – 5.6 2 -4.9		0.7 – 1.4 0.4 – 3.7
Carucci et al. (1996)		10.4	2.9

Table 9. Targets of treatment using SBR process

wastewater	Removal efficiency	Targets	Authors	Remark
artificial municipal wastewater	91.6±1.6% N	CN	Quan, et al(2005)	external carbon source
synthetic wastewater	COD76%, NH_4-N72%, PO_4-P26%, 4-CP34%	CNP	Kargi F., et al., (2005a)	
slaughterhouse wastewater	COD99%, N-$NH_4$85%, P-$PO_4$99%	CNP	Merzouki M., et al.,(2005)	
synthetic wastewater with glucose–organic acid mixtures	P96%	CP	Kargi F, et al., (2005b)	different carbon sources
synthetic wastewater	$BOD_5$45±5.1, COD37±3.6, TKN4.1±1.0, TP0.15±0.80 , SS41±2mg/l (OLD 528±50.8g BOD_5/m^3-d).	CN	Suntud S,et al (2005)	
phenol, *p*-methylphenol, *p*-ethylphenol and *p*-isopropylphenol,	COD 100 mg/l	C	Lee K.M. and Lim P.E. (2005)	phenolic compounds
digested piggery wastewater	N99.8%, P97.8%	CNP	Obaja D., et al., (2005)	
wastewater from the first anaerobic pond in an abattoir wastewater treatment plant.	N95%	N	Pochana K. and Keller J.(1999)	SND
saline wastewater	with NaCl at 0.03% to 0.2%.	NP	Intrasungkha N., et al.,(1999)	Color
domestic wastewater		CN	Bernardes R. S., et al.,(1999)	
synthetic wastewater	Glucose-fed PAOs accumulation	P	Wang J.C. and Park J.K.(1998)	
high quality effluent in regards to carbon, nitrogen and phosphorus compounds	N 190 mg/L 20 mg/l TP 50 mg/l 5 mg/l	CN	Keller J., et al., (1997)	
synthetic wastewater	N96%, P93%.	CNP	Hamamoto Y., et al.,(1997)	
municipal wastewater	$CBOD_5$ 98%, TSS90%, NH_3-N89%	CN	Umble A.K. et al., (1997)	
domestic wastewater	ORP a valuable tool for optimizing N and P removal	CNP	Demoulin G., et al.,(1997)	
actual wastewater emanating from a recreational center	BOD95% SS 89% TN 70% P77%	CNP	Rim Y.-T., et al.,(1997)	
wastewater from the main campus of the National University of Mexico	phosphate removal and nitrification were obtained when the mean organic load was 3 $gCOD/m^2 \cdot d$.	CP	Munoz-Colunga A. et al., (1996)	Biofilm
Nightsoil treatment plant	phosphorus was removed about 42% chemically and about 36% biologically.	P	Choi E., et al., (1996)	

I.3.4 Brief Summary

Opposite to the conventional continuum activated sludge method, the SBR process is a kind of technology which still needs the development and the consummation. Many research works just started, lack of the scientific design basis and the mature management method as well, moreover the SBR own characteristics

will be deepened to solve the question difficulty.

At present SBR developing process has the main problems included:

Basic research:

• About microorganism metabolism theory research of activated sludge when the sewage is in transient state;

• About the anaerobic or aerobic condition are in turn repeatedly, the influence which distributes to the microorganism activeness and population;

• The microorganism mechanism research for dephosphorus and denitrify simultaneously.

Engineering design:

• Lacks of the scientifically reliable design pattern;

• The operation pattern choice and the design method are unmatched.

SBR is a kind of ideal intermittent type activated sludge process, it has the technical process is simple, the processing effect is stable, bears the impact shoulders strong and has denitrify and dephosphorus capability.

I.4 Biofilm Applied to Wastewater Treatment

I.4.1 General Description

The microorganism cell can nearly adhere to the surface in water environment any being which suitable to adhere, stick and cohere reliably, and continue to growth and reproduction. The exopolymers which may assist in binding microbial cells to surface gather to cause the microorganism cell to form the fibrous tangled structure, then is called as biofilm. The biofilm forms on surface of the inert support. Along with the nutrition substrate and spatio-temporal change, biofilm distributes evenly or non-uniformly on carrier, otherwise it is composed by single-layer or quite thicker. A biofilm usually has the whole shape structure and very strong adsorption performance. Finally, a biofilm is composed with the alive cell and lifeless inorganic substance. According to Characklis(1990) research, the biofilm accumulation formation is the combined results of physical, chemical and biological process.

A biofilm mainly is gathered by the exopolymers and carrier. Various microorganisms in biofilm can observe using the light microscope. It can found that the shapes are different, the types are enriched, including: bacterium, fungus, algae (with actinism), protozoon, metazoa, virus additionally. Obviously, biofilm is a complex ecology system which can be used in wastewater treatment possibly.

I.4.2 Description of Mass Transfer Theory

Recently, biofilm structure and mass transfer research, specially the biofilm mass transfer theory will be the focal area. As same activated sludge law, all biological process is the physical chemistry process. In sewage, organic pollutant and the low concentration metallic ion are adsorbed by sludge or biofilm, it is the physical process; afterwards the pollutants are degenerated by microorganism's enzyme, it is chemical process. Since 1970's the reaction-diffusion model was presented, many of researchers carried continually on the biofilm formation and mechanism (Grady C.P.L., *et al.,* 1999). The innovations such as growth-degradation substrate kinetics

(Belkhadir R., 1988a,b) and cellular automation models (Wimpenny J W T,1997) were obtained.

A biofilm is a variable organic coating in thickness (of some micrometers to a few millimeters) formed by adhesion of micro-organisms on a mineral or alive solid support (mucous membrane), typically formed by cells isolated or microphone-colonies drowned in a polymer strongly hydrated. A biofilm is a structure evolving/moving in the course of time, being able to see following one another several microbial populations, dependent on the surrounding physical characters, and likely to incorporate or exchange unceasingly with the ambient conditions of the cells and the macromolecular components (Pelmont, 1993).

1. Formation

The nature and the structure of the support, the environmental conditions as well as the characteristics of the stocks present intervene in the adhesion of the bacteria on a support. The mechanism of adhesion of the bacteria is complex and is characterized by various phases in the formation and the growth from the biofilms:

A. Reversible adhesion

It is a function of the initial attraction of the bacterium for the support. The bacteria colonize the surface of the support via the electrostatic forces, of hydrophobias or of Van Der Waals but are not fixed in a perennial way: a weak agitation of the medium can be enough to detach them. This adhesion is conditioned by the preliminary training of an organic matter film slightly soluble on the surface of the support. These compounds, of hydrophobic nature come from the decomposition of the organic matter, the excretion of living organisms or the lysis of micro-organisms. These molecules hang with surface of support which acquired a load of surface following an ionization of surface or the adsorption of ions (Pelmont, 1993, Maier *et al,* 1999).

The influence of the type of medium on the adhesion and the formation of the biofilm were studied by Gjaltema *et al* (1997). These authors showed that the forces of shearing control the formation of the biofilm. Initial colonization is thus done preferentially in the sites with the shelter of the disturbances of the medium (cavities, hollow, etc.).

B. Irreversible adhesion

The bacteria use the organic substrate present on the support for their metabolism. The bacteria secrete exopolymeres then (mainly polysaccharides). Those create a stencil which surrounds the cell and which, in addition to its sticking action, fills of many functions for the fixed cells: exchange ions for the filtration and the collection of nutrients, protection with respect to factors of stress(drying, effects toxic, variations in temperature, pH, and so on. (Pelmont, 1993, Maier *et al*, 1999).

C. Growth and balance

At the time of the exponential growth of the micro-organisms, the biofilm thickens then until reaching a stable thickness corresponding to a balance between the contribution of new elements and the departure of components torn off by the liquid medium. Thus in a given medium, a distribution between free and motionless cells is established.(Pelmont, 1993)

Beyond this thickness, the speed of consumption of the substrate does not vary any more because of the limitations of diffusion of the oxygen layer.(Lazarova *et al*, 1995).

That involves a stratification of the physiological conditions according to the thickness within a biofilm: in spite of an aerobic medium, the major zone (more than 200 micrometers of depth) of a biofilm can easily become anaerobic.

D. Detachment

The principal mechanism causing this detachment results in first assumption from the collisions between particles but there is not any general rule making it possible to envisage this phenomenon (Nicolella *et al*, 2000).

The detachment of biofilm is due to several phenomena (Nicolella *et al*, 2000):

- The phenomenon of chattering due to consumption by protozoa on the surface of the biofilm
- the periodic loss of great quantities of biofilm
- Erosion, i.e. the permanent loss of small particles on the surface of the biofilm primarily due to the forces of shearing

- The abrasion which causes the same phenomenon as erosion but due here to the collision between particles

The detachment of biofilm is thus a complex function of many parameters including the hydrodynamics, morphology of the biofilm and characteristics of support.

2. Mass transfer and modeling

The growth of the biofilm depends on the quantities available in carbonaceous substrate, oxygen and other essential nutrients (nitrogenizes, phosphorus, etc.). A biological engine using a biofilm fixed on a mobile support comprises three phases: solid (support + biofilm), liquid (water + substrate), and gas (air). The intrinsic quantities available in each phase are controls by the transfers of matter between these various phases. In order to understand these mechanisms of transfers, several models were designed.

The model of diffusion/balance describes the transfers of mass and heat between the various phases of the system. When the biofilm adheres on a solid particle which is used to COD as support, the formed unit is called bioparticle (see Figure 10.).

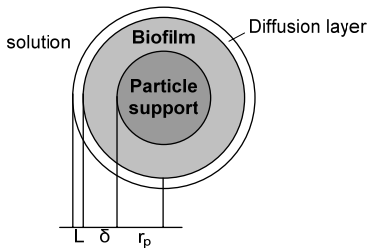


Figure 10. Diagram of the bioparticle (Wu and Huang, 1995)

A. Transport and diffusion of the substrate within the biofilm:

The majority of the models suggested founded on the theory of diffusion-reaction of are composed within the biofilm. Thus, Lay and Shieh (1997) propose the model presented by equation (4):

$$\frac{D_S}{r^2}\frac{d}{d_r}\left(r^2\frac{dS}{dr}\right)=\rho\left(\frac{kS}{K_S+S+S^2/K_i}\right) \qquad (4)$$

$r=r_p,\ S=S_0$

$r=r_s,\ \frac{dS}{dr}=0$

Ds = diffusivity of substance S in biofilm (m^2/h)
R = radial distance since the center of bioparticle (m)
S = concentration of substance S in biofilm (kg COD/m^3)
S_0 = concentration of substance S in solution (kg COD/m^3)
r_p= radii of bioparticle (m)
r_s = radii of particle support (m)
ρ = density dries of biofilm (kg/m^3)
K = maximum rate of substance utilization (kg of S kg VSS.h)

K_s = coefficient of Monod (kg/m^3)
K_i = coefficient of inhibition (kg/m^3)

The left of equation (4) corresponds to the entry of substance in biofilm by phenomenon of diffusion (1st order of Fick) while the right corresponds to the consumption of substrate by the biomass according to the model of Haldane.

This equation presents several limits: it is founded on the assumptions of particles of spherical form with a homogeneous biofilm and coefficient thickness, a resistance to the negligible mass transfer to the interface between the liquid and biofilm. Buffière *et al*, (1998) use almost the same model with the same limiting conditions (Equation 5):

$$\frac{D_S}{r^2}\frac{d}{d_r}\left(r^2\frac{dS}{dr}\right)=\sum_i v_S^i$$
$$v_S=\frac{\mu_{S\max}SX_S}{Y_{X_S/S}K_S+S} \qquad (5)$$

$\mu_{S.max}$ = maximum growth rate of bacterium using S
X_s = concentration of bacteria using S (kg MLSS/m^3)
$Y_{xs/s}$ = output of use of substrate for the bacteria using S (kg MLSS/kg *COD*)
K_s = coefficient of Monod for bacteria using S (kg*COD*/m^3)

The second member of equation 5 corresponds here to the difference, for each substrate between the rate of consumption of the substrate S and the rate production of the substrate S according to the model of Monod.

Indeed, one considers a microflora here understanding several stocks, some using the metabolites produced by others. The induced limitations are here the same one as for the preceding model.

More recently, Vinod and Reddy (2005), for a treating FBBR of strongly phenol water proposed the model described by Equation 6. This model considers at the same time phenol and oxygen as limiting substrates whereas the microbial growth follows kinetics of Haldane.

$$\frac{D_S}{r^2}\frac{d}{d_r}\left(r^2\frac{dS}{dr}\right)=\frac{\rho}{Y_{X/S}}\frac{\mu_{\max}S}{S+K_S+S^2}\frac{C}{K_0+C} \qquad (6)$$

K_s = coefficient of Monod for phenol (kg/m^3)
K_0 = coefficient of Monod for oxygen (kg/m^3)
S = phenol concentration in biofilm (kg/m^3)
C = dissolved oxygen concentration in biofilm (kg/m^3)

The solution of this model makes it possible to envisage the rate of degradation R (kg/s) of the phenol (Equation 7):

$$R=N_p\frac{\rho}{Y_{X/S}}\int_{r=r_p}^{r=r_p+\delta}\frac{\mu_{\max}S}{S+K_S+S^2}\frac{C}{K_0+C}4\Pi r^2dr \qquad (7)$$

The results obtained by this calculation and in experiments were compared under several conditions, the maximum difference obtained is 12%, which proves the relevance of this model.

It is generally allowed that the resistance of transfer of the biofilm is negligible for high speeds of the liquid (Beyenal and Tanyolac, 1998). However, for low speeds, one can define a coefficient of transfer. It was shown that this coefficient increases with the thickness of the biofilm. This increase can be allotted to the increase in the porosity and the roughness of biofilm with the increase thickness (Beyenal and Tanyolac,1998)

B. Transport and diffusion of oxygen:

The coefficient of gas-liquid transfer is a function of the voluminal fraction of gas. The oxygen transfer of gas phase until the solid phase can be represented as shown in Figure 11.

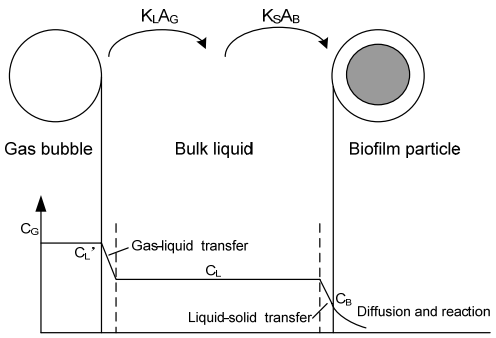


Figure 11. Transfer of oxygen and reactions in biofilm (Nicolella *et al*, 1999)

The coefficient of gas-liquid transfer is a function of the voluminal fraction of gas ε_G in the system as shows in Equation 8 (Nicolella *et al.*,1998):

$$K_{La} = (0.6S^{-1})\varepsilon_G \qquad (8)$$

This relation linear and is not influenced by the quantity of solid particles, their density or their size and thus by the type of solid (solid support or biofilms). It is about an empirical relation which thus requires checking. The liquid-solid transfer is generally described according to the theory of the boundary layer by Equation 9. (Nicolella *et al.*,1998)) :

In this equation, the number of Sherwood represents the relationship between the diameter of the particle and thickness of boundary layer of diffusion. The Reynolds number characterizes the mode of flow (turbulent, laminar) while the Schmidt number characterizes the phenomena of diffusion and viscosity which exploit the flow.

$$Sh = 2 + CRe^{n}Sc^{m} \qquad (9)$$

Sh = Sherwood number $Sh = \frac{K_S d_S}{D}$
k_s = coefficient of liquid transfer solid (m/s)
d_s = diameter of the solid (m)
D = diffusivity of oxygen (m^2/s)
C = concentration of oxygen (g/m^3)
ε_G = fraction voluminal of gas in the engine
Re = Reynolds number according to the theory of the turbulence of Kolmogorov (used for the columns of transfer)
$\mathrm{Re} = \frac{u_g g d_s^4}{v^3}$
u_g = speed of gas (m/s)
g = acceleration of gravity (m^2/s)
v= viscosity of the liquid (m^2/s)
S_c = a Schmidt number $S_c = v/D$

I.4.3 Carrier

It is various for classify the biofilm carriers, in accordance of the stuff, the biofilm carriers may be divided approbatory into the firm, soft, semi soft, assembled and suspend carriers to reach the classes (Table 10.). (http://www.paper.edu.cn)

Table 10. Characteristic of the different carrier

carrier		advantages	probable defects
Firm		- High biology concentration and activity relatively - High volume loading - High power efficiency - Low sludge production	- Weak relative surface area - Smooth surface, biofilm fall off easily - Often stem and bunch up - Asymmetric apportioned gas and water, low aeration capability - High project investment and operation charge relatively
Hanged	Soft	- Avoid the stem - Large relative surface area - Low cost, easy machining	- Bunch up easily - Low oxygen transmission efficiency
	Semi-soft	- Solve the tangle and break problems of the soft carrier	- Academic relatively surface area is smaller than the soft carrier - Cost is expensively than the soft carrier - Smooth surface, biofilm adhere difficultly
	assembled	- Large specific surface, biofilm - Oxygen transmission efficiency is higher than soft carrier - No stem, long using life	Sludge cumulates easily.
Suspend		- Need not fixed bracket - Fluidization equality, low energy consumption - Evident functions of the bubbles iterative incision, high oxygen transmission efficiency	- High cost - Maybe toxicant for microorganism - weak intensity

On the other hand, the biofilm carrier can classify such as inorganic, organic carriers. During the biofilm technology development, the inorganic carriers such as grit, carbonate, glass, zeolite, ceramic, charcoal fibre, slag, activated carbon, metal and so on. The organic carriers such as PVC, PE, PS, PP, resin, plastic, etc. were used broadly as well. Table 11 shows partially the reactors which using the carrier.

Table 11a. Partially the reactors which using the inorganic carrier.

carrier	Biofilm wet weightily (kg/cm^2)	reactor
Flat glass	0.073	Biofilm reactor
Falt aluminum	2.0	Biofilm reactor
Slag	0.24-1.7	Fluidized bed
Rock	0.24-1.7	Fluidized bed
Glass	$4\text{-}12.2*10^{-3}$	Stirring biofilm reactor
Glass	$1*10^{-3}$	Stirring biofilm reactor
Glass	0.2	Biofilm reactor
Glass	$12*10^{-4}$	Biofilm reactor
Stainless steel		Pipe biofilm reactor
Activated carbon		Biofilter
Basalt		Airlift reactor

Table 11b. Partially the reactors which using the organic carrier.

carrier	Biofilm wet weightily (kg/cm^2)	reactor
Plastic	0.25	RBC
Plastic	0.48-1.44	Filter bed
Plastic	0.12-2.55	Filter bed
Tennis ball	0.71	Filter bed
PVC	0.1-0.25	Completely composite reactor
PP	0.1-0.25	Completely composite reactor
PE	0.1-0.25	Completely composite reactor
PS	0.1-0.25	Completely composite reactor
PS	0.05-0.1	Airlift stirring bed
PS	0.05-0.1	Three-phase fluidized bed
Ion charge resin		Completely composite reactor
Plastic soft carrier		Stabilization pond

I.4.4 Biofilm Reactors

The biofilm reactor is the main biological treatment technology, compound with activated sludge, also is used in the biological wastewater treatment. (see Figure 12.)

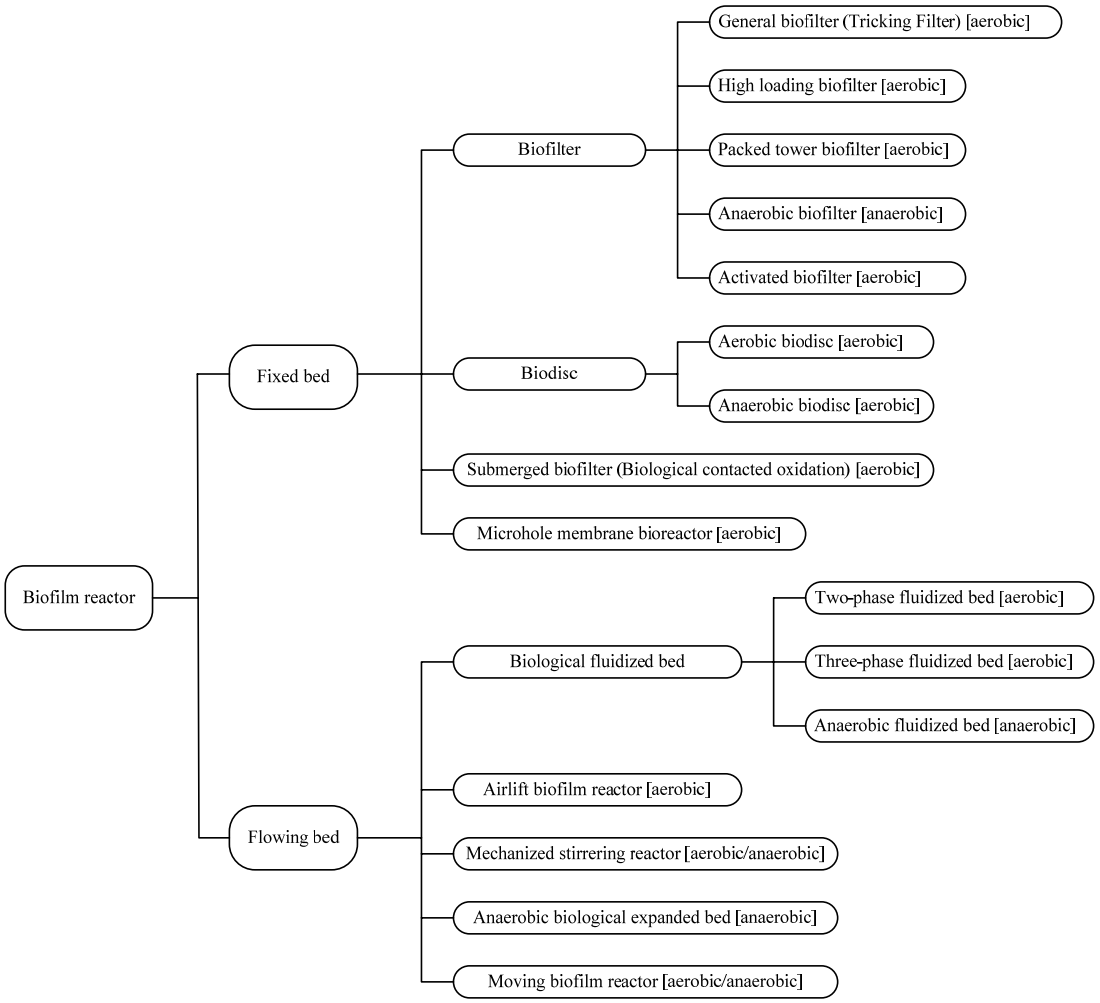


Figure 12. Types of biofilm reactors

I.4.5 Applications with biofilm

Nowadays, the biofilm technology was used in many fields of wastewater treatment, such as Table 12. shows partially:

I.4.6 Brief Summary

Biofilm reactor is the biofilm technology which applies widely in wastewater treatment. And the development is great, biofilm reactor will treat the high-concentration industrial wastewater and sewage. Nowadays biofilm reactor can be playing the important role in the drinking water as well.

Table 12. Experimentation studies and applications using biofilm

	wastewater	carrier	HRT	Organic loading rate (OLR)	Removal efficiency	remark	Authors
1	distillery effluent	perlite	2 - 0.19 day	35 kg COD/m^3d.	COD 84%	fluidized bed reactor	Sowmeyan R. (2008)
2	synthetic wastewater	polyester fiber			COD > 90% E_{SND} 83.3%.	compact suspended carrier biofilm reactor	Xia S.Q., et al., (2008)
3	Seawater	spherical positively buoyant polyethylene		17.7±1.4 g N/ m^2 d	NO_3-N 53→1.7±0.7 mg/L	submerged moving bed biofilm reactor	Labelle M.A. et al. (2005)
4	real raw municipal wastewater.			(20°C,DO=5mg/L) 0.84 gNH_4^+-N /m^2 d		Fixed-Bed Submerged Biofilters without Backwashing	Canziani, R. et al., (1999)
5	Artificial wastewater	Biolite (expanded clay)		2 kg NO_3-N/m^3·d.	15 mgCOD/L (4.5 g COD/g NO_3-N.) 75 mgCOD/L (8 -10 g COD/g NO_3-N.)	packed bed reactor	Æsøy A., et al., (1998)
6	synthetic water containing inorganic carbon and nitrogen compounds			1.5·2 gO_2/gN-NH_4^+		circulating bed reactor (CBR).	Lazarova V., et al., (1998)
7	textile effluent			2.5 kgN/ m^3 d	<10 mgN/L	up-flow sand filter	Canziani R., Bonomo L.,(1998)
8	Sjölunda wastewater treatment plant				10 mg BOD_7 /L 8 mg N/L 0.3 mg P/L	moving bed biofilm reactor (MBBR).	Aspegren H., et al., (1998)
9	synthetic wastewater	hollow fibre	34min(mixed) 47min(plug flow)		89% COD (mixed) 86% COD (plug flow)	membrane aeration bioreactor (MABR)	Pankhania M.,et al. (1999)
10	synthetic wastewater.	corrugated plastic sheets		43g COD_S/m^2d or 3.8kg COD_S/m^3d		biofilm reactor	Rodgers M. (1999)
11	synthetic domestic sewage			6.9–20.7g COD/m^3·d and 0.69–2.09g N/m^2·d,	N 20-68%	three stage rotating biological contactor (RBC).	Gupta A. B., Gupta S. K. (1999)
12	chemical industry wastewater	plastic carrier elements		53 g BOD_5/m^2d	95% BOD_5	Moving Bed Biofilm Reactor (MBBR),	Rusten B., et al.,(1999)
13	domestic sewage		UASB 6 h BF< 11'		SS 94% BOD_5 96% COD 91%	submerged aerated biofilter — BF	Gonçalves R.F.,(1998)
14	synthetic wastewater.	Kaldnes K1	1.5h (15°C)	2.7g NO_x-N/m^2carrier d		suspended carrier biofilm reactor	Welander U., et al., (2003)

I.5 Biological Denitrification and Dephosphorization

I.5.1 General Description

Nutrient compounds frequently present in wastewater are valuable substances which act as fertilizers. They are becoming increasingly significant in water and wastewater management because the discharge of nutrients such as nitrogen and phosphorus into rivers and lakes can cause adverse influences on our environment and life. An excessive increase in the quantities of these nutrients in the aquatic surroundings disturbs the ecological balance, resulting in severe damage to environment(e.g. eutrophication). However the conventional activated sludge system only can eliminate the sewage containing BOD and SS effectively, and does not be aware to remove effectively the nutrients such as nitrogen and phosphorus. Therefore the majority municipal wastewater treatment plants (WWTPs) and industrial wastewater treatment processes will have to consider the dephosphorization denitrogenation technologies. Therefore, the denitrogenation and dephosphorization should be used by the biological treatment process massively.

I.5.2 Nitrogen Cycle and the Technical Rem oval Process

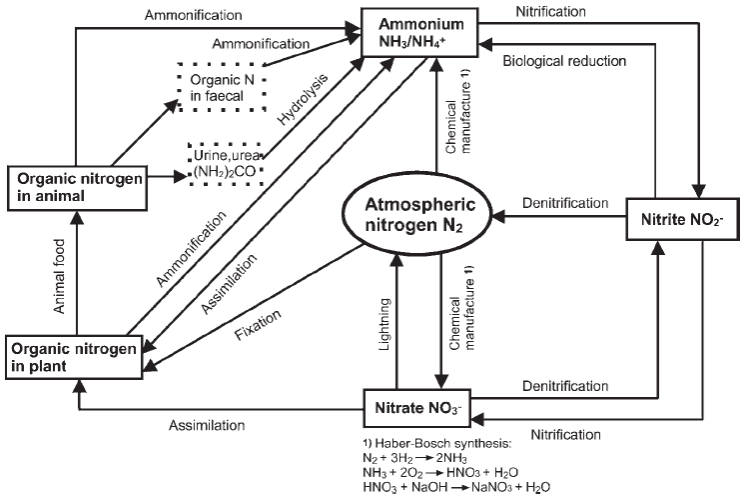


Figure 13. Principal compounds in the nitrogen cycle are nitrogen gas, ammonium, organic nitrogen and nitrate.

The relationship between the various nitrogen compounds and their transformation is presented in Figure 13. as the nitrogen cycle. The transformation reactions include fixation, ammonification, assimilation, nitrification and denitrification. (Wiesmann U., *et al.*, 2007)

I.5.3 Mechanisms of Nitrogen Removal

(a) Ammonification/assimilation

Ammonification is the conversion of organic nitrogen into ammonium, whereas the inverse process, the conversion of ammonium into organic nitrogen, is called bacterial anabolism or assimilation.

$$RNH_2 + H_2O + H^+ \rightarrow ROH + NH_4^+ \quad (15)$$

(b) Nitrification

Nitrification is the biological oxidation of ammonium, with nitrate as the end product. The reaction is mediated by specific bacteria and is a two-step process: in the first step ammonium is oxidized to nitrite by bacterial species such as *Nitrosomonas spp*. The complementary step, oxidation of nitrite to nitrate, is mediated by species such as *Nitrobacter spp*. Both *Nitrosomonas* and *Nitrobacter* can only develop biochemical activity in an environment containing dissolved oxygen.

(c) Denitrification

Denitrification is the biological reduction of nitrate to molecular nitrogen, with organic matter used as a reductor.

(d) Shortcut nitrification denitrification

The concept of Shortcut nitrification denitrification was been presented (Voets J.P., 1974). It is a new denitrogenation craft develops which by Dutch Delft Technology University (Mike S.M. et al., 1997; Verstraete W., 1998). Figure 14. shows the schematic of nitrification and denitrification for achieving nitrite accumulation. Sustained nitrite accumulation via the nitrite pathway ($NH_4^+ \rightarrow NO_2^- \rightarrow N_2$) offers several benefits for nitrogen removal of wastewater, compared to the nitrate pathway ($NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^- \rightarrow NO_2^- \rightarrow N_2$), the disadvantages including: faster kinetics of the nitrification and denitrification processes; up to 25% energy savings during aeration; up to 40% savings from reduced demand for organic

substrate; a higher rate of denitrification; lower biomass production (up to one third of former amount). As disadvantages it can be mentioned: nitrification must be operated and controlled precisely; automatic measurement of NO_2^- concentration in effluent of the anoxic step; results in increasing operating costs.

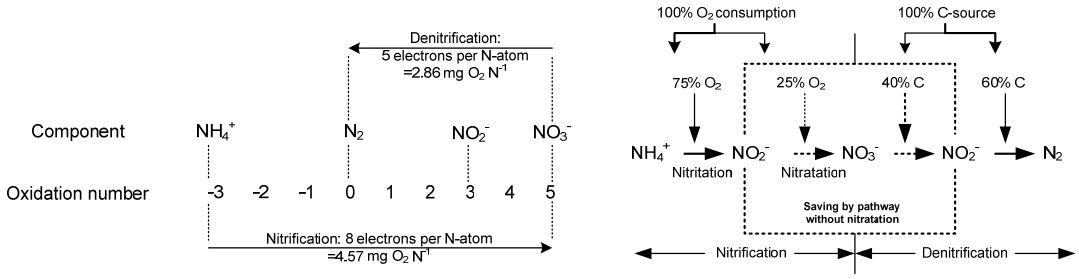


Figure 14. Schematics for Nitrogenous compounds produced and the accumulation of nitrite during nitrification and denitrification

(e) ANAMMOX (ANaerobic AMMonium OXidation)

ANAMMOX means that under the anaerobic condition the ammonia nitrogen is directly oxidized to the nitrogen process by the nitrito-nitrogen as the electron acceptor. As early as in the 20th century 70's intermediate stages, Broda forecasted that it should be existed the ANAMMOX phenomenon in the nature by the free energy theoretical calculation, but its reality discovery is 10 years after the theory forecasts. Mulder(1992) discovered firstly this phenomenon used the denitration fluidized bed. Nowadays the ANAMMOX microorganism separately has been successfully cultured and enriched to certain concentrate in the laboratory fluidized bed and the SBR reactor (van de Graaf A.A, *et al.*,1996; Strous M., *et al.*1996,1999).ANAMMOX reaction has the activeness in temperature ranges of 10-43℃, and its suitable pH is 6.7-8.3. ANAMMOX needs not the organic carbon source existence, the carbonate/carbon dioxide is the inorganically carbon source for ANAMMOX microorganism needs.

(f) Simultaneous nitrification and denitrification (SND)

Simultaneous nitrification and denitrification (SND) (Hyungseok Y., 1999) which has advantages over the separated nitrification and denitrification processes, means that nitrification and denitrification occur concurrently in the same reaction vessel under identical operating condition. In continuously operated plants, SND offers the potential to save cost for a second (anoxic) tank, or at least reduce its size, if

it can be ensured that a considerable amount of denitrification takes place together with nitrification in the aerated tank. If SND is accompanied by the inhibition of the second step of nitrification (oxidation of nitrite to nitrate), theoretically a saving of organic energy of up to 40% could result. This is of particular interest when biologically removing nitrogen from wastewater with low COD: nitrogen ratio.

I.5.4 Traditional Nitrogen Removal Processes

Denitrify is one of the important links in wastewater treatment. Nitrogen which contained in the wastewater can be coped with by the physical, chemical and biological methods. Generally biological denitrify is recognized as the most economical efficacious method and adopted mostly in wastewater treatment at present. Figure 15. shows the Typical biological nitrogen removal schemes.

I.5.5 Novel Nitrogen Removal Processes

Anaerobic ammonium (nitrogen) oxidation can realize chemo-autotrophic denitrify with nitrosation supplement.

(a) SHARON (Single reactor for High Ammonium Removal Over Nitrite)

In SHARON the end-product of ammonia nitrogen is oxidized nitrito-nitrogen (Turk,1989; Rahmani, *et al.*,1995; Brouwer, *et al.*1996; Hellinga, *et al.*1998, 1999). The ANAMMOX process creates the new technical condition for the denitrify continual processing for the industrial wastewater or sewage (van Loosdrecht M.C.M.,1997; Jeeten M S M, *et al.*,1997). And the nitrosation process with ANAMMOX may be realized as the SHARON or in the biofilm. This chemo-qutotrophic denitrify process mainly aims at the high concentrated ammonia nitrogen sewage. At present, in the world the first example project application using SHARON has realized in the Holland Rotterdam's Dokhaven sewage treatment field(van Dongen U, *et al.*,2001). Several year operation passed, the results indicated that the performance of nitrosation process is significant, nitrify efficiency nearly reach 100% (may control pH).

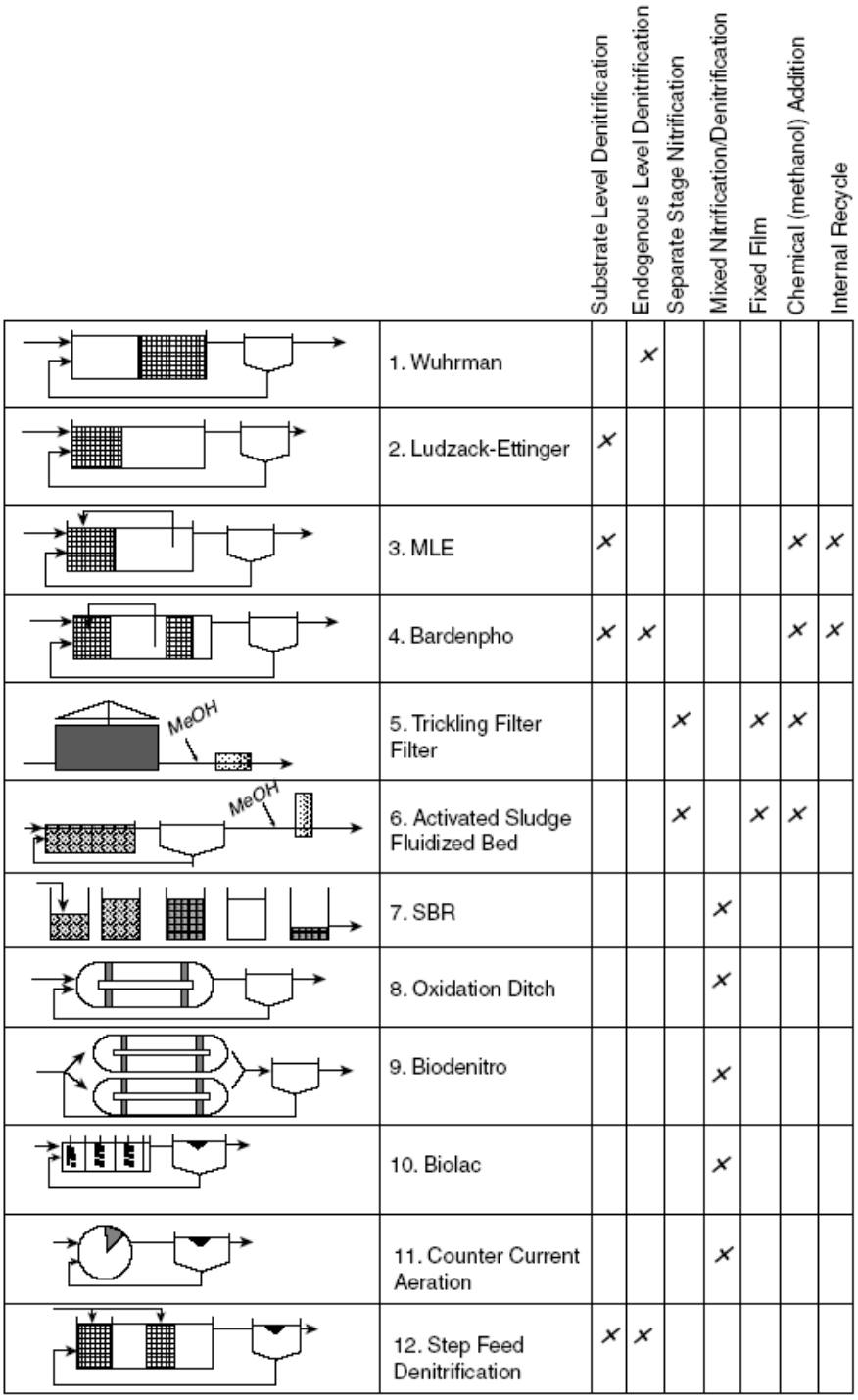


Figure 15. Schemes for typical biological nitrogen removal system (David L., Russell, P.E. 2006)

(b) Combined process of SHARON and ANAMMOX

In fact, SHARON nitrosation unit mentioned above will be the preliminary technical preparation for treat the sludge digestive juice p by the ANAMMOX process. At present, combined with SHARON and ANAMMOX process is completed in the laboratory.

(c) Chemo-autotrophic denitrify in biofilm (CANON)

If the ANAMMOX microorganism can also grow in the biofilm system, then in the biofilm the chemo-autotrophic denitrify process can be realized possibly. In the practice, the phenomenon is already observed truly in some projects or the experiment.(Strous M., *et al.*,1997, Siegrist H., *et al.*, 1998; Helmer C., *et al.*,1999). The kind of chemo-autotrophic denitrify process is already named as CANON(Completely Autotrophic N removal Over Nitrite). Based on the ANAMMOX microbiology research(Strous M., *et al.*, 1999), the mathematical simulation technology which is done (Hao X.D., *et al.*,2002) already carried on the theory analysis to CANON each unknown factor and the influence factor, and identified the main influence factor, thus the project application using CANON process will be provided.

A general overview of the different nitrogen pathways and biochemical conversions for traditional is presented by simplified equations in Table 13.(Paredes D. *et al.*,2007) and Table 14. descried the operational characteristics of wastewater treatment processes.

Table 13. Simplified equations for selected microbial nitrogen transformation processes.

No.	Process	Biochemical conversion
1	Nitritification	$NH_4^+ + 1.5\ O_2 + 2\ HCO_3^- \rightarrow NO_2^- + 2\ CO_2 + 3\ H_2O$
2	Nitratation	$NO_2^- + 0.5\ O_2 \rightarrow NO_3^-$
1+2	Nitrification	$NH_4^+ + 2O_2 + 2\ HCO_3^- \rightarrow NO_3^- + 2\ CO_2 + 3H_2O$
3	Denitratation	$2\ NO_3^- + C \rightarrow 2NO_2^- + CO_2$
4	Denitrification via nitrite. (Denitritification)	$4NO_2^- + 3\ C + 2H_2O + CO_2 \rightarrow 2N_2 + 4\ HCO_3^-$
3+4	Denitrification	$4\ NO_3^- + 5\ C + 2H_2O \rightarrow 2N_2 + 4\ HCO_3^- + CO_2$
5	Partial nitrification (50 % conversion)	$NH_4^+ + 0.75\ O_2 + HCO_3^- \rightarrow 0.5\ NO_2^- + 0.5\ NH_4^+ + CO_2 + 1.5\ H_2O$
6a	Anammox (without cell synthesis)	$NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O$
6b	Anammox (with cell synthesis)	$NH_4^+ + 1.32\ NO_2^- + 0.066\ HCO_3^- \rightarrow 1.02\ N_2 + 0.26\ NO_3^- + 0.66\ CH_2O_{0.5}N_{0.15} + 2.03\ H_2O$
1+2+3+4	Traditional nitrification denitrification	$NH_4^+ + 8O_2 + 5\ C + 4\ HCO_3^- \rightarrow 2N_2 + 9CO_2 + 10\ H_2O$
1+6	CANON	$NH_3 + 0.85\ O_2 \rightarrow 0.11\ NO_3^- + 0.44\ N_2 + 0.14\ H^+ + 1.43\ H_2O$
7	OLAND	$NH_4^+ + 0.75\ O_2 \rightarrow 0.5\ N_2 + H^+ + 1.5\ H_2O$

Table 14. Operational characteristics of wastewater treatment processes for nitrogen removal (Ingo Schmidt. et al.,2003)

	Conventional nitrification denitrification	NOx	OLAND	SHARON	Anammox	Canon	Aerobic deammonification
Aerobic ammonia oxidizers	many	N. *eutropha*	unknown	N. *eutropha*	absent	N. *eutropha*	unknown salt tolerant ammonia oxidizer
Aerobic nitrite oxidizers	many	absent	unknown	absent	absent	absent	Nitrobacter
Anaerobic ammonia oxidizers	absent	absent	unknown	absent	*B. anammoxidans, K. stuttgartiensis*	*B. anammoxidans, K. stuttgartiensis*	*K. stuttgartiensis*
Biofilms or suspension NH_4^+ loading (kg N/m^3 reactor day)	biofims/suspension 2-8	suspension	biofims 0.1	suspension 0.5-1.5	biofilms 10-20	biofilms 2-3	bifilms 1-2
N-removal efficiency	95%	95%	85%	90%	90%	90%	60%
Process complexity	separate oxic and anoxic compartments or periods, methanol dosing	separated oxic and anoxic compartments, methanol dosing, membrane for sludge retention	aeration needs to be tuned to ammonia loading	separate oxic and anoxic compartments or periods, methanol dosing	preceding partial nitrification needed	aeration needs to be tuned to ammonia loading	aeration needs to be tuned to ammonia loading
Application status	established	pilot plant	laboratory	two full-scale plants	full scale initiated	laboratory	two full-scale plants
Investment costs	medium	medium	medium	medium	low	medium	medium
Operational costs	high	low	unknown	low	very low	low	low

I.5.6 Phosphorus Removal

Firstly, Srinath et al. (1959) have mentioned the sewage biology dephosphorus phenomenon, the various countries' scientist carries on long reaches for the biological dephosphorus mechanism more than 20 years. However, the early biological dephosphorus research often used the actual sewage treatment process as the main research object, also the attention concentrates greatly the biology absorbs the phosphorus process under the aerobic condition, certainly has not noticed the relations between the phosphorus anaerobic release and aerobic absorb together harmoniously. Until above century the beginning of 80's, Rensink(1981) reported that the phosphorus aerobic absorb with the anaerobic release process exists some kind inevitably contacts. In this foundation, one complete biochemistry metabolism model of the biological dephosphorus then consummates by the following some scientists. Figure 16. demonstrated the biological dephosphorus biochemistry metabolism model which has basically finalized (Mino T, et al.,1998; van Loosdrecht M.C.M, et al.,1997.)

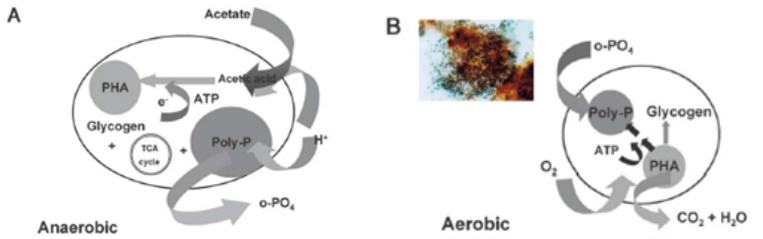


Figure 16. Biochemistry metabolism model of biology dephosphorus (Robert J. *et al.,* 2003)

Generally, under the anaerobic condition matrix (COD) in the sewage is transformed firstly as polymerization matter of the bacteria cell -PHA (namely PHB+PHV, take PHB as principal constituent), in this process cell gathers the phosphate and provides the energy which needs. Finally, the phosphate is released besides the cell. After environment change for aerobic condition, PHB which under the anaerobic oxygen condition stores is used for to act as the matrix because of short of COD in the environment. Under this condition the matrix provides the energy and the bacterium excessive absorbs the phosphate of the environment then forms the poly-phosphate in the cell, simultaneously the bacterium obtains multiplication. In addition, the sugar source also obtains the supplement under the aerobic condition. The bacterium can be separated after the aerobic

condition which multiplies the phosphorus then can be removed along with bacteria cell. PAOs (Phosphate Accumulating Organisms) in the cell phosphorus content may reach as high as 12% (counts by net cell weight), but in the ordinary cell phosphorus content only is 1%-3% (van Loosdrecht M.C.M, *et al.*,1997). Obviously, after the phosphorus biological adsorb bacterium separation may remove effectively the phosphate of sewage.

The function of the biological phosphorus absorbed/release of the amphoteric denitrifying bacteria is confirmed not only opens up the phosphorus removal way, but also more importantly this kind of bacterium which has the phosphorus biological absorb/release function can take organically the denitrification denitrify and the biological dephosphorus gather two to one. This might establish the sewage continual treatment process and apply the development with the extremely powerful technical foundation. As Figure 17 and Table 15. show, under the anoxia condition (oxygen deficit but exists nitric acid nitrogen), denitrifying bacteria DPB(Denitrifying Phosphorus removing Bacteria) can be acted as the electron acceptor like under the aerobic condition using the nitric acid nitrogen, has the similar the phosphorus biological absorbs function. Simultaneously the nitric acid nitrogen can be deoxidized to the nitrogen. Obviously, the denitrifying dephosphorus merged by the DPB the process can save suitable COD and the aerobic capacity, simultaneously also means less synthetic cells.

Table 15. Comparison of different configurations for biological phosphorus removal

Configuration	Advantage	Disadvantage
Phoredox /AO	**-Small and simple system** **-Short residence time**	**-No nitrogen removal** **-In hot or moderate climate the system will not be reliable**
Modified Pre-D / A2O	**-High denitrification rate** **-Short sludge age**	**-Might not function properly (due to recirculation of nitrate)** **-Denitrification incomplete** **-Tendency to induce sludge bulking**
Modified Bardenpho (3 or 5 reactors)	**-Excellent configuration for nitrogen removal**	**-If denitrification is incomplete then nitrate will be recycled to the anaerobic zone, adversely affecting P-removal**
UCT	**-Prevents recirculation of nitrate**	**-The utilization of the denitrification capacity is inefficient.**
Modified UCT	**-Ensures absence of nitrate in the anaerobic reactor**	**-The utilization of the denitrification capacity is inefficient (even more so than in UCT system).**
Johannesburg	**-Efficient use of denitrification reactor**	**-Denitrification incomplete**

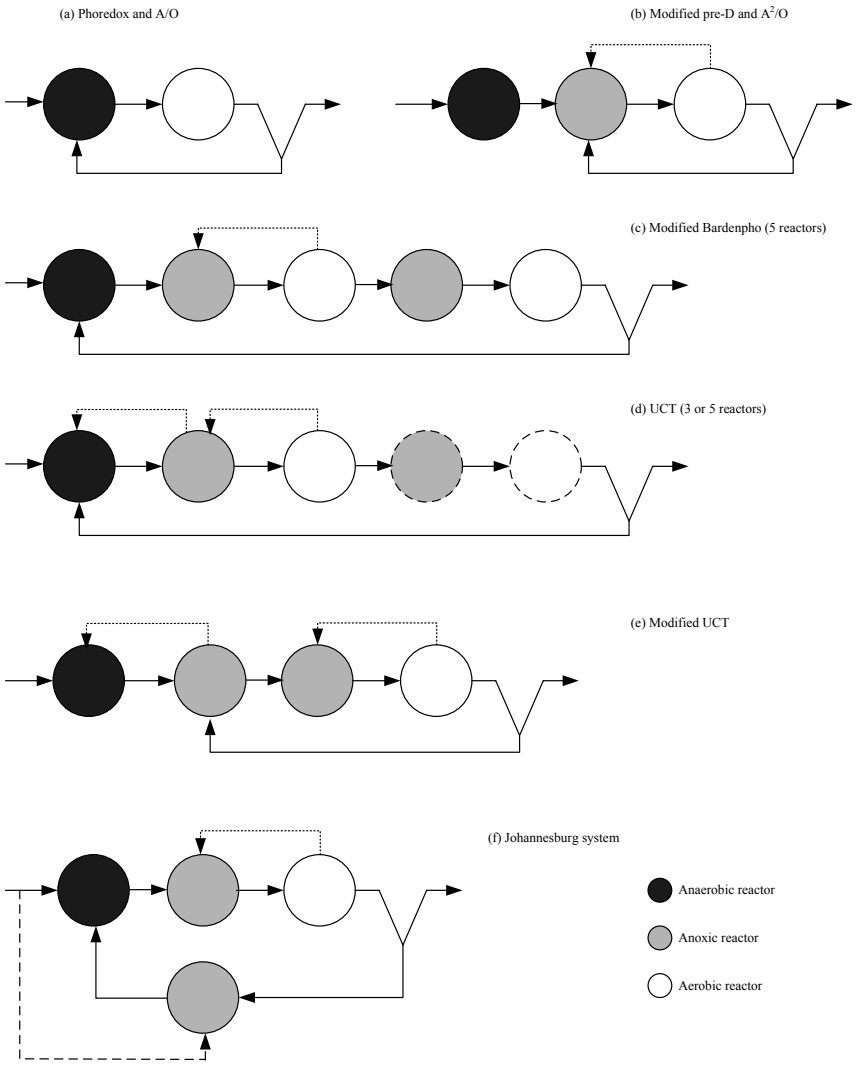


Figure 17. System of phosphorous removals. (Adrianus van Haandel,2007)

I.5.7 Nitrogen and Phosphorus Removal

At present people take solely reduces COD as the goal of sewage treatment process which is not as a rule, the denitrifying and dephosphorus act the main goals (BNR, Biological Nutrient Removal). On the one hand, the effluent discharges whose standard unceasingly enhances; the COD oxidation can consume energy, and disobeys to the sewage continuable treatment concept. From this significance, during the sewage treatment process it should reduce the COD consumption maximum limit and cause the surplus COD change to methane. This kind of concept plays the pivotal role to realize the

sewage continuable treatment.

Therefore study and apply of the new technologies on develop the sewage bio-treatment continuable process have the epoch-making significance, and the impetus function is great. There the principle and engineering practice of the denitrifying dephosphorization are focused on.

Table 16. shows the characteristics of different zones in biological nutrient removal process. In fact the wastewater treatment processes which used nowadays are focused on not only the COD removal, but also the denitrifying and dephosphorization, and the concepts were changed as well. The processes treated the simple contamination no more, the combinatorial goals would be accepted by contraries, therefore the sundry novel processes are effective for all the contaminations. The process assembled neatly under the spatio-temporal condition using the anaerobic, anoxic and aerobic zones and meet the effectual targets.

As above sections mentioned, nowadays the nitrification, denitrification and phosphorus removal play the important role in wastewater treatment and the alternative processes are selected expediently.

Table 16. Characteristics of different zones in the biological nutrient removal process.

Zone	Biochemical transformation	Function	Removed component
Anaerobic	Phosphorus release	Enrichment of PAOs[a)]	Phosphorus
	Formation of readily biodegradable organic matter by fermentation		Carbon
	Uptake and storage of volatile fatty acids by PAOs		
Anoxic	Denitrification	Reduction of NO_3-N to N_2	Nitrogen
	Metabolism of exogenous substrate by facultative heterotrophs	Selection of denitrifying bacteria	Carbon
		Uptake of PO_4 [b)]	
	Production of alkalinity		Phosphorus
Aerobic	Nitrification	Oxidation of NH_4-N to NO_2-N and/or NO_3-N	Nitrogen
	Consumption of alkalinity	Nitrogen removal via gas stripping	
	Phosphorus uptake	Formation of polyphosphate	Phosphorus
	Metabolism of stored and exogenous substrate by PAOs	Uptake of PO_4 [c)]	
	Metabolism of exogenous substrate by heterotrophs		Carbon

a) Phosphate-accumulating organism.
b) In the presence of easily biodegradable organics, nearly all the PO_4-P is taken up.
c) If all the easily biodegradable organics are used in the anoxic stages without complete PO_4-P uptake, additional PO_4-P is removed within the aerobic stage using organic lysis product.

I.6 Conclusions

The literature review was concerned to give a progress report on four necessary fields for the development and optimization of the process including equipment, process, microorganisms state and factors of wastewater treatment.

Among the available different processes, the fluidized bed bioreactor (FBBR) seems to be the best one and present many advantages relating to hydrodynamics and mass transfer phenomenon. The use of fluidization in biotechnology field gained considerable importance. And it is applied widely in biological wastewater treatment and obtained the satisfied results. During the operational process, the practicability and advantages of SBR are observed. The multifarious SBR processes were innovated and used in different occasions. Along with the computer technology development, SBR would have the more capacious application foreground in future. SBR would be indispensable actor in the wastewater treatment field. Nowadays, people pay attention to the activated sludge and biofilm usually. Although both have the advantages and disadvantages respectively, there are the suitable application as well. People focus the interesting on the biofilm development and the combined process bring into play the excellences. Summarized the wastewater treatment processes, the nitrification, denitrification and phosphorus removal technologies are developed as well.

Our work use the equipment (extra-loop fluidized bed) in which the biofilm and activated sludge coexist, and operate the model of the sequencing bath reactor, consider the carbon, nitrogen and phosphorus removal and the process optimization.

Chapter II. Results and Discussion

II.1 Experimental Studies of a Novel Extra-loop Fluidized Bed Bioreactor (EFBBR) Part I: *Hydrodynamics and Oxygen Transfer*

The performance and characteristics of reactor are the important parameters to estimate the reactor. The mixing time characterizes the mixing degree and judges the validity of the reactor. The oxygen transfer is an extremely important process in many biological systems. The oxygen is the foundation that the aerobic microorganism depends on for existence, and in water the transmission path is closed to the biodegradation of the carrier which covered on with the biofilm, maintains the reactor operates normally and reduces the consumption. In this section, the innovative apparatus which called a novel extra-loop fluidized bed bioreactor (EFFBBR) was developed. A laboratory-scale experiment employing the pouzzole or PVC tubes as a carrier media was performed and the hydrodynamic characteristics and mass transfer were demonstrated.

Experimental Studies of a Novel Extra-loop Fluidized Bed Bioreactor (EFBBR)

Part I: *Hydrodynamics and Oxygen Transfer*

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Abstract: In this paper the characteristics of fluid mixing time in a novel extra-loop fluidized bed were studied. The results showed that: the mixing time was been shortened with the increase of fluid velocity. All the discrete numbers of the reactor were above 0.2. The serial number *n* was 2.5~3. It was judged accordingly that the reactor fluid state was CSTR mainly. When the inspiratory capacity increased the mixing time of the reactor was shortened. Thus the air input was beneficial for the fluid mixing. During the three phases mixing process, the mixing time of the reactor could be decreased by the n increase of carrier and air loading together, but the change was not significant. The parameters affecting the reactor fluid state were fluid velocity, inspiratory capacity and carrier. The inspratory capacity maximum can ascend quickly following an increase of the liquid velocity and the acceleration was also quick. The inspratory capacity Qg can be described as $Q_g = 190.35\{(\rho \cdot \frac{u_1^2}{2})[(\frac{S_1}{S_2})^2 - 1]\} - 95.088$.

K_{La} can be increased following the air loading increase, and at the same gas/liquid ratio when the pressure drop was high, K_{La} value was increased. The amount of carrier had a complex influence on K_{La}. As the carrier loading continued to increase, its value has the dropped but the changes was not significant and optimization condition was found at above 800-1000g carrier loading (Pouzzolane) or 600g (PVC). Under gas/liquid ratio of 0.8-5.2%, K_{La} was be 0.62-1.37 10^{-2} s^{-1}.

Key words: extra-loop fluidized bed, mixing time, oxygen transfer, fluid velocity, Venturi aero-ejector, carrier

Nomenclature

$\frac{D}{UL}$	discrete number
φ	random variable
σ_{φ}^{2}	random variance
θ	residence time of each reactor (s)
C	concentration of the reactor (V)
C^*	dimensionless concentration
C_0	original concentration of the reactor (V)
C_n	concentration of the n^{th} reactor (V)
D	diffusion coefficient
K_{La}	volumetric mass transfer coefficient (h^{-1})
n	serial number
Qc	Circulation flow (m^3/s)
Q_g	inspratory capacity (gas) (L/h)
r	reaction rate
S_1,	area of the circle pipe and (m^2)
S_2	Area of Venturi aero-ejector pipe
t	average mixing time (s)
U	average velocity of the flow (m/s)
u_1	liquid velocity in the circle pipe (m/s)
Z^*	dimensionless length
ΔP	pressure drop of the Venturi aero-ejector (pa)
ρ	liquid density (kg/m^3)

1 Introduction

The fluidized bed reactor is one kind of reactor which carries on the mass transfer or heat transfer operation using the fluidization concept. The fluidized bed reactor has a history of several dozens of years. At first it was mainly used in the chemical synthesis and the petrochemistry industry. Because this kind of reactor displayed in many aspects its unique superiority, its application scope was enlarged gradually to metal smelting, air purification and many other fields [1]. Since 1970's [2], people have successfully applied the fluidization technology to the wastewater biochemical process field.

Nowadays, with the advantages of simple mechanical design, better mixing and improved capacity, the airlift reactor has gained much attention from researchers and manufacturers [3]. Numerous investigations have been made on the performance and characteristics of such reactors [4,5]. Much work has been conducted on the reactor structures and the hydrodynamics of the multiphase flow [6.7], such as the liquid circulation velocity and the average gas holdup in the reactor [8,9]. The mixing time, is a parameter of particular importance for design, modeling and operate [10-13]. About 20 years ago, Chisti and Moo-Young [14] investigated the hydrodynamics and oxygen transfer in airlift reactor, and predicted liquid circulation velocity reactors with biological media. For the airlift reactors containing a three-phase flow (TPAL), the hydrodynamic behavior in internal-loops and multiphase mass transport in the external-loop have been studied by Livingston and Zhang [15] and Mao *et al*. [16]. Many workers have paid much attention in the field of airlift reactor investigations [17-22]. In recent decades external loop reactors are gaining interest for application in bioprocesses, wastewater treatment and chemical industry due to following advantages [23]: simple construction without internals or moving parts, good mass transfer capacity and mixing properties as the gas phase in the reactor serves the dual functions of aeration and agitation.

With the biological fluidized bed technology innovated gradually, people have tried to use many different carriers as the solid-phase, such as zeolite, activated carbon [24], plastic ball [25], basalt [26] and Chalk [27], etc. Xing *et al.* [28] presented a single continuous-flow fluidized-bed bioreactor system consisting of porous carrier particles for

retaining microbes, the system was constructed to simultaneously remove carbonaceous and nitrogenous substances in wastewater under different C/N (mass ratio) values. A TOC removal of >91% and a maximum total nitrogen removal of 85% were achieved under a moderate C/N value. TiO_2-coated mm-size spherical ceramic particles, which are very stable for dynamical impact and whose specific density is very near to unity were developed and applied to a fluidized bed reactor for water purification. Tatsuo Kanki *et al* [29] prepared two types of test-scale fluidized bed photocatalytic reactors. It was shown that aqueous phenol and bisphenol A can be decomposed rapidly in about 200 min and TOC originated from their byproducts can eventually be mineralized in a short time of 300 min. Thus solid-phase carrier choice plays an important role in the fluidized bed for wastewater treatment.

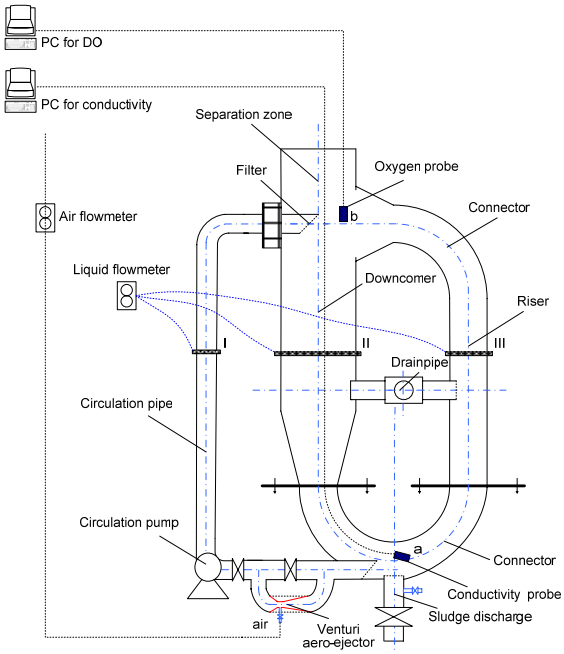
Oxygen transfer is an extremely important process in many biological systems. Oxygen is the foundation that aerobic microorganisms depend on for existence. Different types of the reactors and carriers have different oxygen transmission paths. The efficient oxygen transmission can guarantee sufficient dissolved oxygen. In the reactor the water current will be mixed fully with aeration, and form turbulent flow. That lets the water and the biofilm contact, enhances mass transfer efficiency, promotes biofilm renewals and prevents carriers' escape [30,31]. Therefore, study oxygen transmission characteristic in the reactor, strengthen and spread the performance, seek the rational air supply way and realize the greatest coefficient of oxygen utilization, study and develop biofilm characteristics, which is one of the important routes of the craft innovation. Fluidized-bed with circulation can enhance oxygen transmission is an effective method for enhancing transmittance $K_{La.}$ For this reason, this research exams the effects of on $K_{La.}$ different gas flow amount with a novel aeration method and different gas/liquid rates, carrier loading

In this study a novel extra-loop fluidized bed is investigated without considering biochemistry responses, whose the mixing time is critical to reactor performance. This research determines the mixing time and through a modeling approach, analyzes its hydrodynamic characteristics.

2 Experiments and methods

2.1 Laboratory-scale fluidized bed

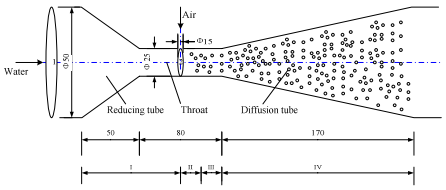
Figure1 shows the schematic diagram of the extra-loop fluidized bed reactor, which is made of PVC. The reactor is composed of a riser and a downcomer and a circulation pipe, whose inner diameter is 100mm, 200mm and 50mm, respectively. The working height is 1.0m with the total working volume of 38L.



(a) extra-loop fluidized bed

Table 1. Parameters of the extra-loop fluidized bed reactor (EFBBR)

Index	
Total height t of FB (m)	2.2
Effective height of riser (m)	1.0
Inner diameters of riser (m)	0.1
Effective height of downcomer (m)	0.8
Inner diameter of downer (m)	0.2
Effective volume (L)	38
Replace the volume (L)	25



(b) Venturi aero-ejector

Figure 1. Schematic diagram of the experimental apparatus (with Venturi aero-ejector)

Venturi aero-ejector

The Venturi aero-ejector is one kind of the aeration equipments whose inspiratory collection and mixing operate simultaneously. Its internal structure divides into the reducing pipe, the throat, the air feeder and the diffusion tube, as shown Figure 1(b).

The flow state may divide into 4 stages:

1. The liquid continual motion stage (I). The pressurized water is from the water pump and enters the reducing pipe blowout, this jet flow is close-grained and columnar, passes the reducing pipe and in front of throat section.

2. The relative motion between liquid and gas section (II). Because of the agglutination between the jet flow boundary layer and the gas, the kinetic energy of the high speed water current forms negative pressure in the throat, the gas is brought to enter the throat, and the two phases moved relatively. Both phases are continuous media. Its experience section is in the middle and back end of the throat.

3. Liquid drop movement section (III). As a result of the scattering of the liquid particles, the liquid is cutted and dispersed into liquid drop, the drop through striked with the gas membrane whose collision can bequeath the energy to the gas, thus gas is accelerated and compressed. In this section, the liquid is the continuous media. Its experience section is the back end of the throat.

4. The water with dissolved gas movement section (IV). As it passes through the diffusion tube and velocity head is transformed to discharge head, the tiny air bubble is compressed further, solubility of the air in the under-water is increased, formed the water with dissolved gas, and the liquid drops re-got together as the liquid phase continuous media.

Finally the water with dissolved gas is blowout from the jet flow diffuse tube. The turbulent agitation is intense in the basin. The massive oxygen dissolved in the water with the small air bubbles, completes the oxygen transfer process.

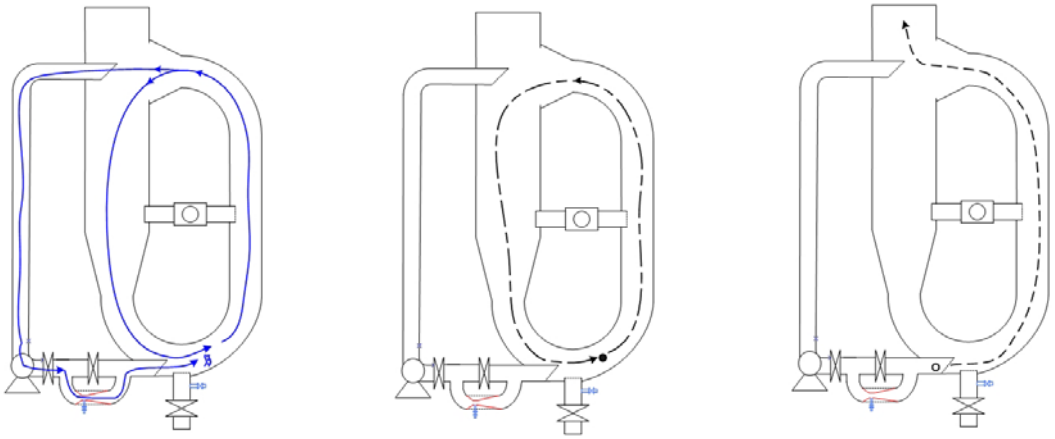
From this process, in sections III IV, the interface area which the fluid and the gas contact is quite big, enhancing mass transfer. Therefore, the Venturi aero-ejector is one kind of highly efficient mass transfer oxygen replenishing equipment.

When there is no need for increasing dissolved oxygen, through water pump supplying high pressurized water with spray nozzle blowout, liquid stirring can be completed.

2.2 Operating conditions

The fluidization is realized by controlling the flow of the circulation pump. The Venturi aero-ejector is the gas device whose flow is controlled by the circulation pump and the air flowmeter. Figure 2 shows the liquid, solid and gas circulations in the

fluidized bed.



(a) Liquid cycles (b) Solid cycle (c) gas cycle

Figure 2. Liquid, solid and gas circulations in the fluidized bed

- *Liquid cycles (2 cycle)*
  No.1 riser → upconnector → downcomer → subconnector
  No.2 riser → upconnector → circulation pipe → Venturi aero-ejector (selective) → subconnector
- *Solid cycle (1 cycle)*
  riser → upconnector → downcomer → subconnector
- *Gas cycle (semi-cycle)*
  Venturi aero-ejector (selective) → subconnector → riser → upconnector → separation area

Liquid cycle:

When the circulation pump operates, there are two cycles in the fluidized bed. First the pump inhales water which runs through the filter from top of the bed (upconnector) to the circulation pipe. Then the water passes the Venturi aero-ejector to the riser part by the subconnector. Simultaneously the water carries out the other cycle, passing the upconnector, downcomer, subconnector orderly, and back to the riser finally.

Solid cycle:

With the circulation pump in operation, the solid medium achieves its fluidization state. The solid can be fluidized in the riser and the upconnector. Due to gravity, the solid will drop from the upconector to the downcomer and return to the bottom of the bed. Then another cycle begins continuously.

Gas cycle:

Also because of the circulation operation, the Venturi aero-ejector which is installed

as a bypath inbreathes the air from the feed-tube that connects with the outside atmosphere. The air will be diffused. The mixing air carries out the cycle from the bottom through the riser to the upconnector, and releases back to the atmosphere at the separation zone.

2.3 Materials

In this study the pouzzole or PVC tubes were used as the carriers. Their physical properties are shown in Table 2. and Figure 3.

Table 2. Physical properties of the carriers

Type	Range of diameter(mm)	Ture density(g/mL)	Stacking density(g/mL)
Pouzzolane (brown)	1~10	2.30	0.83
Pouzzolane (black)	4~8	1.72	0.70
PVC tube	ϕ10(s=1mm), H=10-15mm	1.2	0.387

(a) Pouzzolane (brown) (b) Pouzzolane (black) (c) PVC tube

Figure 3. photos of the carriers

2.4 Methods

The experimental medium is the tap water at the normal temperature, makes the tracer made of NaCl (C.P.) solution is injected into the system at point "b" (see Figure1.) pulse of the tracer was injected at a volume of 10mL NaCl (0.5g/L). The experimental process fluid state is stable. Using conductivity meter (ponselle mesure CTCEN) at point "a"(see Figure1.) fluid conductivity change was determined to monitor in the reactor the

intermixture NaCl density change. Conductivity is recorded by a PC for direct testing. Simultaneously the circulation liquid velocity was determined with the flowmeter (Greyline PDFM-IV).

The volumetric mass transfer coefficient was determined by a physical dynamic method. The liquid was deoxygenated by stripping with $Na_2S_2O_3 \cdot 5H_2O$ (A.R.) with $CoCl_2$ (A.R.) as the catalyzer. The dissolved oxygen (DO) concentration in the solution was measured until equilibrium was reached. DO was measured continuously by polarographic dissolved oxygen electrodes connected to a dissolved oxygen meter (Sonde Orbisphere Modele 3600) and recorded using a PC based data acquisition system. The electrode response time was determined by the amount of time required to record the saturation DO concentration after a step change in concentration. The volumetric mass transfer coefficient K_{La} was determined by the dynamic method described by Chisti [32] and Benyhaia *et al* [33].

2.5 Hydrodynamic model

There are two methods for studying the fluid state of reactor:

1 discrete model

Generally the fluid state of the actual reactor is between a PFR (plug flow reactor) and a CSTR (continuous stirred tank reactor). Thus there is longitudinal mixing to a certain degree. Put the mixing effect to each cross section of the PFR and a model that approximates to the actual reactor can be received. Such a model is called a discrete model. Based on the mass balance equation the normal derivative equation of the discrete model can be described as follows:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial Z^2} - U\frac{\partial C}{\partial Z} + r \qquad (1)$$

In the tap water experiment, the tracer is conservative, so r=0. Using C*, φ, Z* respectively for dimensionless concentration, time and length, equation (1) can be written as:

$$\frac{\partial C^*}{\partial \varphi} = (\frac{D}{UL})\frac{\partial^2 C^*}{\partial Z^{*2}} - \frac{\partial C^*}{\partial Z^*} \qquad (2)$$

$\frac{D}{UL}$ is a discrete number. It means the degree of the longitudinal mixing, or back mixing. When $\frac{D}{UL}$ is close to 0, the fluid state belongs to PFR，on the other hand when $\frac{D}{UL}$ tends to infinite, the reactor belongs to CSTR. The actual reactor is somewhere in bewteenness.

As long as the back mixing is not signifiable, the solution of the equation (2) is:

$$C^* = \frac{1}{2\sqrt{\pi \cdot \frac{D}{UL}}} \exp\left[-\frac{(1-\varphi)^2}{4 \cdot \frac{D}{UL}} \right] \qquad (3)$$

It is consistent with the Gaussian distribution. The variance σ_φ^2 of the random variable φ can be calculated:

$$\sigma_\varphi^2 = 2 \cdot \frac{D}{UL} \qquad (4)$$

When the back mixing increases, σ_φ^2 can be calculated with $\frac{D}{UL}$ as:

$$\sigma_\varphi^2 = 2 \cdot \frac{D}{UL} - 2 \cdot (\frac{D}{UL})^2 (1 - e^{-\frac{UL}{D}}) \qquad (5)$$

σ_φ^2 can be derived with a C-t curve in the actual reactor，and $\frac{D}{UL}$ can be obtained as well. The fluid state characteristic can then be estimated.

2 Serial CSTR models

The actual reactor can also be simulated as a series of the ideal CSTR combined equal in volume. As soon as the reactor is made up of n CSTR series combination, the tracer concentration C_n of n^{th} reactor outlet is shown below:

$$C_n = \frac{1}{(n-1)!} C_0 \left[\frac{t}{\theta}\right]^{n-1} e^{-t/\theta} \qquad (6)$$

Where θ is the residence time of each reactor, C_0 is the concentration of the first CSTR at t=0. The total residence time of the reactor is $n\theta$. Equation (6) descried dimensionless:

$$C^* = \frac{1}{(n-1)!} (n\varphi)^{n-1} e^{-n\varphi} \qquad (7)$$

The random variance of the function is $\sigma_\varphi^2 = \frac{1}{n}$ (8)

The serial number n reflects the back mixing degree. When n=0, the reactor is a PFR. On the other hand, when n=1, the reactor is a CSTR. The actual reactor is somewhere in bewteenness.

3 Results and discussions

3.1 Single phase

In this study the fluid circulation is operated with an external force (the circulation pump). Different fluid velocity leads to different mixing effectiveness. Figure4 shows the results under different velocity.

The diagram shows that the time curve changed its periodicity and the fluid state such as circulation characteristic of the reactor is been rendered as well. Based on the fluid state models, the average mixing time t, random variance σ_φ^2, discrete number $\frac{D}{UL}$, CSTR serial number n can be obtained.

Obviously the mixing time is shortened with the flow rate increased (showed in Figure 5.). When the circulation rate is 0.283 m^3/s, the pilot needs a long 125 s to reach a complete mixing. As the circulation rate increases, the mixing time decrease. The results show that when the circulation rate is 1.632 m^3/s, mixing is achieved in only about 22s.

They also show that the circulation velocity and the mixing time are the linearly correlated with a negative slope. All the discrete numbers of the reactor are greater than 0.2 (showed in Figure 6.), indicating the presence of back mixing in the reactor to some extent. Moreover the serial number n is between =2.5~3, suggesting that the reactor fluid state is CSTR mainly.

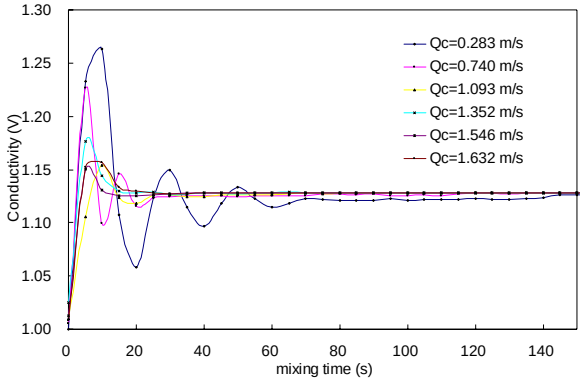


Figure 4. Diagram of circulation time

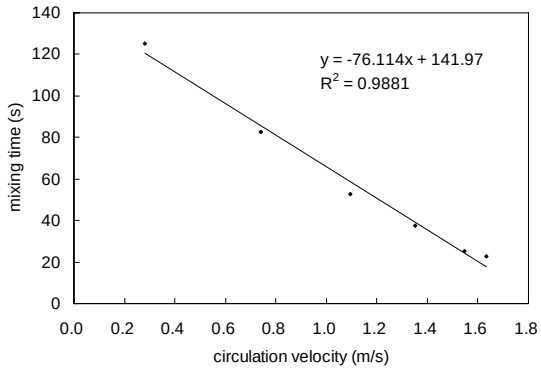


Figure 5. effect of circulation velocity on mixing time

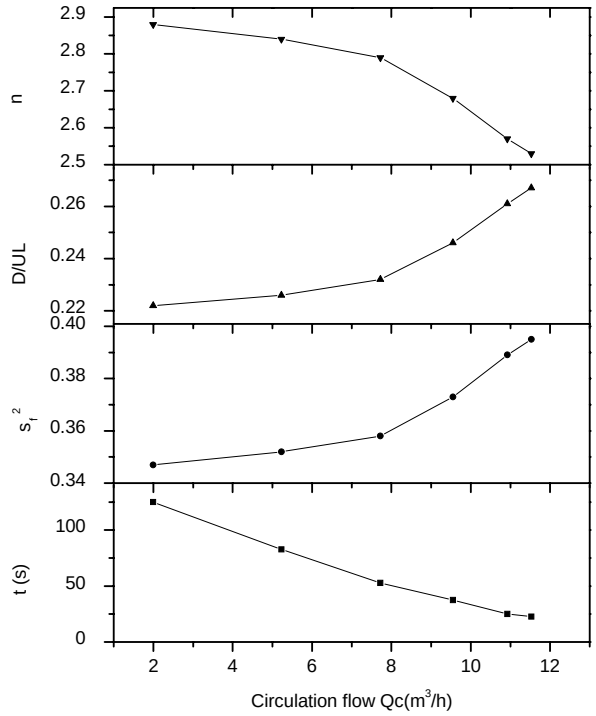


Figure 6. Discrete number and serial number under the different fluid velocity

Generally mixing time and circulation time would be inspected at the same time when the hydrodynamic characteristics are discussed. There mixing time expresses the duration required to completely mix added material in the reactor. Influencing factors are fluid circulation velocity, the installation structure, mixedness, and so on. Circulation time represents the duration required for the fluid to complete one circulation in the reactor. Because the mixing time of the reactor is too short, and the reactor is used as the equipment for wastewater treatment, so the circulation time can be omitted basically.

3.2 Two phase

Inspiratory capacity

The Venturi aero-ejector is the gas device and guarantees air supply. Inspiratory capacity is controlled by the air flow meter as long as the on-off rate of the valve on the circulation pipe is fixed. The experimental results showed that: when the inspiratory capacity increases the fluid circulation velocity also increased, but the amplitude of the latter is less than 5% of the former. Figures 7a,b show the results under different circulation flows and inspiratory capacities as follows.

Obviously when the inspiratory capacity increased the mixing time of the reactor were shorten when using the pouzzolane brown as carrier. Thus the air input is beneficial for the fluid mixedness. The results show that the circulation flow was between 10.32 and 10.75 m^3/h, the inspiratory capacity was changed from 0 to 500 L/h. That means that under high circulation flow, the mixing time can be decreased from 37.60 to 25.13s. The air addition can shorten the mixing time because the air can increase the turbulence of the fluid. The fluid state is also changed. The discrete number increases introduced that the degree of the back mixing was increased as well. And the serial number decreases also testified that the fluid state tended to become CSTR even more with the air addition. However the influence range was not large according the results.

When PVC tubes used as the carrier, the fluid state tended to become CSTR as well. The results show that the circulation flow was between 6.893 and 6.988 m^3/h. When the inspiratory capacity was changed from 0 to 120 L/h under a high circulation flow, the

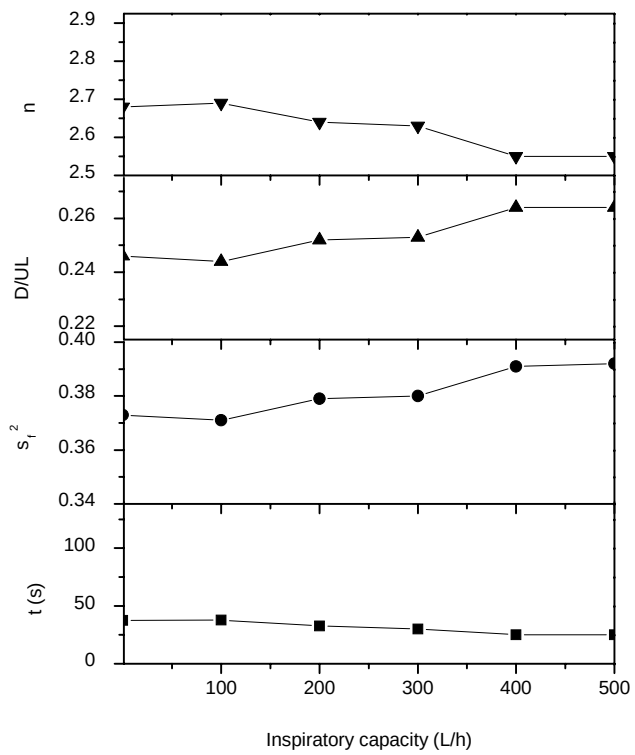
mixing time followed from 35.22 to 28.01s. While the discrete number and the serial number changed irregularly.

Compared different circulation flows with inspiratory capacities, it can be found that under low circulation flows, the fluid state changed mildly and the mixing time was shortened lightly. The inspiratory capacity played an important role, nevertheless, although to a lesser degree.

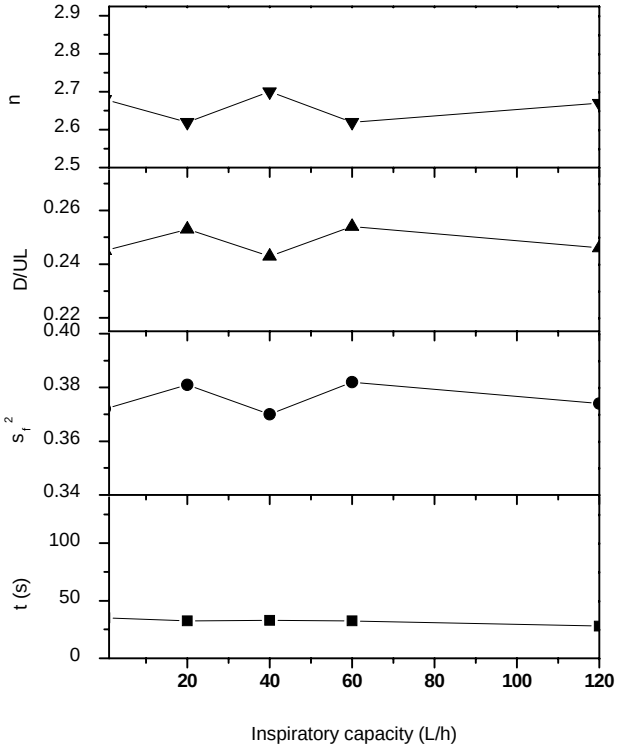
Carrier

As long as the on-off rate of the valve on the circulation pipe is fixed, and the carrier can circulate in the reactor. It was found that increasing the carrier capacity different affect the fluid circulation velocity during the operation. Figure8 shows the results as follows.

Similarly drawn into the carrier can stand the fluid mixedness in good stead, and the fluid state tended to become CSTR even more, and the phenomenon existed with the carrier loading certainly and was independent of to the quantity. For example, under the circulation flow of 9.553m^3/h and with the pouzzolane brown as the carrier, the mixing time can be changed from 37.60 to 25.19s (Figure 8a). The result shows that he carrier loading can affect the turbulence of the fluid but the reactor can be complex. When the pouzzolane black was the carrier, although the fluid state happen the analogous rule whose mixing time would be shortened, but not be orderliness. Because the density of the pouzzolane black is smaller than the brown, in the fluidized bed the pouzzolane black carrier solid collided and frictioned with each other, thus the fluid state was more comply than others. When the PVC tubes were the carrier, because of the holes the fluid state changed irregularly as well. When the carrier capacity becomes large, the disadvantage would come into being. For example, when the pouzzolane black capacity exceed at 1000g the reactor mixing time would increase, the fluid state would be tardiness. So the carrier can stand the fluid mixedness in good stead and whose capacity would be testified. When using the PVC tubes as the carrier, the fluid state also can be called as CSTR.



(a) Circulation flow Qc(m^3/h)=[10.32, 10.75]



(b) Circulation flow Qc(m^3/h)=[6.893, 6.988]

Figure 7. Discrete number and serial number under the different inspiratory capacity

3.3 Three phases

With the on-off rate of the valve on the circulation pipe fixed, and the pouzzolane brown or PVC tubes at 600g used as the carrier, and the Venturi aero-ejector supplying the air, mixing in the reactor as a function of inspiratory is shown in Figure 9.

The results show that during the three phase mixing process, the mixing time of the reactor can be decreased by either the carrier or air supply. However the change is significant when all liquid, solid and gas three phases existed in the same pilot, the fluid state was complex. As a whole the mixing time can be shortened and the fluid state can be called CSTR, although the carrier's collided and frictioned with each other, and the bubble's combination and decentralization.

By comparing all the results, it can be found that the parameters affecting the reactor fluid state are fluid velocity, inspiratory capacity and carrier, in the order of high to low effect.

3.4 Operation Curve of Venturi aero-ejector

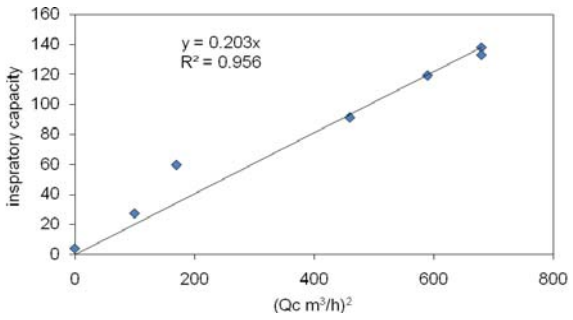
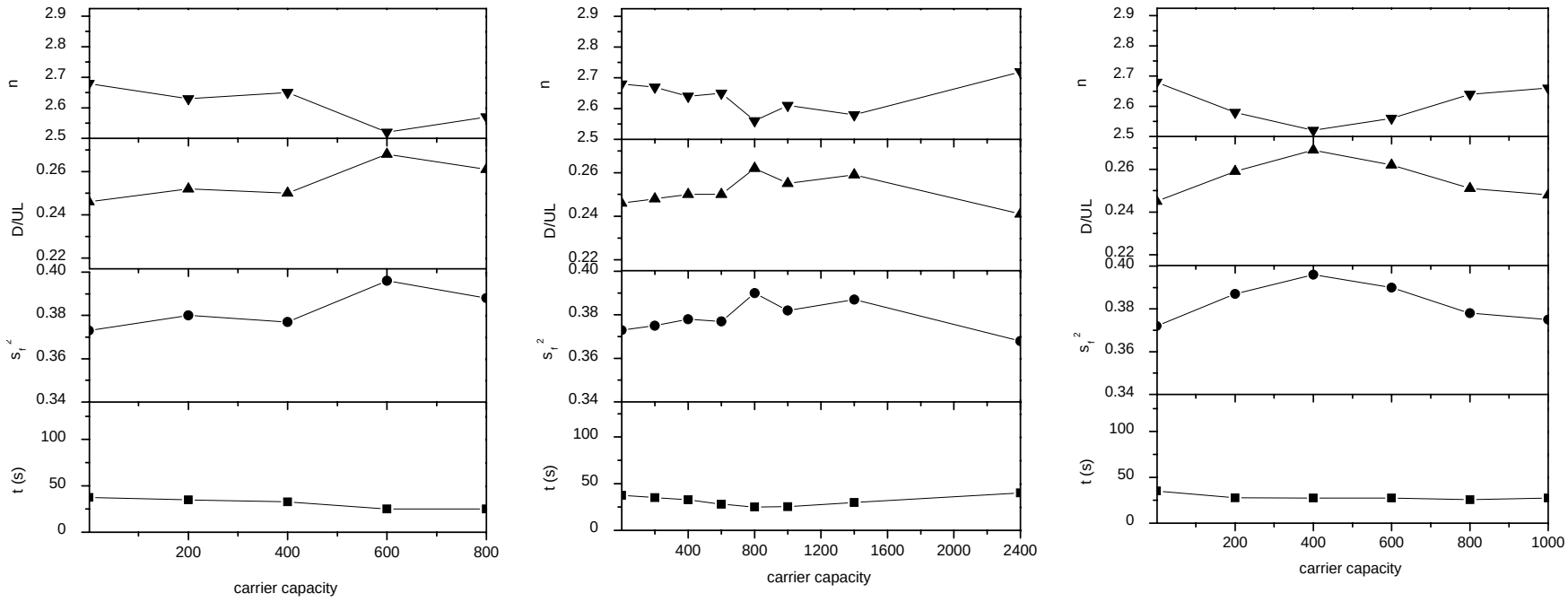


Figure 10. Effect of circulation velocity on inspiratory capacity maximum

The operation curve of the Venturi aero-ejector is shown in Figure 10. Obviously the results showed that: when the liquid velocity was slower, the inspratory capacity became smaller and the increase trend was tardiness as well. There were the hydro-resistance and friction at the Venturi aero-ejector start-up. However the inspiratory capacity should overcome these resistances. On the other hand the inspiratory capacity maximum can ascend quickly following the liquid velocity and its acceleration is also quick. This is because the hydro-resistance and friction increases slowly and meets the maximal. Fortunately it can be found that the liquid velocity of 8m/s is one locus point.

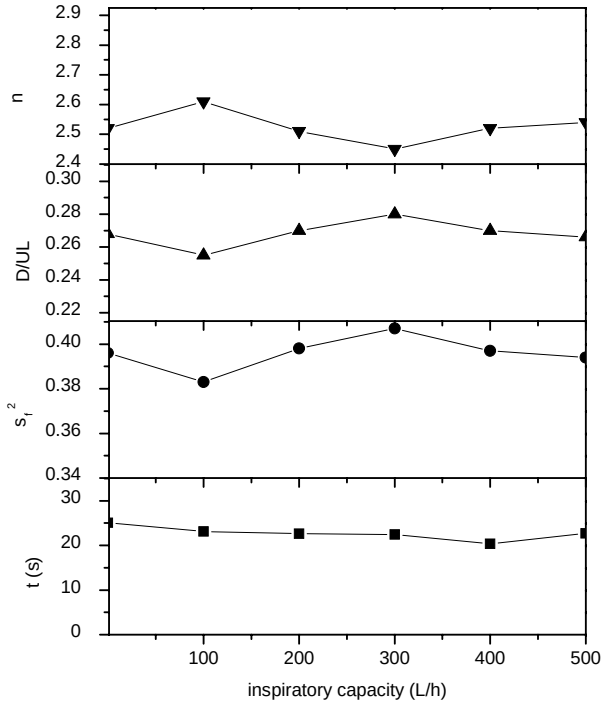


(a) Circulation flow Qc=9.553m^3/h, pouzzolane brown

(b) Circulation flow Qc=9.553m^3/h, pouzzolane black

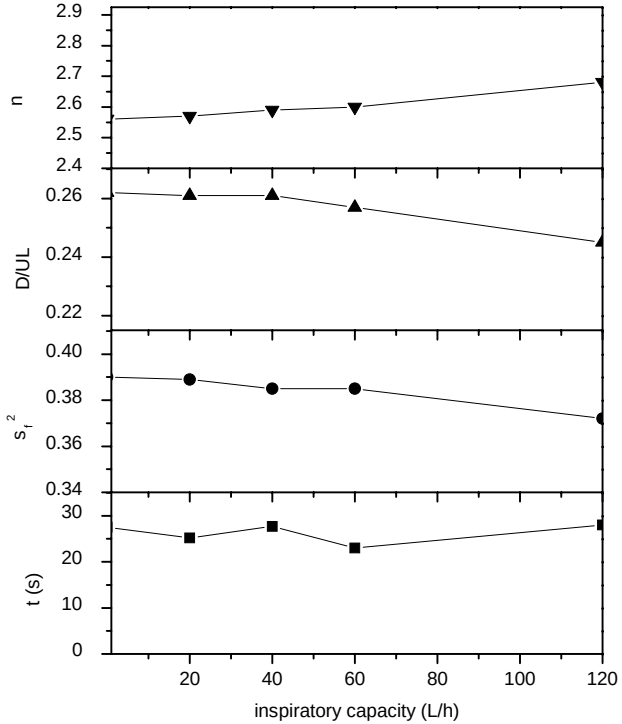
(c) Circulation flow Qc=6.966-7.254m^3/h, PVC tube

Figure 8. Discrete number and serial number under the different carrier capacity



(a) carrier capacity (600g), Circulation flow Qc=9.553m^3/h,

(pouzzolane brown)



(b) carrier capacity (600g), Circulation flow Qc=6.998-7.111 m^3/h

(PVC)

Figure 9. Discrete number and serial number under the three phases mixing

Base on the principle of the Venturi aero-ejector, Qg can be described as:

$$Q_g = 190.35\{(\rho \cdot \frac{u_1^2}{2})[(\frac{S_1}{S_2})^2 - 1]\} - 95.088 \quad (9)$$

$$\Delta P = P_2 - P_1 = (\rho \cdot \frac{u_1^2}{2})[(\frac{S_1}{S_2})^2 - 1] \quad (10)$$

3.5 Gas/Liquid Rate

Pouzzolane brown

The influence of gas/liquid rates on K_{La} is shown in Figure11 and Figure12. The results show that : K_{La} was increased when the air loading was higher. And the formulas for K_{La} are depicted in Table 3. From the results shown in Figure 12, at the same gas/liquid ratio but different corresponding pressure drops, K_{La} value is higher with a higher pressure drop.

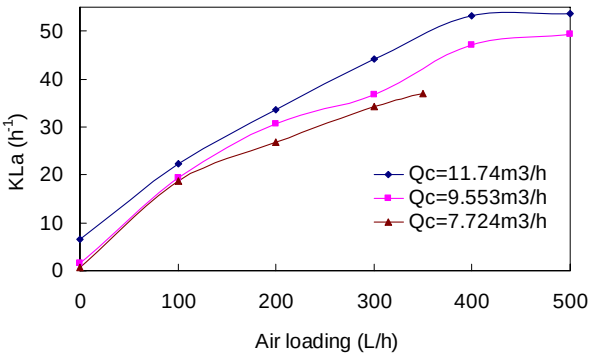


Figure11. Effect of air loading on K_{La} under different liquid velocity

Table 3. The formula for K_{La}

Qc (m^3/h)	K_{La} (h^{-1})	R^2	ΔP
11.74	K_{La} =1138.2Qg+11.371	0.9458	4.14
10.92	K_{La} =896.4Qg+7.33	0.9437	2.32
7.742	K_{La} =217.81Qg+3.8158	0.9493	1.64

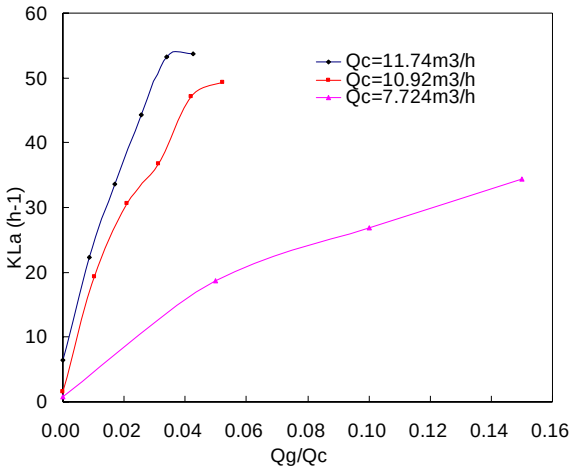


Figure 12 Effect of gas/liquid rate on K_{La}

PVC tubes

The influence of gas/liquid rate on K_{La} with PVC tubes is shown in Figure13 and Table4. The results show that K_{La} can be increased as air loading increases.

Table 4. Effect of air loading on K_{La} (Ws=0)

Qg(L/h)	0	20	40	60	120
K_{La} (h^{-1})	1.1483	4.1798	6.6367	7.3235	12.811

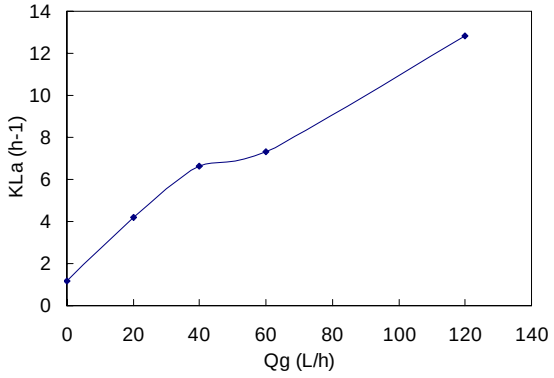
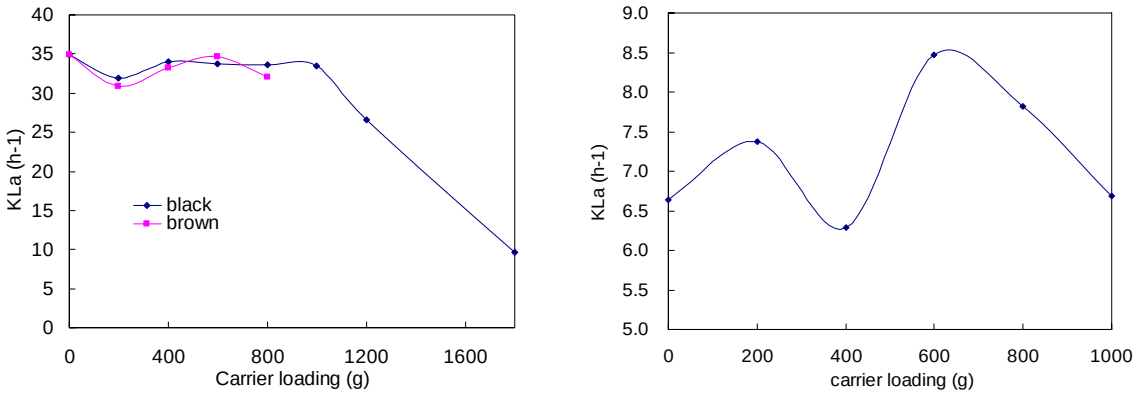


Figure 13. Effect of air loading on K_{La} under different liquid velocity

3.6 Carrier Loading

The amount of carrier exerts complex influence to K_{La} (shown in Figure14). When gas flow was at 10.92m^3/h, the carrier (Pouzzolane brown) increased from 0 to 200g (Ve = 38L), K_{La} dropped little (Figure 14a). As carrier loading continued to increase, K_{La} value also dropped but the changes was not significant, This phenomenon can be attributed to the complexity of the K_{La} function: On the one hand the carrier introduction can destroy big air bubbles causing to the fluid contact area to increase, hence enhancing oxygen transmission, on the other hand the carrier may prorate air bubbles to gather causing to the fluid contact area to reduce, and inhibiting oxygen transmission. There two effects can cancel out each other. However the negative effects eventually become dominant. For example, when the Pouzzolane (black) loading exceeded 1000g (Ve = 38L), K_{La} dropped suddenly and the carrier seat to the bottom of the reactor. It can be found that the optimization condition is above 800-1000g (compactness was between 21.05 and 26.32 g/L).(see Figure 14a)

When using the PVC tubes as carrier, the K_{La} change was complex as well. Based on the results the optimization condition was about 600g.(see Figure 14b)



(a) Pouzzolane (b) PVC tube

Figure 14. Effect of carrier loading on K_{La}

4 Conclusions

It was shown that the mixing time was shortened when the fluid velocity was increased, and all the discrete number of the reactor were above 0.2. Thus the back mixing existed in the reactor to some extent. Moreover the serial number n was 2.5~3. it was judged accordingly that the reactor fluid state showed CSTR characteristics mainly.

When the inspiratory capacity increased the mixing time of the reactor would be shortened. Thus the air input was beneficial for fluid mixing. The discrete number increase suggested that the degree of the back mixing increased as well. And the decrease of the serial number testified that the fluid state tended to become CSTR even more with the air addition. But the influence range was no significant.

Similarly drawn into the carrier can stand the fluid mixings in good stead, and the fluid state tended to become CSTR even more. This phenomenon existed certainly for the carrier loading. When the carrier capacity was too large, the disadvantage would come into being.

During the three phases mixing process, the mixing time of the reactor can be decreased by the carrier and air together, But the change was not significant.

By compared all the results, it can be found that the parameter affecting the reactor fluid state were fluid velocity, inspiratory capacity and carrier.

The inspiratory capacity maximum can ascend quickly following an increase of the liquid velocity and acceleration was also high. Base on the principle of the Venturi aero-ejector, Qg can be described as

$$Q_g = 190.35\{(\rho \cdot \frac{u_1^2}{2})[(\frac{S_1}{S_2})^2 - 1]\} - 95.088$$

K_{La} can be increased following the air loading increase, and at the same gas/liquid ratio. However the corresponding pressure drop was different, the pressure drop was higher when K_{La} value was increased.

The amount of carrier used had a complex influence on the K_{La} When gas flow amount was 10.92m^3/h, the carrier (pouzzolane brown) increased from 0 to 200g (Ve =

38L), K_{La} dropped little. As carrier loading continued to increase, K_{La} value also dropped but the changes was not significant. It can found the optimization condition was above 800-1000g of the carrier loading (compactness was between 21.05 and 26.32 g/L) . When PVC tubes were used as the carrier, the K_{La} change was complex as well. Based on the experimental results the optimization condition was about 600g.

We have inserted the performance of our reactor in a general comparative table (Table 5) showing the work of literature [34].

Table 5. Mass transfer performance of the aero-ejector compared to other gas/liquid contactors.

Type	Gas/liquid rate (%)	K_{La} (10^{-2} s^{-1})
Countercurrent packed column	2-25	0.04-7.0
Concurrent packed column	2-95	0.04-102.0
Bubble cap plate column	10-95	1.00-20.0
Sieve plate column	10-95	1.00-40.0
Bubble column	60-98	0.50-24.0
Packed bubble column	60-98	0.50-12.0
Horizontal and coiled tube reactor	5-95	0.50-70.0
Vertical tube reactor	5-95	2.0-100.0
Spray column	2-20	0.07-1.5
Mechanical agitated bubble reactor	20-95	0.30-80.0
Submerged and plunging jet	94-99	0.03-0.60
Hydrocyclone	70-93	2.00-15.0
Ejector reactor	-	-
Venturi	5-30	8.00-25.0
Aero-ejector	5-30	1.00-12.0
our work	0.8-5.2	0.62-1.37

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II.2 Experimental studies in a novel extra-loop fluidized bed bioreactor (EFBBR) Part II. *nitrification denitrification and phosphorus removal*

During the past long period of time, biological wastewater treatment has been traditionally designed for organic carbon removal purposes only. Although the process allows for some removal of nitrogen in the form of nitrification, the fact is that nitrate and/or nitrite discharges standards are still high. And the phosphorus removal efficiency is at the low level as well. The resulting needs to develop compact wastewater treatment facilities or to up-grade existing plants for nitrogen and phosphorus removal provides an opportunity in a novel wastewater treatment apparatus research. In this section, a novel extra-loop fluidized bed bioreactor (EFFBBR) with anaerobic, aerobic and anoxic stages employing PVC tubes as a carrier media for the simultaneous removal of carbon, nitrogen and phosphorus from synthetic wastewater was discussed. The EFBBR was performed to select the SBR operation mode, and investigate the influences of the factors on the pollutants elimination.

Experimental Studies of a Novel Extra-loop Fluidized Bed Bioreactor (EFBBR)

Part II: *nitrification denitrification and phosphorus removal*

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Abstract: In this paper, the performance of a novel extra-loop fluidized bed bioreactor (EFBBR) with SBR (total 12h: anaerobic 1.5h, aerobic 5h, anoxic 4.5h, settle 1h and idle 1h) and employing PVC tube as a carrier media for the simultaneous removal of carbon, nitrogen and phosphorus from synthetic wastewater was discussed. The EFBBR was operated the system commissioning and optimization lasted for about 300 d. During the operation, the CFBB was able to achieve carbon (C), total ammonia nitrogen (NH_4-N) and phosphorous (P) removal efficiencies of 90%, 95% and 100% respectively. The results show that: C/N is insignificant for COD removal, and at C/P=10.4, COD removal efficiency is only about 32%; At C/N=33.2, there are the productions including NO_2-N and NO_3-N, however at C/N=10.4, nitrification is restrained; When TKN/COD from 0.0805 to 0.139, the phosphorus purify completely. Temperature influence relatively light to carbon, nitrogen and phosphorus removal. Therefore, the EFBBR is a novel high-powered equipment for carbon, and phosphorus removal simultaneous with a Shortcut nitrification denitrification process.

Keywords: extra-loop fluidized bed bioreactor (EFBBR), SBR, Shortcut nitrification denitrification process, phosphorus removal

1. Introduction

Nowadays, a great interest is conceded to the biologic treatment processes, which prove to be economic and efficient. Among these available different processes, fluidized bed bioreactor (FBB) seems to be the best one and present many advantages relating to hydrodynamics and mass transfer phenomenon. (Reese J, et al., 1999). The FBB outperforms other bioreactor configurations used in wastewater treatment, such as (1) very high biomass concentration up to 30-40 kg/m^3 can be achieved due to immobilisation of cells onto or into the solid particles; (2) the limit on the operating wastewater flow efficiencies imposed by the microbial maximum specific growth rate, as encountered in a continuous stirred-tank bioreactor (CSTR), is eliminated due to the decoupling of the residence time of the liquid phase and the microbial cells growth; (3) intimate contact between the liquid and solid phases is achieved; (4) the use of supporting particles allows the partial replenishment of the fluidized bed without interrupting the operation in order to maintain high microbial activity (Boumehdi Toumi L, et al., 2008).

The biological carbon, nitrogen and phosphorus removal in the alternating FBBR processes were described in the literatures. Fdez-Polanco F, et al.,(1994) used the FBBR with aerobic and anaerobic areas for municipal wastewater treatment and obtained SCOD, BOD_5, N-TKN, TN removal efficiencies were 80%, 90%, 80% and 70%, respectively. In the studies, Rovatti M, et al.,(1995) investigated the FBBR working as sequencing batch reactor (SBR) and demonstrated that at the end of this cycle COD uptake reached 87.1% and phosphorus removal was 50.2%. Rabah FKJ, et al., (2004) studied the performance of the FBBR with sand as the biofilm carrier for the treatment of high-strength nitrate wastewater and observed that at a loading rate of 6.3 kg N/m^3_{bed} ·d almost complete denitrification was achieved with a removal efficiency of 99.8%. Botrous AEF, et al.(2004). utilized a laboratory-scale fluidized-bed reactor with an external aeration loop was used for nitrification of high-strength ammonium wastewater (up to 500 mg NH_4-N/L) and demonstrated that the system was capable of handling ammonium removal efficiencies of up to 2.5 kg NH_4-N/m^3·d, while removal efficiencies were as high as 98%. Alvarado-Lassman A, et al., (2008) studied two anaerobic inverse fluidized bed reactors to evaluate organic matter removal from brewery wastewater and observed COD removal efficiencies

greater than 90%. Xing XH, et al., (2000) constructed a single continuous-flow fluidized-bed bioreactor system consisting of porous carrier particles for retaining microbes to simultaneously remove carbonaceous and nitrogenous substances in wastewater under different C/N (mass ratio) values. The suspended microbial concentration in the bioreactor was extremely low compared with that of retained microbes. A TOC removal of up to 91% and a maximum total nitrogen removal of 85% were achieved under a moderate C/N value.

Simultaneous nitrification-Denitrification (SND) was successfully demonstrated in the FBBR as well. In Aslan S and Dahab M (2008) studies that fluidized-bed biofilm nitritation and denitritation reactors (FBBNR and FBBDR) were operated to eliminate the high concentrations of nitrogen by nitritation and denitritation process. The dissolved oxygen (DO) concentration was varied from 1.5 to 2.5 g/m^3 at the top of the reactor throughout the experiment. NH_4-N conversion and NO_2-N accumulation in the nitritation reactor effluent was over 90 and 65%, respectively. Patel A, et al., (2006) presented the performance of the circulating fluidized bed bioreactor (CFBB) with anoxic and aerobic beds and employing lava rock as a carrier media for the simultaneous removal of carbon, nitrogen and phosphorus from municipal wastewater. Compared to with particles or not, the results showed that Without particles' recirculation, the CFBB was able to achieve carbon (C), total nitrogen(N) and phosphorous (P) removal efficiencies of 94%, 80% and 65% respectively, whereas with bioparticles' recirculation, 91%, 78% and 85% removals of C, N and P were achieved. In the above literatures simultaneous nitrogen and phosphorous removal in FBBR investigated feasibility as well.

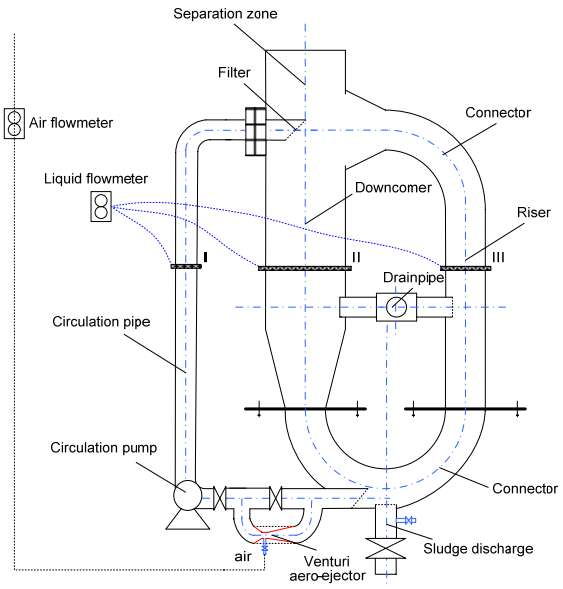
On one hand, the FBBR as a type of equipments has attracted considerable interest as an alternative to the conventional wastewater treatment processes due to its high performance efficiency. On the other hand, SBR as a mode for wastewater treatment has widely application yields as well. Li J, et al. (2003) developed a biofilm reactor that is operated in an SBR mode employing fibrous carrier media treating artificial sewage at an HRT of 9 h and observed 90% phosphorous removal. Kargi F and Eyiisleyen S, (1995) investigated a fluidized bed with sponge particles surrounded by stainless-steel wires as support particles for synthetic wastewater in operating in batch mode, and obtained the kinetics of biological removal of COD and nitrogen.

While the main goal of the study was to demonstrate simultaneous carbon, nitrogen, and phosphorous removal in the EFBBR with anaerobic, aerobic and anoxic processes working as sequencing batch reactor (SBR), the specific objectives of this paper are to evaluate the biological carbon, nitrogen and phosphorous removal in the system.

2. Materials and methods

2.1 Laboratory-scale fluidized bed

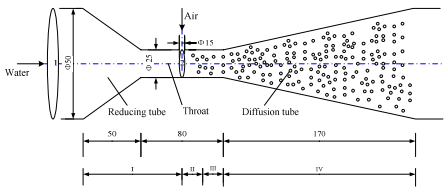
Figure 1 shows the schematic diagram of the extra-loop fluidized bed reactor, which is made of PVC. The reactor is composed of a riser and a downcomer and a circulation pipe, whose inner diameter is 100mm, 200mm and 50mm, respectively. The working height is 1.0m with the total working volume of 38L.



(a) extra-loop fluidized bed

Table 1. Parameters of the extra-loop fluidized bed reactor (EFBBR)

Index	
Total height t of FB (m)	2.2
Effective height of riser (m)	1.0
Inner diameters of riser (m)	0.1
Effective height of downcomer (m)	0.8
Inner diameter of downer (m)	0.2
Effective volume (L)	38
Replace the volume (L)	25



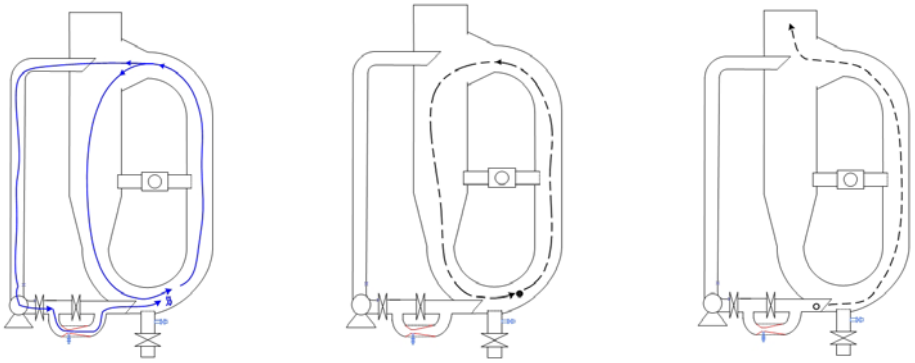
(b) Venturi aero-ejector

Figure 1. Schematic diagram of the experimental apparatus (with Venturi aero-ejector)

2.2 Operating conditions

Hydrodynamics cycle

The fluidization is realized by controlling the flow of the circulation pump. The Venturi aero-ejector is one kind of the aeration equipments whose inspiratory collection and mixing operate simultaneously. The inspiratory capability is controlled by the circulation pump and the air flowmeter. Figure 2 shows the liquid, solid and gas circulations in the fluidized bed.



(a) Liquid cycles (b) Solid cycle (c) gas cycle

Figure 2. Liquid, solid and gas circulations in the fluidized bed

- *Liquid cycles (2 cycle)*
  No.1 riser → upconnector → downcomer → subconnector
  No.2 riser → upconnector → circulation pipe → Venturi aero-ejector (selective) → subconnector
- *Solid cycle (1 cycle)*
  riser → upconnector → downcomer → subconnector
- *Gas cycle (semi-cycle)*
  Venturi aero-ejector (selective) → subconnector → riser → upconnector → separation area

Liquid cycle:

When the circulation pump operates , there are two cycles in the fluidized bed. First the pump inhales water which runs through the filter from top of the bed (upconnector) to the circulation pipe. Then the water passes the Venturi aero-ejector to the riser part by the subconnector. Simultaneously the water carries out the other cycle, passing the upconnector, downcomer, subconnector orderly, and back to the riser finally.

Solid cycle:

With the circulation pump in operation, the solid medium achieves its fluidization state. The solid can be fluidized in the riser and the upconnector. Due to gravity, the solid will drop from the upconnector to the downcomer and return to the bottom of the bed. Then another cycle begins continuously.

Gas cycle:

Also because of the circulation operation, the Venturi aero-ejector which is installed as a bypath inbreathes the air from the feed-tube that connects with the outside atmosphere. The air will be diffused. The mixing air carries out the cycle from the bottom through the riser to the upconnector, and releases back to the atmosphere at the separation zone.

Wastewater treatment process

In this work, the process of anaerobic, aerobic, anoxic are used, the operation steps including: anaerobic time, aerobic time, settle time, discharge time, idle time, and restart system for water feed.

- **Anaerobic step:** Open the electromagnetic valve of pipeline of circulation and circulation pump automatically after water feeding, begin to hydrolyze, acidifying until the enactment time.
- **Aerobic step:** After anaerobic stage, open the valve of circulation pipeline automatically, the Verturi aero-ejector inspires and the aeration starts simultaneously, thus aerobic decomposition continues until the enactment time.
- **Anoxic step:** Shut off the valve and stop the Verturi aero-ejector, the circulation pump still operates like anaerobic stage. However, the semi-manufactured wastewater with lower dissoluble oxygen in this stage.
- **Settle step:** shut off the circulation pump automatically after the anoxic step, the system begins to subside quietly until the enactment time
- **Discharge step:** Open the valve of the discharge pipeline and begin to drain.
- **Idle step:** After discharge, the system keeps the idle step.

- **Restart step:** start the new period for wastewater treatment.

At different craft stages, the originally systematic reactor has function of liquid-solid two-phase fluidized bed and gas-liquid-solid three-phase fluidized bed concurrently.

Liquid-solid two phase fluidized bed

It is anaerobic stage that liquid-solid two-phase fluidized bed is operated, after at one time entering water in the fluidized bed reactor, through the pipeline of circulation, some water is taken in at the top the fluidized bed out, enter the bottom of the fluidized bed after the efflux via the circulation pump pressurizes. Under the hydrodynamic action, the liquid do the circulation, water will circulate passing the riser - top connection pipe - downcomer. The liquid flowing drives carriers to flow and fluidize, thus make carriers do circulation to move in the same place, realize the hydrolysis of the waste water acidifies function. And at the anoxic stage, the liquid-solid two-phase fluidized bed is operated as well.

Gas-liquid-solid three-phase fluidized bed

It is aerobic stage that gas-liquid-solid three-phase fluidized bed is operated. When the Venturi aero-ejector does the aeration, the density of the fluid in the riser is less than in the downcomer, under the condition of the density difference, fluid circulate by riser and downcomer, The liquid flowing drives carriers to flow and fluidize, thus make carriers do circulation to move in the same place. Thus in the gas-liquid-solid three fluidized bed, the gas, fluid, solid three phase circulate all, reach the bio-decomposition of wastewater.

Ascending sport perturbation in liquid phase of bubble in the riser, make and bring about the trouble, the liquid phase interface brings renewal constantly, strengthen mass transfer between the gas and liquid greatly. The sports of the bubble have strengthened the mass transmission between liquid and carrier too, so the reaction efficiency is high. In the procedure, dissolved oxygen concentration is higher in riser, the aerobic bio-decomposition rate is great, but most gas appear easily while passing downcomer, only some small bubbles insert and bring into and enter downcomer, it is relatively that DO is weak in downcomer.

2.3 carrier

In this study the PVC tubes are used for the carriers and the physical properties are showed in Table 2.

Table 2. Physical properties of the carriers

Type	Range of diameter(mm)	Ture density(g/mL)	Stacking density(g/mL)
PVC tube	ϕ10(s=1mm), h=10-15mm	1.2	0.387

2.4 Synthetic Wastewater

The pilot-plant was located at the ENSIL (Limoges, France). The characteristics of the synthetic wastewater are reported in Table 3. Table 3 clearly shows that the extra-loop fluidized bed reactor is fed by a mixture of sugars (containing the powdered milk and glucose) and salt such as NH_4Cl g/L and KH_2PO_4. Not only the powdered milk provided the basic nutritive elements which the organic matter and other microorganisms need, the glucose has provided the carbon source, the ammonium chloride has provided the nitrogen source, the sodium bicarbonate has provided the inorganic carbon source and the alkalinity, the phosphate provides the phosphorus element which the microorganism need, also increased the pH buffer capacity. According to the need, may make the adjustment. The experimental water temperature is 15-42℃.

Table 3. The characteristics of the synthetic wastewater

	Parameter	Concentration (g/L)
powdered milk, glucose	COD	0.4n, 0.6n
NH_4Cl	NH_4-N	0.28n
K_2HPO_4	Orthophosphate	0.028n

Note: n=1,2,…n

2.5 Analysis method

All analyses were performed on grab samples taken from the reactors influents, effluents, and completed in accordance with Standard Methods. Samples were withdrawn daily from the reactors and filtered using 0.45 μm, white, 47mm radius filters. All samples were tested for NH_4-N, NO_3-N, NO_2-N and PO_4-P concentrations

using a Chromatographie ionique DIONEX DX120, respectively. And the support of TOC metre Dohrmann Phoenix 8000 for measures the TOC concentrations. The COD, total Nitrogen (TN) and total Phosphorus (TP) were determined using a Hach 2010 spectrophotometer with Hach Chemicals. The DO was measured by the DO meters (Sonde Orbisphere Modele 3600). The pH was monitored with WTW 320.

3. Results and discussions

3.1 start-up *(domestication and biofilm formation)*

The pilot plant was seeded simultaneously with the PVC tubes as carrier and the suspended nitrifying sludge (2000-3000 mg/L MLVSS) from the Wastewater Treatment Plant of Limoges. The synthetic wastewater containing the nutrients such as ammonium chloride, bicarbonate and phosphate, was one-off fed into the reactor. The experimental run was conducted with constant aerated gas by Ventrui aero-ejector. First start-up conditions include: normal temperature (about 20℃), aeration flow 120 L/h, influent TOC 90.75~233.95 mg/L, operation period 12 h. During the continuous 11 d experimental runs, sludge expanded and qualities effluent were dissatisfactory, a few sludge escaped following on the heels of effluent. The color of carrier surface was not changed. By microscopical exam procedure, it was not founded that the microorganism adhering to carrier. Figure 3. depicts the influent and effluent concentrations of TOC versus the operation days. TOC removal efficiencies were up to 60%. Obviously, the biofilm of carrier have not effected of on nutrients removal, contrarily the activated sludge. Because of 12 h operation period, it is beneficial for activated sludge growth and reproduction, thereby sludge captured the nutrients which should be fed to microorganism of carrier surface, and thus biofilm formation was difficult. Moreover sludge expanded also restrained biofilm formation. Based on activated sludge played dominant function in reactor, even a few microorganisms could adhere above the carrier, biofilm formation cannot achieve using the weak nutrients.

Thus change the operation conditions, operation period was shortened to 6 h. The start-up process renewed. After 7 days operation, the color of carrier changed

significantly and the adhesion phenomenon carried on carrier surface. By microscopical exam procedure, microorganisms acculturated and cumulated on carrier surface, biofilm was buff and clarity. During the experiment, sludge was not expanded, the concentration of sludge maintain steadily. Figure 3. shows biofilm formation versus the operation days.

At the later experiment, biofilm formation was steadily, the thickness was above 300 μm which adhering the interior. Because of PVC tube structure, biofilm formation carried on stronger the interior than exterior. When biofilm formation was obtained, the operation period backed to 12 h, biofilm did not fall off. It declared that the initial bacteria adhesion was important for biofilm formation; the exoteric infection was weak when biofilm achieved. Thereinafter studies were under different condition according to the necessaries.

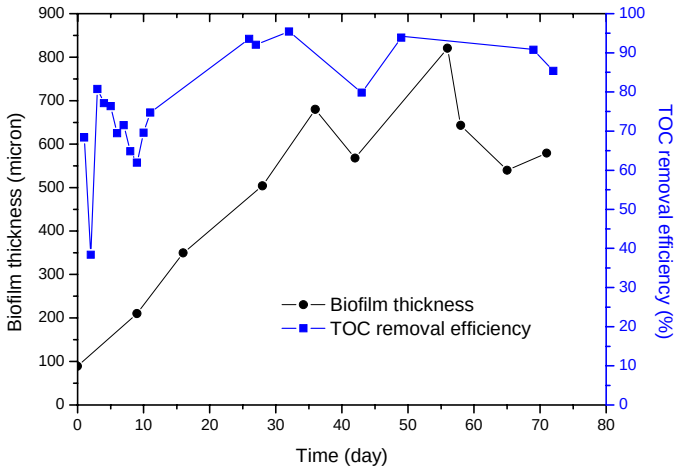


Figure 3. Influent and effluent concentrations of TOC versus the operation days

3.2 Design SBR process

Anaerobic time:

As above mentioned the pilot-plant aims to removal the organic pollutant and the nitrogen and the phosphorus, the anaerobic period plays the important roll in phosphorus removal. Phosphorus release under anaerobic conditions and phosphorus uptake under aerobic conditions is significant. This phenomenon is consistent with the conventional enhanced biological phosphorus removal (Chiou RJ and Yang YR, 2008). So for confirm the anaerobic period, it must be attention for the phosphorus

uptake time. The operation follows that: at first under the anaerobic condition and analysis the samples, when the phosphorus concentration is steady to begin the aeration. According to the Figure 4, it shows that the phosphorus concentration rises at operation beginning stage (1 h), at 2 hours phosphorus accumulated at maximum, during the subsequent process phosphorus concentration drops a certain extent but maintains ultimate steadily. So that for biological phosphorus accumulation the anaerobic time about 2 hours is sufficient.

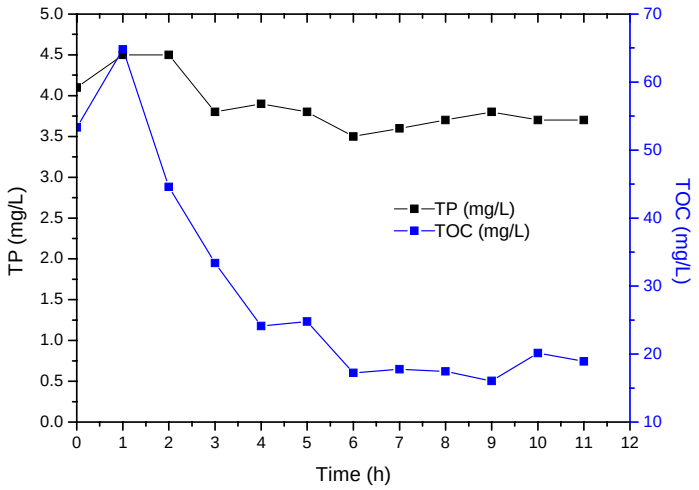


Figure 4. Phosphorus concentration change during anaerobic period

Aerobic time:

Increasing the nitrification in the mainstream aerobic reactor can be obtained by several approaches (Salema S, et al., 2003). Figure 5. shows the process with 2h anaerobic and 9h aerobic stages and during the process NH_4-N, NO_2-N, NO_3-N concentration curves. In anaerobic stage NH_4-N concentration drops continually with a small quantity of NO_2-N, NO_3-N produce. In the stage anaerobic ammonium oxidation maybe carrier out. However, the main nitrification is obtained during the aerobic stage. NH_4-N is degraded continually until 9h; and NO_2-N happen to accumulate, its accumulation achieved maximum with 7h aerobic stage; But NO_3-N produce is weak none the less. Therefore, short nitrification is actualized. According to the removal efficient, for economic reason 5h aerobic is acceptant.

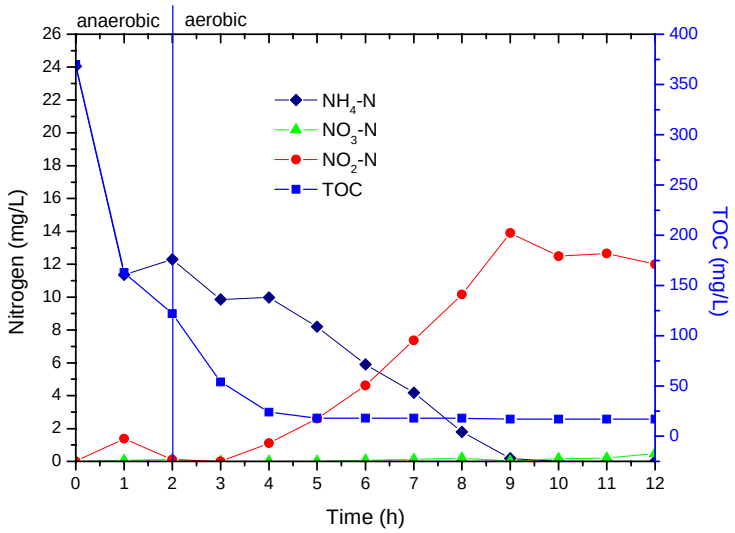


Figure 5. Nitrogen concentration change during the anaerobic-aerobic period

Anoxic time:

It is designed anoxic stage for denitrification as well and the total process is completely.

Thus, the pilot-plant whose sequential operation selected has as a base the alternation of phases (1.5h of anaerobic, 5h of aerobic, 4.5h of anoxic, 1h of settle and 1h of idle) thus ensuring the treatment of carbon, nitrification, denitrification and phosphorus removal. The flow of recirculation is 7 m^3/h and ventilation is assured with a flow of about 2 L/min if necessary. Figure 6 presents the SBR arrange as below.

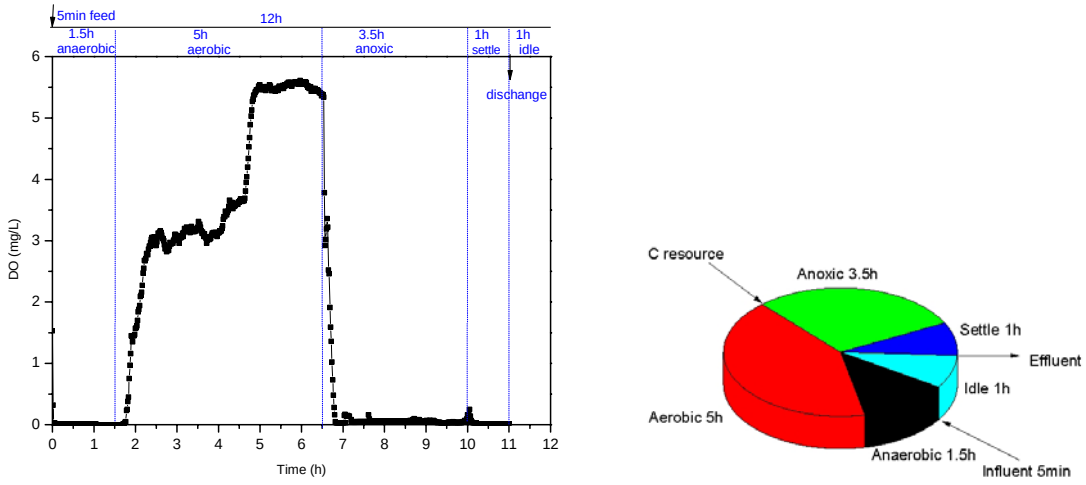


Figure 6. The SBR arrange according to dissolvable oxygen (DO)

3.3 Carbon removal

Adopt the treatment procedure described above, the system commissioning and optimization lasted for about 300 d. Figure 7 presents the partial temporal variation of TOC and COD.

Influence of initial concentration

Under different initial COD concentrations, deal with the removal results of COD of in the influent and effluent as shown in Figure 8. Based on SBR characteristics whose notable anti-impingement capabilities and the EFBBR's high-powered operation, the results showed that during experiment period, the influence of the initial COD is lightly, removal efficiencies of COD are up to 90%.

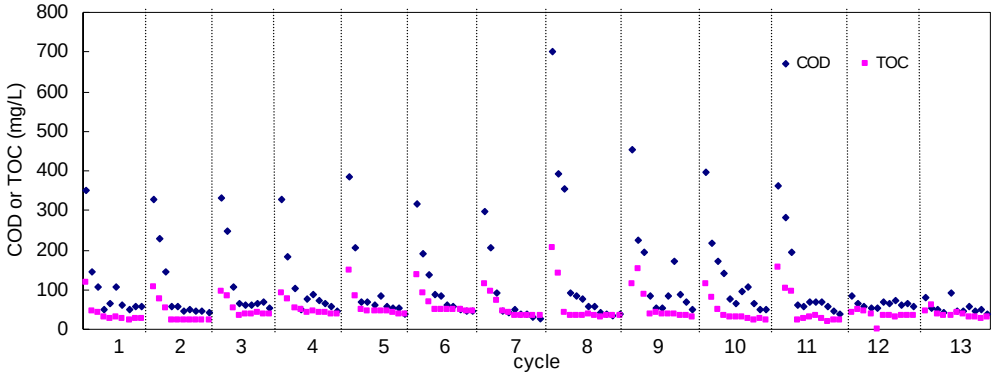


Figure 7 the temporal variation of TOC and COD

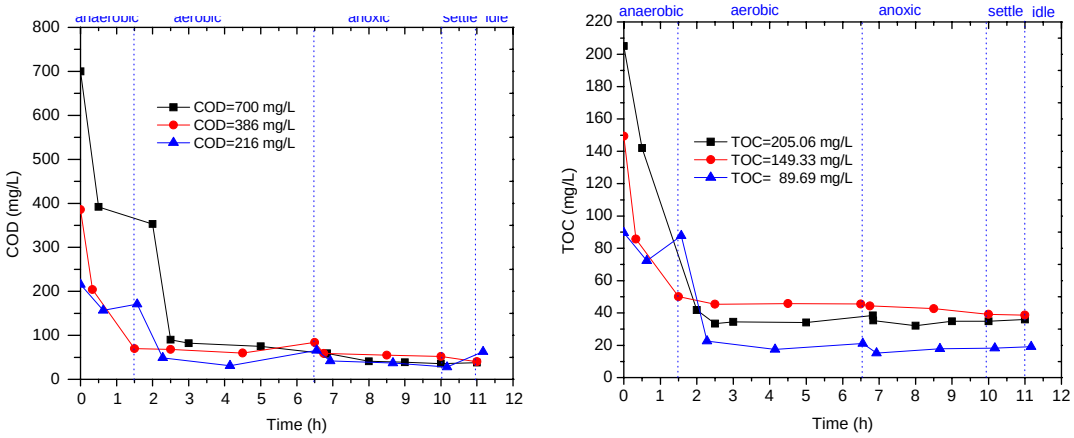


Figure 8 Effect of the initial COD/TOC on removal efficiencies

Influence of C/N

Be fixed wastewater COD and changed the ammonia concentration, make wastewater able to obtain different C/N. Investigate COD removal efficiencies under

different C/N, the results are as shown in Figure 9. The results demonstrate that different C/N to wastewater COD removal efficiencies have not almost been influenced, removal efficiencies of COD all keep above 90%, this is mainly because they all have fixed COD loading, and COD loading is not high. The N quantity does not exert an obvious influence on the organic compounds biodegradation. And it can be owed to the SBR characteristics whose notable anti-impingement capability and the EFBBR's high-powered operation as well.

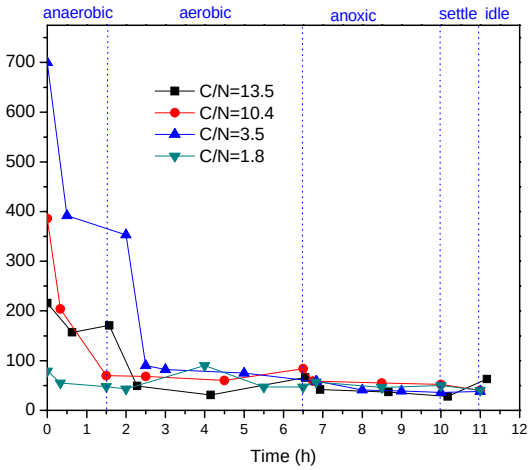


Figure 9. Effect of C/N on COD removal

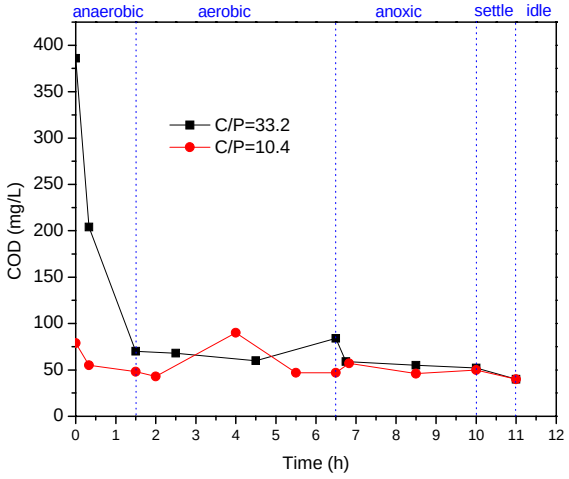


Figure 10. Effect of C/P on COD removal

Influence of C/P

Changed the COD concentration, make wastewater able to obtain different C/P. Investigate COD removing efficiencies under different C/P, the results are as shown in Figure 10. Andrew considered that enhanced biological phosphorus removal (EBPR) in wastewater treatment involves at least two types of bacterial metabolism: a polyphosphate-accumulating metabolism (PAM) and a glycogen-accumulating metabolism (GAM). Influent phosphorus/chemical oxygen demand (COD) ratio can affect PAM and GAM on inner-cell energy competition. Punrattanasin W (1997) investigated the robust enhanced biological phosphorus removal (EBPR). Specific COD removal efficiencies were met up to 90% at the COD/TP ratios of 20, 30, 40 and 60. In the work, the results demonstrate that different C/P influence to the wastewater COD removal efficiencies; At C/P=33.4, the COD be treated quite completely, the removal efficiency is up to 90%. The conclusion is accorded with Punrattanasin's

studies; But when C/P=10.4, the COD removal efficiency is only about 32%.

Influence of temperature

Be fixed wastewater COD and investigated COD removal efficiencies under different temperature, the results are as shown in Figure 11. As can be seen: Different temperature to the wastewater COD removal efficiencies have not influenced, removal efficiencies of COD all keep above 90%. This is at a certain extent the influence temperature on organic compound biodegradation is lightly. Lim B.R. et al.,(2001) presented that BOD removal rate in the bioreactor increased when the temperature increased from 20ºC to 30ºC, 40ºC, and 50ºC, but it decreased when the temperature increased from 50ºC to 60ºC. In the work, the conclusion is inosculated to Lim's studies.

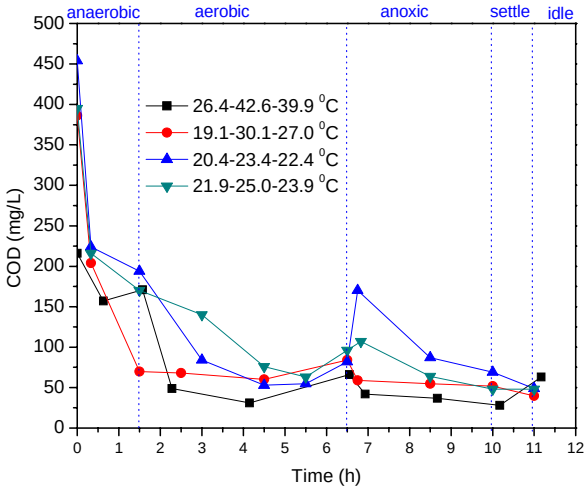


Figure 11. Effect of temperatures on COD removal

3.4 Nitrification and Denitrification

The performance of the EFBBR for nitrification and denitrification was excellent. Figure 12 presents the temporal variation of influent ammonia and effluent ammonia, nitrates and nitrites observed during the EFBBR operation. During all the periods, on average the system achieved up 95% ammonia removal efficiency, with an influent NH_4-N concentrations of 13.8, 34.9, 44.6 mg/L, respectively.

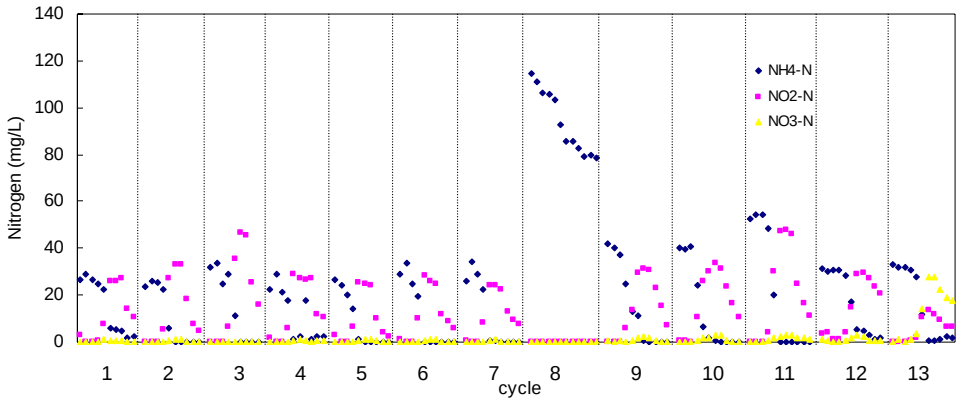


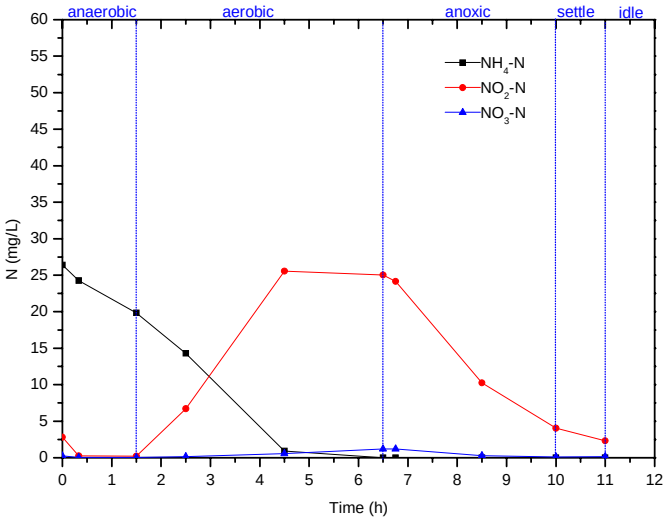
Figure 12. Temporal variation of influent ammonia and effluent ammonia, nitrates and nitrites

Influence of initial concentration

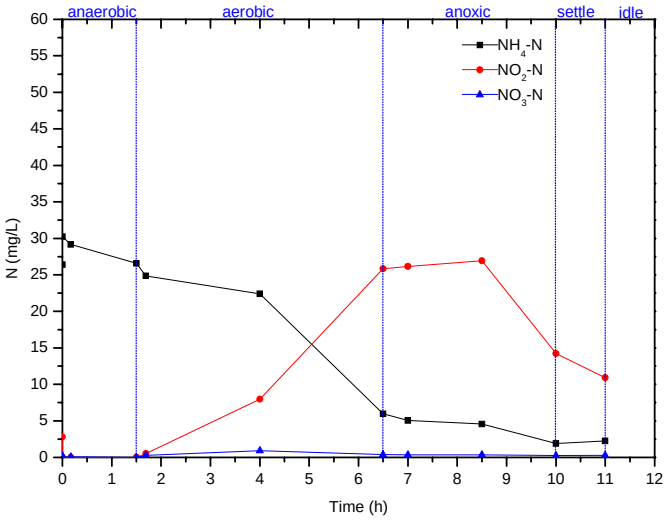
Because of experiment selection, the removal changes of the ammonia nitrogen which demonstrate mainly based on the changes of the NH_4-N and COD volume loading. The total variation tendency is: With the improvement of NH_4-N volume loading, the removal rate of the ammonia nitrogen and total nitrogen drops.

The experimental results of the variations of the nitrogen oxidation components and their concentrations in EFBBR are showed in Figure 13. The experimental temperature are not controlled and changed by the pump operation within 19.1-33.0℃ unequally. Simultaneously, FA concentration are obtained such as 0.20, 0.35, 0.57 mg/L according to the initial temperature, respectively. Under different initial NH_4-N concentration the productions are followed with the same transformation. During the anaerobic stage, different initial NH_4-N of influents begins to be eliminated with lower NO_2-N, NO_3-N productions except the hangover of last operation. Within the aerobic stage, NH_4-N keeps continual elimination, NO_2-N produces quickly but NO_3-N concentration still holds on lower level. At the end of aerobic stage, the NH_4-N is transformed to NO_2-N nearly completely, their transformed efficiencies are 94.5%, 85.5% and 91.58%, respectively. Similarly the nitrite accumulations (NO2-N/NOx-N) are achieved to 95.4%, 98.5% and 94.16%, respectively. The results showed that the different initial NH_4-N effect on the process of the productions including the nitration and nitrition. During all the process, the nitrition production is weaker than the nitration. When the initial concentration is higher, the amount of nitrition is more plenitudinous. And the nitrite accumulation efficiency is obtained highly during the aerobic step. The denitrification happened obviously during the anoxic step, but the initial concentration is lower that the denitrification carries on

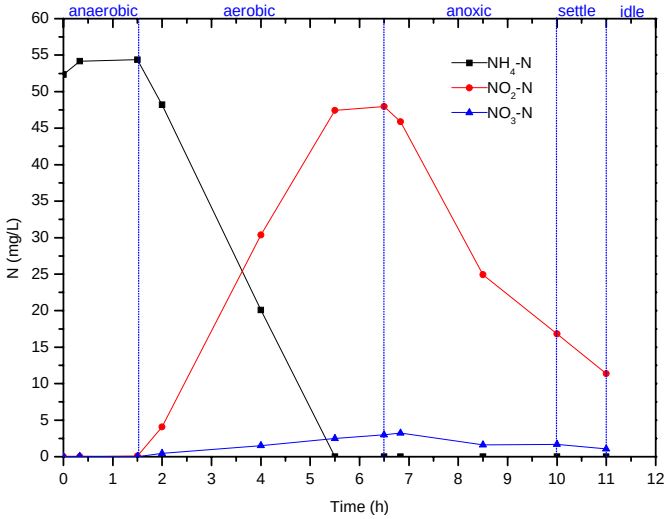
slightly.



a. pH=7.24, 19.1-30.1-27.1℃ (24.6±5.5℃)



b. pH=7.35, 21.2-33.0-30.6℃ (27.a±5.9℃)



c. pH=7.34, 20.7-33.1-30.4℃ (26.9±6.2℃)

Figure 13. Effect of the initial NH_4-N on the nitrogen removal rate

Influence of initial C/N

Changed the wastewater COD and ammonia concentration, make waste water able to obtain different C/N. Investigate denitrification rate under different C/N, the results are as shown in Table 4. Different C/N to the wastewater denitrification efficiencies have the almost been influenced; At C/N=33.2, there are the production including NO_2^--N and NO_3-N, but at C/N=10.4, NO_2-N and NO_3-N exist rarely. Therefore, the nitrogen quantity does exert an obvious influence on the denitrification, especially the type of the productions.

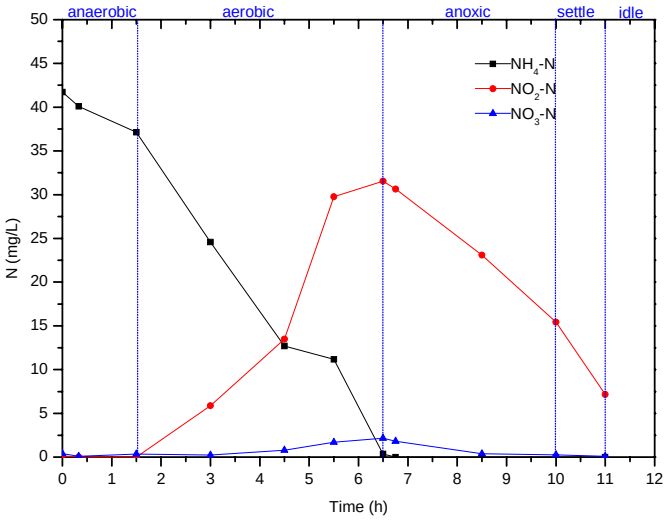
Table 4. Effect of different C/N on denitrification (mg/L)

	Time	influent	anaerobic effluent	aerobic effluent	anoxic effluent	effluent
C/N=33.2	NH_4-N	26.42	19.83	0.00	0.00	0.10
	NO_2-N	2.81	0.22	25.02	4.03	2.31
	NO_3-N	0.23	0.05	1.19	0.12	0.15
	TN	33.00	25.00	23.00	13.00	9.00
C/N=10.4	NH_4-N	11.51	9.88	7.37	7.38	7.35
	NO_2-N	0.00	0.00	0.00	0.00	0.00
	NO_3-N	0.00	0.00	1.61	0.45	0.05
	TN	27.80	31.20	23.00	14.00	16.80

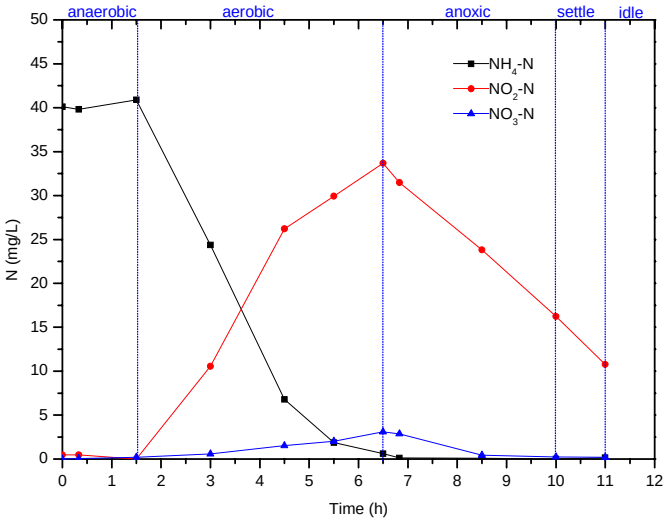
Influence of temperature

The experiments are designed as follows: the influent NH_4-N concentration about 40.11 mg/L and 41.73 mg/L whose FA concentration 0.48 mg/L and 0.31 mg/L, pH controlled at 7.34 and 7.18; the temperature controlled at the change range of 1.5 ℃, the work temperature is during 20.4-23.4 ℃ and 21.9-25.0 ℃, respectively. Figure 14. shows that at the end of aerobic stage, the NH_4-N is transformed to NO_2-N partially, their transformed efficiencies are 75.6% and 83.4%, similarly the nitrite accumulation (NO_2-N/NO_x-N) are achieved to 93.6%, and 91.6% , respectively. Compared with Figure 14., each nitrite accumulation rate is high up to 90%, with temperature controlled their efficiencies are less than without temperature, but the difference is not significant. However, the ammonia transformation efficiencies are

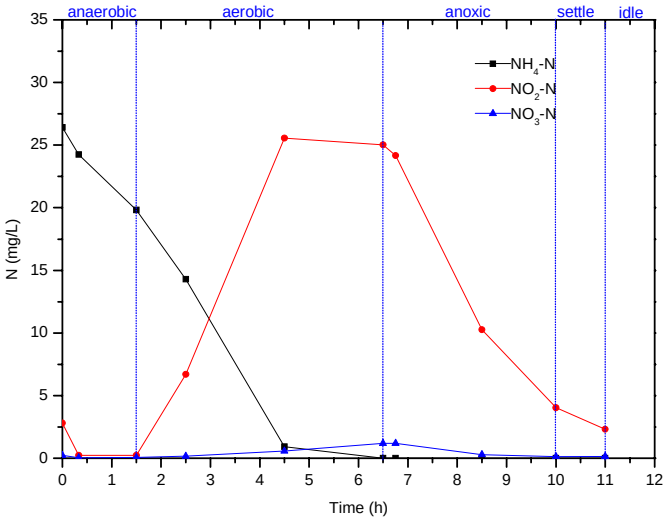
dropped obviously. Thus, the wide temperature change is benefic to the nitrite accumulation, and the temperature range is not the key factor, because the results commend that the nitrite accumulation is obtained at the range of 20-25 ℃ (experimental condition). Therefore, the EFBBR supplies the possibility for a novel nitrite accumulation process. Compared with a, b, c curves, it's obvious that under the different temperature, the nitrification present the same rule. From the literatures(Munch EV, et al.,1996; Sandu SI, et al.,2002; D. Obaja S, et al., 2003; Botrous AEF, et al.,2004), when studies on factors influencing the nitrification and/or denitrification efficiency, the operation temperature was steady ultimately. In the work, it can be seen that at the appropriate temperature range, nitrification also can be obtained. Thus, temperature has a wide application for nitrification, but different temperature range can effect on the quality and quantity of the productions.



a: 20.4-23.4-22.4℃(21.9±1.5℃)



b: 21.9--25.0-23.9℃(23.4±1.5℃)



c: 19.1-30.1-27.1℃ (24.6±5.5℃)

Figure 14． Effect of temperature on the nitrification

In this work, it is discovered that the SBR process is following the nitrite accumulation phenomenon. According to the traditional nitration theory, in the nitrification process, the energy using efficiency of nitrobacteria is lower than the bacillus nitrosomonas, therefore should not have the too many NO_2-N accumulation. The reason of nitrite accumulates possibly is:

- Inhibitory action of Free ammonia (FA) on nitric acid fungus. Anthonisen discovered that FA has the inhibitory action for nitrobacteria and bacillus nitrosomonas, but nitrobacteria are more sensitive, and this function may realize at FA concentration only 0.1-1.0mg/L. During the process, NH_4Cl was used for synthetic wastewater, the initial FA concentration is less than 0.6 mg/L.
- Effect of the environment transforms on bacillus nitrosomonas and nitrobacteria. Some research discovery, from anaerobic stage to aerobic stage, bacillus nitrosomonas activeness can restore very quickly under the anaerobic/anoxic condition, but nitrobacteria activeness restoration needs period of time to be able to achieve gradually. Therefore in the initial aerobic stage, nitration speed can lag in nitrition speed, the nitrite accumulation is obtained.

The concept of Shortcut nitrification denitrification was been presented by Voets JP at 1974. It is a new denitrogenation craft develops which by Dutch Delft Technology University (Jeeten MSM, et al., 1997; Verstraete W and Philips S,1998).

Based on the results of our work, it can be called a Shortcut nitrification denitrification as well.

Sustained nitrite accumulation via the nitrite pathway ($NH_4^+ \rightarrow NO_2^- \rightarrow N_2$) offers several benefits for nitrogen removal of wastewater, compared to the nitrate pathway ($NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^- \rightarrow NO_2^- \rightarrow N_2$):

As disadvantages it can be mentioned:

• nitrification must be operated and controlled precisely,

• automatic measurement of NO_2^- concentration in effluent of the anoxic step

• results in increasing operating costs.

3.5 phosphorus removal

Anaerobic habitat

Barnard pointed out the necessity of anaerobic area in the biological phosphorus removal system. The anaerobic habitat which already indicates that does need dissolvable oxygen in the anaerobic stage. Because oxygen is the easiest electronic receptor finally, if the oxygen exist, and concurrently anaerobic bacterium would not start its fermented and metabolize, will neither produce fatty acid and nor induce the phosphorus release. On the contrary, so long as a small amount of oxygen exists, and it is enough to result the sludge which phosphorus release before in the phosphorus adsorption. Generally, DO of in the anaerobic area should be smaller than 0.2mg/L. According to the Figure 4, for biological phosphorus accumulation the anaerobic time about 2 hours is sufficient.

Figure 15 depicts the concentrations of PO_4-P and total phosphates(TP) in each stage, such as: influent, anaerobic, aerobic, anoxic and final effluent during the EFBBR for the period of 11 cycles. The performance of EFBBR for P removal was satisfactory. The data of Figure 17 suggest that significant phosphorus release occurred across the anaerobic stage even though the actual increment in the PO_4-P concentration was accumulated 15-77% unequally.

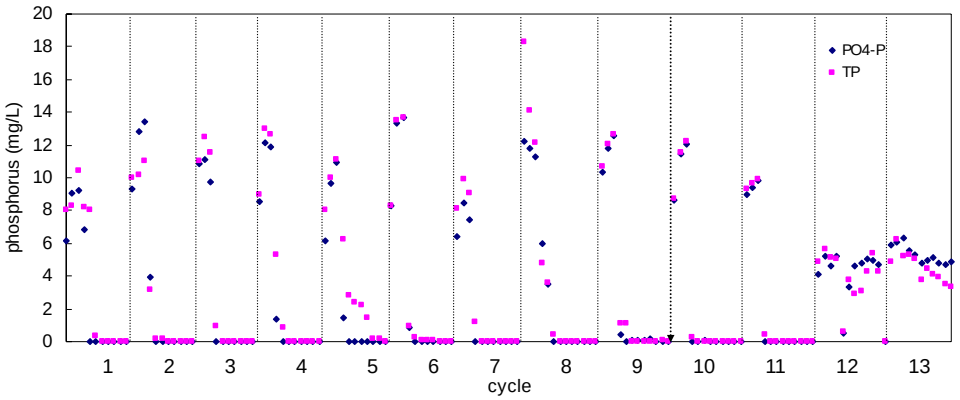


Figure 15. The temporal variation of phosphorus

Influence of NO_3-N and NO_2-N

Be similar as DO, NO_3-N and NO_2-N in anaerobic area will influence to the phosphorus removal in two paths:

a. The sour bacterium which produce the acid can used NO_3-N and NO_2-N as the electronic receptor oxidizes the organic ground substance finally, so NO_3-N and NO_2-N existence can inhibit from the ferment and fatty acids volatile;

b. The bacterium utilizes NO_3-N and NO_2-N as the denitrification, consumes the organic ground substance which exchanges biodegradation at the same time, thus competitiveness has restrain the anaerobic phosphorus release by the bacterium.

In this work, the nitrition drops rapidly during the anoxic step, and the preponderance in the denitrification production effect slightly on the phosphorus removal. According to the synthetic wastewater has not NO_3-N and NO_2-N import, the data are the leftover of the last cycle with low concentration. The experiment suggests that the concentrations varieties in different stages.(See Table 5. and Figure 16) At the end of aerobic stage, NO_2-N and NO_3-N achieve accumulation (25.02-47.95 mg/L and 0.40-2.97 mg/L), respectively. During anoxic stage operation, P concentration drop to zero. At a word, nitrification and denitrification does not affect on the p removal in EFBBR. The EFBBR is a novel high-powered equipment for nitrification, denitrification and phosphorus removal simultaneous.

Table 5. Effect of NO_3-N, NO_2-N on P removal

	influent	anaerobic effluent	aerobic effluent	anoxic effluent	effluent
NO_2-N	2.81	0	25.84	26.94	10.92
NO_3-N	0.23	0	0.40	0.36	0.28
PO_4-P	6.17	9.22	0	0	0
TP	8.04	10.462	0.32	0	0
NO_2-N	0	0	33.37	18.24	4.96
NO_3-N	0.05	0	1.05	0.16	0.13
PO_4-P	9.33	13.432	0	0	0
TP	9.98	11.042	0.14	0	0
NO_2-N	1.57	0.01	27.34	27.27	10.73
NO_3-N	0.10	0.04	0.93	0.29	0.37
PO_4-P	8.56	11.842	0	0	0
TP	8.98	12.66	0	0	0
NO_2-N	2.81	0.22	25.02	10.26	2.31
NO_3-N	0.23	0.052	1.19	0.30	0.15
PO_4-P	6.17	10.912	0	0	0
TP	8.04	11.142	2.42	1.42	0.13
NO_2-N	0.15	0	31.53	23.07	7.18
NO_3-N	0.40	0.36	2.17	0.38	0.10
PO_4-P	10.36	12.56	0.10	0.13	0
TP	10.69	12.62	0	0	0.09
NO_2-N	0.48	0	33.68	23.81	10.77
NO_3-N	0	0.21	3.09	0.43	0.20
PO_4-P	8.65	12.04	0	0	0
TP	8.69	12.21	0	0	0
NO_2-N	0	0.07	47.95	24.91	11.37
NO_3-N	0	0	2.97	1.62	1.04
PO_4-P	8.98	9.82	0	0	0
TP	9.30	9.88	0	0	0

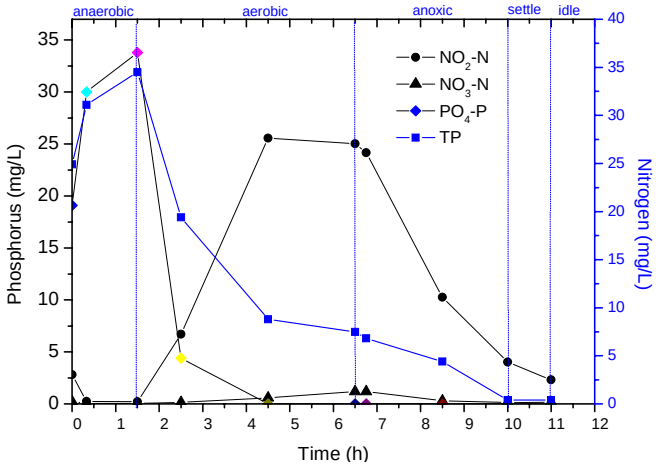


Figure 16. Effect of NO_3-N, NO_2-N on P removal (sample)

Influence of C/N

Another factor to phosphorus release is the influent organic compound density, the research works found that influent TKN/COD<0.1, it is complete to denitrification instead and effectual to phosphorus removal, TKN/COD is at 0.10-0.13, it should be careful to manage. At TKN/COD<0.08 in Phoredox the phosphorus eliminate effectively; at 0.14, even if UCT process eliminate the phosphorus result is not good. There is the report point out that when TKN/COD=0.13, the phosphorus removal effectively still is better in wastewater treatment plant of Western Europe. In the work, TKN/COD from 0.0805 to 0.139, the phosphorus purify completely.(See Table 6.)

Table 6. P removal under the different TKN/COD

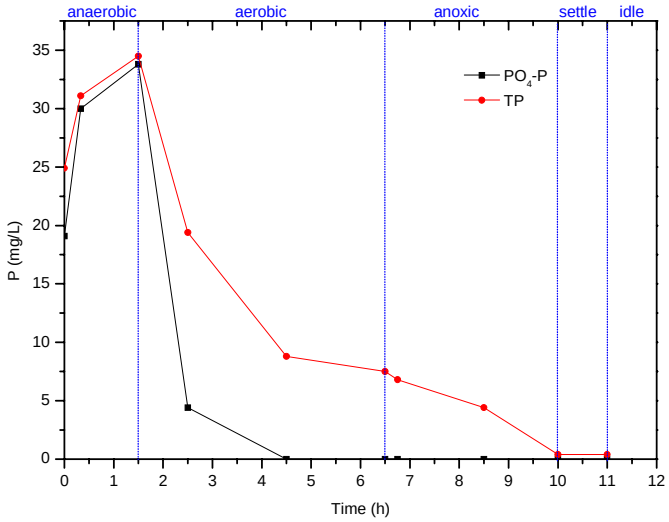
Data	COD(mg/L)	TKN(mg/L)	TKN/COD	TP(influent) (mg/L)	TP(effluent) (mg/L)
2006-11-22	351	48.95	0.139	24.6	0
2006-11-29	327	33.95	0.104	30.9	0
2006-12-6	332	43	0.129	34.1	0
2006-12-20	386	33	0.085	24.9	0
2006-12-28	315	35	0.111	25.8	0
2007-1-3	297	32.5	0.109	25.1	0

Influence of C/P

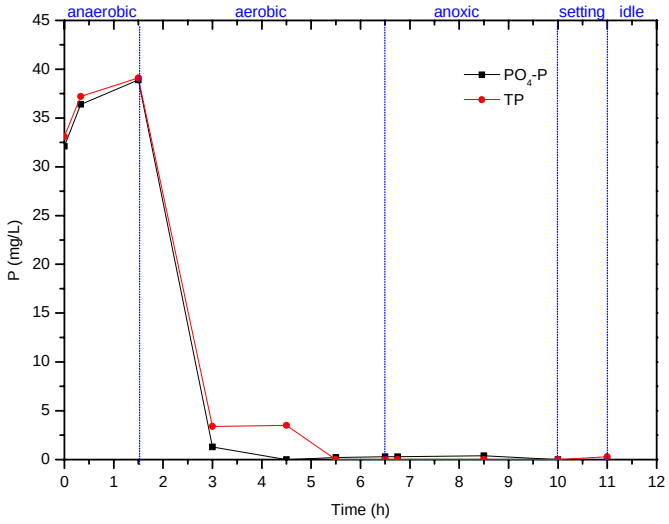
In addition, someone has investigated TBOD/P and the relation of the phosphorus removal quantitatively, the result indicates that will use water and dissolve phosphorus <1mg/L, it must be about 20-30 to influent TBOD/TP. Hong, et al. propose the influent TBOD/TP will higher than 15 at least, can make the phosphorus concentration of the effluent to be lower in the sludge age shortly phosphorus removal system.

Influence of temperature

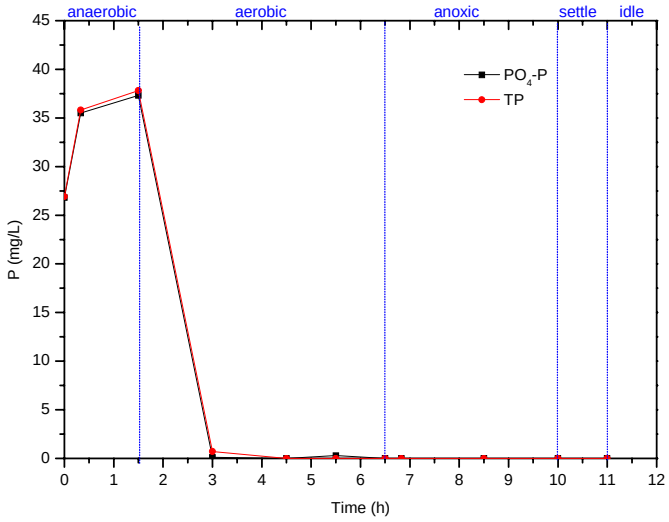
Temperature influence relatively light to phosphorus removal, along the accumulate phosphorus fungus grow. Temperature influence on the phosphorus removal is influence to produce sour of the fermented fungus mainly (see Figure 17.). In addition, must reach the denitrification at the same time, it demands to reduce load and lengthen sludge age.



a:19.1-28.4℃



b: 20.4-23.6℃



c: 21.9-23.1℃

Figure17. Effect of temperature on the phosphorus removal

4. Conclusions

A novel extra-loop fluidized bed bioreactor (EFBBR) employing SBR (1.5h of anaerobic, 5h of aerobic, 4.5h of anoxic, 1h of settle and 1h of idle) operating was successfully demonstrated to achieve close to excellent effluent quality, as reflected by TOC, COD, NH_4-N, PO_4-P and TP removal efficiencies, respectively. The system could achieve high biological carbon, nitrogen and phosphorus removal efficiencies.

Based on SBR characteristics whose notable anti-impingement capabilities and the EFBBR's high-powered operation, the results showed that during experiment period, the influence of the initial COD is lightly; different C/N to wastewater COD removal efficiencies have not almost been influenced, removal efficiencies of COD all keep above 90%. At C/P=33.4, the COD be treated quite completely, the removal efficiency is up to 90%. The conclusion is accorded with Punrattanasin's studies; But when C/P=10.4, the COD removal efficiency is only about 32%. At a certain extent the influence temperature on organic compound biodegradation is lightly as well.

The performance of the EFBBR for nitrification and denitrification was excellent. During all the periods, on average the system achieved up 95% ammonia removal efficiency, with an influent NH_4-N concentrations of 13.8, 34.9, 44.6 mg/L, respectively. Different initial NH_4-N effect on the process of the productions including the nitration and the nitrition. And the nitrition reaction takes place during the aerobic step. The denitrification happened obviously during the anoxic step, but the initial concentration is lower that the denitrification carries on slightly. At C/N=33.2, there are the production including NO_2-N and NO_3-N, but at C/N=10.4, NO_2-N and NO_3-N exist rarely. In a word, the EFBBR is a Shortcut nitrification denitrification process.

The performance of EFBBR for P removal was satisfactory. At the end of aerobic stage, NO_2-N and NO_3-N achieve accumulation (25.02-47.95 mg/L and 0.40–2.97 mg/L), respectively. During anoxic stage operation, P concentration drop to zero. The EFBBR is a novel high-powered equipment for nitrification, denitrification and phosphorus removal simultaneous. In the work, TKN/COD from 0.0805 to 0.139, the phosphorus purify completely and temperature influence relatively slight to phosphorus removal.

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II.3 Nitrite Accumulation Phenomenon in a Novel Extra-loop Fluidized Bed Bioreactor (EFBBR)

During the experiment study, the nitrite accumulation phenomenon was discovered in EFBBR. Generally, in activated sludge includes the ammonia oxidizing bacteria and nitrite oxidizing bacteria simultaneously, both bacteria have the habitat for which each one is suitable. Compares with the nitrite oxidizing bacteria, the ammonia oxidizing bacteria has the advantages such as: short generation period, quick growth speed, and strong adaptation environmental variation capability. Therefore, through the temperature control, pH, dissolved oxygen(DO), sludge resident time and inhibitor, can suppress the nitrite oxidizing bacteria activeness even eliminate them, and the ammonia oxidizing bacteria of the ecology superiority will be formed, thus the nitrosation process will be obtained. In this section, a laboratory-scale experiment with anaerobic, aerobic and anoxic stages was described. And the functions of nitrite accumulation were explained. The free ammonia (FA), pH, dissolved oxygen (DO) and SBR operation mode can effect on the nitrite accumulation.

Nitrite Accumulation Phenomenon in a Novel Extra-loop Fluidized Bed Bioreactor (EFBBR)

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Abstract: In this paper, the nitrite accumulation phenomenon is obtained in EFBBR. The results showed that on the different free ammonia (FA) concentration, the high nitrite accumulation efficiency are obtained obviously, the FA is not the significant influence factor on nitrite accumulation. pH influence is complex; at the pH range of 7-8 is selected in EFBBR. The EFBBR operation without the temperature control (naturally 19-33℃) and with temperature control at 20-25℃, can realize the nitrite accumulation successfully. The SBR process supplies the anaerobic, aerobic and anoxic stages, the high and low DO concentration operates alternately can achieve successfully the nitrite accumulation. The famine and feast period of the nitrite oxidizing bacteria is discovered.

Keywords: extra-loop fluidized bed bioreactor (EFBBR), temperature, famine and feast period, free ammonia (FA), DO

1. Introduction

Generally, the conventional biological nitrogen removal technologies do not catch sight of the nitrite and/or nitrate accumulation. The nitrite is the substance of partial nitrification, and it is dangerous for aquatic environment (i.e. eutrophication) and human being (i.e. cancer). Nowadays, nitrification at high ammonia loading rates studies (Campos JL, et al., 1999; Ruiz G, et al., 2003) and shortcut biological nitrogen removal technologies (Wang S, et al., 2004; Chung J, et al., 2007; Zhang S, et al., 2007) impel people to scrutinize the nitrite accumulation once more.

The novel nitrogen removal technologies developed including the shortcut nitrification denitrification (Jetten MS, et al., 1998; Verstraete W,1998) and Simultaneous nitrification- denitrification (SND) (Hyungseok Y, 1999), such as SHARON (Hellinga C, et al.,1998), ANAMMOX (Schmidt I and Bock E, 1997), combined SHARON and ANAMMOX (Hwang IS, et al., 2005), OLAND (Windey K, et al.,2005) and CANON (Sliekers AO, et al.,2003), etc.. The common principle described as follow: nitrification and denitrification is only for achieving nitrite accumulation, and sustained nitrite accumulation via the nitrite pathway ($NH_4^+ \rightarrow NO_2^- \rightarrow N_2$) offers several benefits for nitrogen removal of wastewater. Compared with the nitrate pathway ($NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^- \rightarrow NO_2^- \rightarrow N_2$), the advantages including: faster kinetics of processes, savings energy consumption, saving-costs, etc.

Generally, in activated sludge includes the ammonia oxidizing bacteria and nitrite oxidizing bacteria simultaneously, both bacteria have the habitat for which each one is suitable. Compares with the nitrite oxidizing bacteria, the ammonia oxidizing bacteria has the advantages such as: short generation period, quick growth speed, and strong adaptation environmental variation capability. Therefore, through the temperature control, pH, dissolved oxygen(DO), sludge resident time and inhibitor, can suppress the nitrite oxidizing bacteria activeness even eliminate them, and the ammonia oxidizing bacteria of the ecology superiority will be formed, thus the nitrosation process will be obtained. Afterwards, pH, DO, temperature, ammonia concentration and inhibitor were discussed by researchers. Kim DJ, et al., (2006) investigated the cause of seasonal failure of a nitrifying municipal landfill leachate

treatment plant utilizing a fixed biofilm. The results showed that high free ammonia (NH_3-N) inhibited not only nitrite oxidizing bacteria (NOB) but also ammonia oxidizing bacteria (AOB). Leachate was completely nitrified up to a load of 1.5 kg NH_4-N $m^{-3}d^{-1}$ at 28℃. The activity of NOB was inhibited by NH_3-N resulting in accumulation of nitrite. Bipin K, et al., (2007) detected and quantified that anaerobic ammonium oxidizing (anammox) bacteria present in microbial communities in two laboratory scale upflow anoxic reactors supplied with small amounts of ammonium (<3mg/L) at low temperature and complete ammonium and nitrite removal with greater than 92% total nitrogen removal efficiency was achieved. Carta F, et al., (2001) presented that bacteria in activated sludge are subjected to periods of substrate availability and absence of external substrates. The response of bacteria to such dynamic conditions was studied in a 2L sequencing batch reactor (SBR) by subjecting a mixed microbial population to successive periods of external substrate availability (feast period) and no external substrate availability (famine period). In previous studies, acetate or glucose was used as single substrate leading to the storage of polyhydroxybutyrate or glycogen, respectively. Chuang HP, et al., (2007) investigated partial nitrification by implementing a closed down-flow hanging sponge (DHS) reactor operated at controlled oxygen concentrations and found that oxygen concentration played an important role in the production of nitrous oxide, which increased with decreasing oxygen concentration. The ratio of nitrite produced relative to ammonium oxidized increased by decreasing oxygen concentration. Partial nitrification was satisfactorily accomplished under oxygen limitation at around 0.5% in the gas phase (0.2mgDO/L). In fact, the influences of nitrite accumulation are complex, including the interrelated, coadjutant and interdependent or internecine, etc... Thus the studies were divergent normally.

While the main goal of the study is to demonstrate nitrogen removal in the EFBBR with anaerobic, aerobic and anoxic processes working as sequencing batch reactor (SBR), the nitrite accumulation phenomenon is obtained steadily.

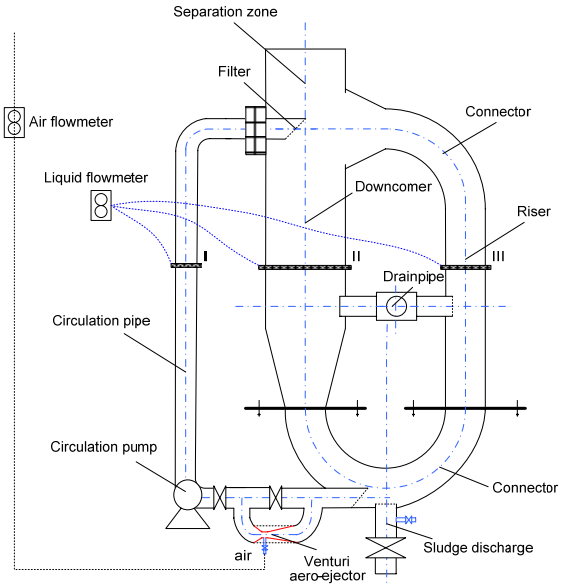
2. Materials and methods

2.1 Laboratory-scale fluidized bed

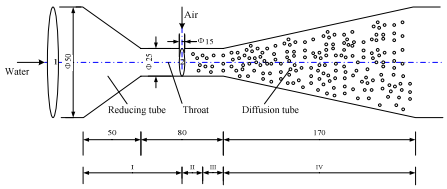
Figure 1 shows the schematic diagram of the extra-loop fluidized bed reactor, which is made of PVC. The reactor is composed of a riser and a downcomer and a circulation pipe, whose inner diameter is 100mm, 200mm and 50mm, respectively. The working height is 1.0m with the total working volume of 38L. (see Table 1.)

Table 1. Parameters of the extra-loop fluidized bed reactor (EFBBR)

Index	
Total height t of FB (m)	2.2
Effective height of riser (m)	1.0
Inner diameters of riser (m)	0.1
Effective height of downcomer (m)	0.8
Inner diameter of downer (m)	0.2
Effective volume (L)	38
Replace the volume (L)	25



(a) extra-loop fluidized bed



(b) Venturi aero-ejector

Figure 1. Schematic diagram of the experimental apparatus (with Venturi aero-ejector)

2.2 Operating conditions

Hydrodynamics cycle

The fluidization is realized by controlling the flow of the circulation pump. The Venturi aero-ejector is one kind of the aeration equipments whose inspiratory collection and mixing operate simultaneously. The inspiratory capability is controlled by the circulation pump and the air flowmeter. Figure 2 shows the liquid, solid and gas circulations in the fluidized bed.

Liquid cycle:

When the circulation pump operates, there are two cycles in the fluidized bed. First the pump inhales water which runs through the filter from top of the bed (upconnector) to the circulation pipe. Then the water passes the Venturi aero-ejector to the riser part by the subconnector. Simultaneously the water carries out the other

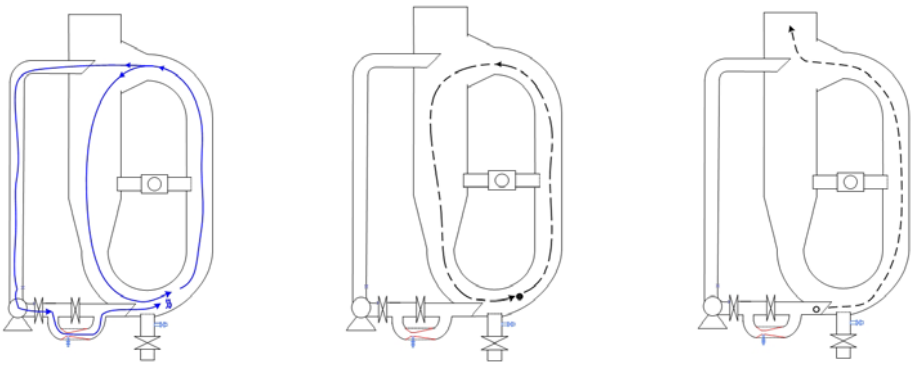
cycle, passing the upconnector, downcomer, subconnector orderly, and back to the riser finally.

Solid cycle:

With the circulation pump in operation, the solid medium achieves its fluidization state. The solid can be fluidized in the riser and the upconnector. Due to gravity, the solid will drop from the upconnector to the downcomer and return to the bottom of the bed. Then another cycle begins continuously.

Gas cycle:

Also because of the circulation operation, the Venturi aero-ejector which is installed as a bypath inbreathes the air from the feed-tube that connects with the outside atmosphere. The air will be diffused. The mixing air carries out the cycle from the bottom through the riser to the upconnector, and releases back to the atmosphere at the separation zone.



(a) Liquid cycles (b) Solid cycle (c) gas cycle

Figure 2. Liquid, solid and gas circulations in the fluidized bed

- *Liquid cycles (2 cycle)*
  No.1 riser → upconnector → downcomer → subconnector
  No.2 riser → upconnector → circulation pipe → Venturi aero-ejector (selective) → subconnector
- *Solid cycle (1 cycle)*
  riser → upconnector → downcomer → subconnector
- *Gas cycle (semi-cycle)*
  Venturi aero-ejector (selective) → subconnector → riser → upconnector → separation area

Wastewater treatment process

In this work, the process of anaerobic, aerobic, anoxic are used, the operation

steps including: anaerobic time, aerobic time, settle time, discharge time, idle time, and restart system for water feed.

- **Anaerobic step:** Open the electromagnetic valve of pipeline of circulation and circulation pump automatically after water feeding, begin to hydrolyze, acidifying until the enactment time.
- **Aerobic step:** After anaerobic stage, open the valve of circulation pipeline automatically, the Verturi aero-ejector inspires and the aeration starts simultaneously, thus aerobic decomposition continues until the enactment time.
- **Anoxic step:** Shut off the valve and stop the Verturi aero-ejector, the circulation pump still operates like anaerobic stage. However, the semi-manufactured wastewater with lower dissoluble oxygen in this stage.
- **Settle step:** shut off the circulation pump automatically after the anoxic step, the system begins to subside quietly until the enactment time
- **Discharge step:** Open the valve of the discharge pipeline and begin to drain.
- **Idle step:** After discharge, the system keeps the idle step.
- **Restart step:** start the new period for wastewater treatment.

At different craft stages, the originally systematic reactor has function of liquid-solid two-phase fluidized bed and gas-liquid-solid three-phase fluidized bed concurrently.

Liquid-solid two phase fluidized bed

It is anaerobic stage that liquid-solid two-phase fluidized bed is operated, after at one time entering water in the fluidized bed reactor, through the pipeline of circulation, some water is taken in at the top the fluidized bed out, enter the bottom of the fluidized bed after the efflux via the circulation pump pressurizes. Under the hydrodynamic action, the liquid do the circulation, water will circulate passing the riser -top connection pipe – downcomer. The liquid flowing drives carriers to flow and fluidize, thus make carriers do circulation to move in the same place, realize the hydrolysis of the waste water acidifies function. And at the anoxic stage, the liquid-solid two-phase fluidized bed is operated as well.

Gas-liquid-solid three-phase fluidized bed

It is aerobic stage that gas-liquid-solid three-phase fluidized bed is operated. When the Venturi aero-ejector does the aeration, the density of the fluid in the riser is less than in the downcomer, under the condition of the density difference, fluid circulate by riser and downcomer, The liquid flowing drives carriers to flow and fluidize, thus make carriers do circulation to move in the same place. Thus in the gas-liquid-solid three fluidized bed, the gas, fluid, solid three phase circulate all, reach the bio-decomposition of wastewater.

Ascending sport perturbation in liquid phase of bubble in the riser, make and bring about the trouble, the liquid phase interface brings renewal constantly, strengthen mass transfer between the gas and liquid greatly. The sports of the bubble have strengthened the mass transmission between liquid and carrier too, so the reaction efficiency is high. In the procedure, dissolved oxygen concentration is higher in riser, the aerobic bio-decomposition rate is great, but most gas appear easily while passing downcomer, only some small bubbles insert and bring into and enter downcomer, it is relatively that DO is weak in downcomer.

2.3 carrier

In this study the PVC tubes are used for the carriers and the physical properties are showed in Table3. and Figure 2.

Table 2. Physical properties of the carriers

Type	Range of diameter(mm)	Ture density(g/mL)	Stacking density(g/mL)
PVC tube	ϕ10(s=1mm), h=10-15mm	1.2	0.387

2.4 Synthetic Wastewater

The pilot-plant was located at the ENSIL (Limoges, France). The characteristics of the synthetic wastewater are reported in Table 3 in which clearly shows that the extra-loop fluidized bed reactor is fed by a mixture of sugars (containing the powdered milk and glucose) and salt such as NH_4Cl g/L and KH_2PO_4. Not only the powdered milk provided the basic nutritive elements which the organic matter and

other microorganisms need, the glucose has provided the carbon source, the ammonium chloride has provided the nitrogen source, the sodium bicarbonate has provided the inorganic carbon source and the alkalinity, the phosphate provides the phosphorus element which the microorganism need, also increased the pH buffer capacity. According to the need, may make the adjustment. The experimental water temperature is 15-42℃.

Table 3. The characteristics of the synthetic wastewater

	Parameter	Concentration (g/L)
powdered milk, glucose	COD	0.4n, 0.6n
NH_4Cl	NH_4-N	0.28n
K_2HPO_4	Orthophosphate	0.028n

Note: n=1,2,…n

2.5 Analysis method

All analyses were performed on grab samples taken from the reactors influents, effluents, and completed in accordance with Standard Methods. Samples were withdrawn daily from the reactors and filtered using 0.45 μm, white, 47mm radius filters. All samples were tested for NH_4-N, NO_3-N, NO_2-N and PO_4-P concentrations using a Chromatographie ionique DIONEX DX120, respectively. And the support of TOC metre Dohrmann Phoenix 8000 for measures the TOC concentrations. The COD, total Nitrogen (TN) and total Phosphorus (TP) were determined using a Hach 2010 spectrophotometer with Hach Chemicals. The DO was measured by the DO meters (Sonde Orbisphere Modele 3600). The pH was monitored with WTW 320.

3. Results and discussions

3.1 Effect of free ammonia (FA) on nitrite accumulation

The pH influence of nitrosation process on two aspects: on the one hand pH can affect the microorganism in the system on its electrolyte balance, hence on its activeness. The most suitable environmental pH which the ammonia oxidizing bacteria grows is 7-8.5, the nitrite oxidizing bacteria is 6-7.5; On the other hand, pH has the significant influence on FA concentration.

The FA concentration formula is written as:

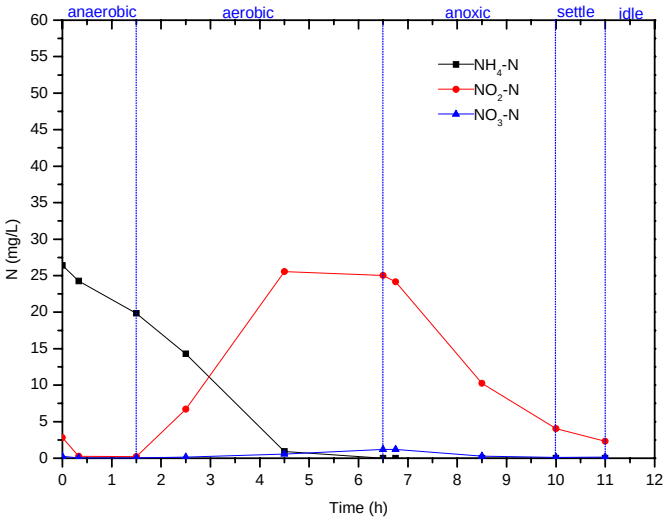
$$[FA] = \frac{17}{14} \times \frac{[NH_4^+ - N] \times 10^{pH}}{K_b / K_w + 10^{pH}}$$

Where, K_b is ammonia dissociation constant, and K_w is water ionization constant.

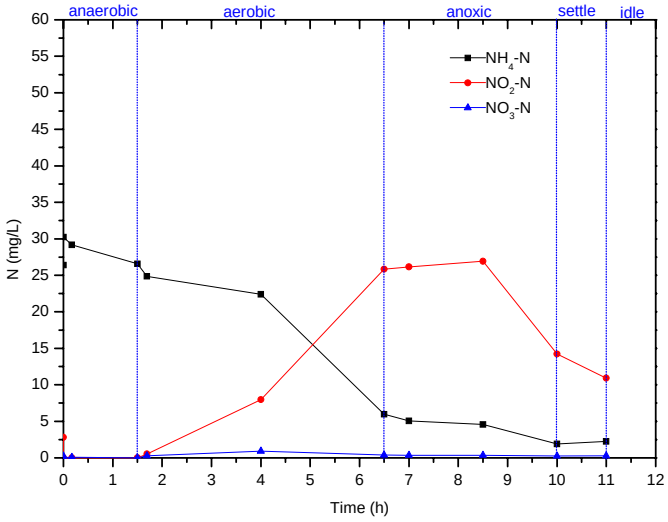
Based on formula, the FA concentration increases along with pH. The FA has the inhibitory action to the ammonia oxidizing bacteria and nitrite oxidizing bacteria. The inhibition concentration of nitrite oxidizing bacteria and ammonia oxidizing bacteria is 0.1-1.0 mg/L, above 10 mg/L, respectively. Previous research Yang S.F. et al., (2004) summarized that FA concentration of 10-150 mgN/L would significantly inhibit the activities of both *Nitrobacter* and *Nitrosomonas.*

The experimental results of the variations of the nitrogen oxidation components and their concentrations in EFBBR are showed in Figure 3. The experimental temperature are not controlled and changed by the pump operation within 19.1-33.0℃ unequally. Simultaneously, FA concentration are obtained such as 0.20, 0.35, 0.57 mg/L according to the initial temperature, respectively. Under different initial NH_4-N concentration the productions are followed with the same transformation. During the anaerobic stage, different initial NH_4-N of influents begins to be eliminated with lower NO_2-N, NO_3-N productions except the hangover of last operation. Within the aerobic stage, NH_4-N keeps continual elimination, NO_2-N produces quickly but NO_3-N concentration still holds on lower level. At the end of aerobic stage, the NH_4-N is transformed to NO_2-N nearly completely, their transformed efficiencies are 94.5%, 85.5% and 91.58%, respectively. Similarly the nitrite accumulations (NO2-N/NOx-N) are achieved to 95.4%, 98.5% and 94.16%, respectively.

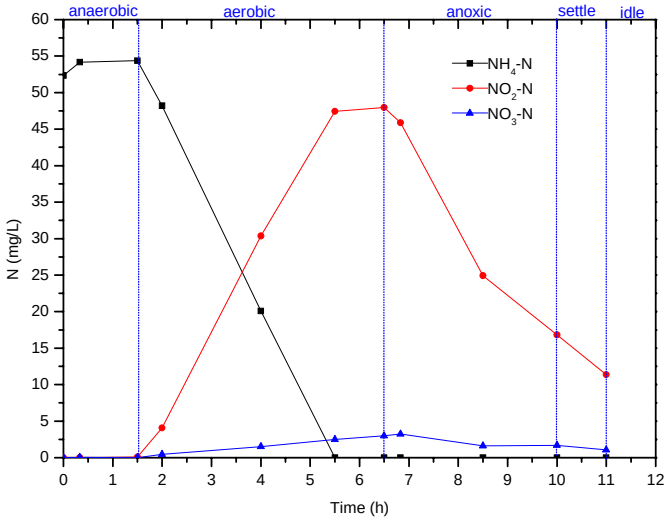
The results showed that the nitrite accumulation efficiency is obtained highly in EFBBR, and it is can be obtained that the FA is not the significant influence factor on nitrite accumulation as well. Based on Anthonisen (1976) selective inhibition theory, he discovered that FA has the obvious inhibition to the nitrification, 0.6 mg/L FA nearly may inhibit completely the nitrite bacteria activities, but when FA achieved above 5mg/L, the inhibition start to effect the ammonia oxidizing bacteria activities, at 40mg/L FA can inhibit seriously to the nitrite accumulation. In this study, FA concentration can meet up to 0.57 mg/L, and with the high nitrite accumulation efficiency obviously.



a. pH=7.24, 19.1-30.1-27.1℃ (24.6±5.5℃)



b. pH=7.35, 21.2-33.0-30.6℃ (27.a±5.9℃)



c. pH=7.34, 20.7-33.1-30.4℃ (26.9±6.2℃)

Figure 3. Effect of FA on nitrite accumulation

3.2 Effect of pH on nitrite accumulation

According the above results and mechanisms, FA concentration is the function of pH, temperature, initial NH_4-N concentration and etc. Because FA is not the significant factor in EFBBR, so the experiments check the influence of pH on nitrite accumulation. Table 5. shows the effect of different pH on nitrite accumulation. Whereas the nitrite accumulation is obvious, the ammonia transformation rates are different and ruleless. However, it is also can found that when pH exceeds 8, FA concentration raised as well, and the nitrite accumulation is inhibited at a certain extent. Although the nitrite accumulation and the ammonia transformation efficiencies still keep 97.7% and 93.9% at pH=6.72, respectively. At pH=7.18, the ammonia transformation is not satisfied. Based on the influence is complex, the nitrite accumulation realization is the integrative result of all the factors, at the pH range of 7-8 is selected in EFBBR.

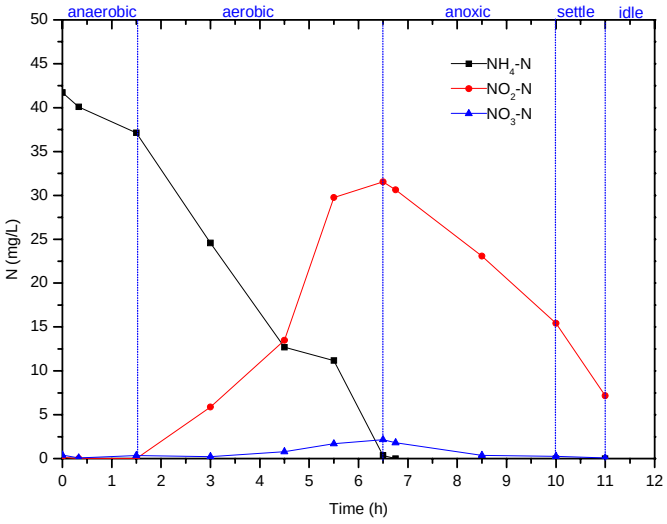
Table 5. Effect of different pH on nitrite accumulation

pH	NH_4-N(mg/L)	NO_3-N(mg/L)	NO_2-N(mg/L)	FA (mg/L)	NO_2-N/NO_X-N (%)	NO_2-N/NH_4-N (%)
6.72	25.90	0.56	24.31	0.35	97.7	93.9
7.18	41.73	2.17	31.53	0.33	93.6	75.6
7.24	26.41	0.57	25.56	0.23	97.8	96.8
7.35	30.22	0.34	26.15	0.35	98.7	86.5
7.86	52.00	0.16	46.77	1.80	99.7	89.9
8.03	29.35	0.06	8.15	1.41	99.3	27.8
8.46	35.81	0.12	18.08	4.69	99.3	50.5

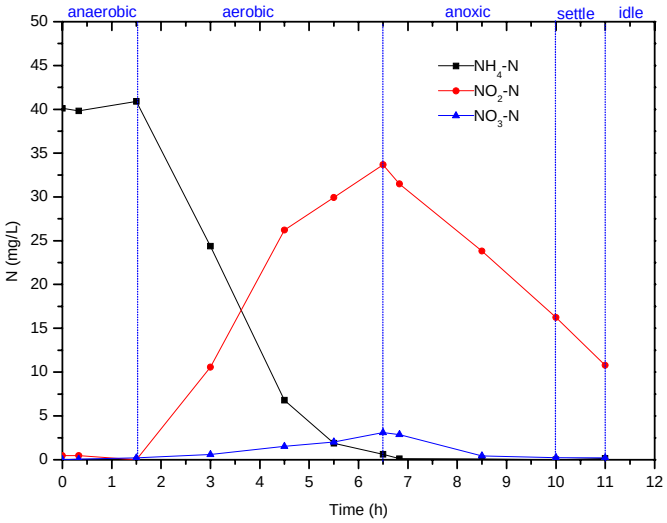
3.3 Effect of temperature on nitrite accumulation

The ammonia oxidizing bacteria and nitrite oxidizing bacteria grow suitably in different temperature scope, respectively. With controlled wastewater temperature, the ammonia oxidizing bacteria can grow fast in a certain temperature range, and the generation period shortens; but because of the disadvantageous ambient temperature, the activities of nitrite oxidizing bacteria are inhibited, the generation period increases. Through the selection of sludge age in the system, the nitrite bacteria will be washed out during the effluent stage, thus nitrosation process will be realized. The biological nitration reaction may occur at the range of 5-45℃; Generally, within 15-30 ℃ the

nitrite produced by biological ammonization can oxidized by the nitrite oxidizing bacteria to be the nitrate in further, hence the NO_2-N accumulation can not be existed steady. The optimum temperature for nitrite accumulation is 30-36 ℃, the nitration rate reduces obviously less than 15 ℃. But the influences of low temperature on two kinds of nitrifying bacteria are different. In the activated sludge, the activities of the nitrite oxidizing bacteria will be inhibited more seriously than ammonia oxidizing bacteria within 12-14 ℃, and also can occur the NO_2-N accumulation.



a. pH=7.34, 20.4-23.4-22.4℃ (21.9±1.5℃)



b. pH=7.18, 21.9-25.0-23.9℃ (23.4±1.5℃)

Figure 4. Effect of temperature on nitrite accumulation

The experiments are designed as follows: the influent NH_4-N concentration about 40.11 mg/L and 41.73 mg/L whose FA concentration 0.48 mg/L and 0.31 mg/L, pH controlled at 7.34 and 7.18; the temperature controlled at the change range of 1.5 ℃, the work temperature is during 20.4-23.4 ℃ and 21.9-25.0 ℃, respectively. Figure 4. shows that at the end of aerobic stage, the NH_4-N is transformed to NO_2-N partially, their transformed efficiencies are 75.6% and 83.4%, similarly the nitrite accumulation (NO_2-N/NO_x-N) are achieved to 93.6%, and 91.6% , respectively. Compared with Figure 3., each nitrite accumulation rate is high up to 90%, with temperature controlled their efficiencies are less than without temperature, but the difference is not significant. However, the ammonia transformation efficiencies are dropped obviously. Thus, the wide temperature change is benefic to the nitrite accumulation, and the temperature range is not the key factor, because the results commend that the nitrite accumulation is obtained at the range of 20-25 ℃ (experimental condition). Therefore, the EFBBR supplies the possibility for a novel nitrite accumulation process.

3.4 Effect of DO on nitrite accumulation

Regarding the ammonia oxidizing bacteria and nitrite oxidizing bacteria exist simultaneously in activated sludge, both are strict aerobic bacterium. The effect of DO on the ammonia oxidizing speed and the productions is complex: The DO concentration is too low to the insufficient of oxygen supplying, thus does not be favorable for the nitrite production, and the higher DO is more advantageous to nitrosation process. However, the exorbitant DO can oxidize further the nitrite to nitrate, and it is disadvantageous for the nitrite accumulation. The research discovered that the oxygen saturation coefficient of ammonia oxidizing bacteria and nitrite oxidizing bacteria is 0.2- 0.4 mg/L and 1.2-1.5 mg/L, respectively. Compared with the nitrite oxidizing bacteria, the ammonia oxidizing bacteria has a stronger affinity to the DO in water. Therefore the ammonia oxidizing bacteria has the competitive advantage under the low DO condition, and the ammonia oxidizing bacteria will be accumulated and the nitrite accumulation be occurred possibly.

Jayamohan S, et al., (1988) discovered that at 25 ℃, the influent ammonia nitrogen is 80 mg/L, DO 0.5 mg/L, the ammonia oxidizing bacterium multiplication will accelerate up nearly 1 time, the nitrite oxidization process has not the obvious

influence, but nitrifying bacteria multiplication rate in low DO(0.5 mg/L) has not any enhancement. The nitrite accumulation occurs possibly. However, Jang A. and Kim I.S. (2004) declared that the oxygen uptake rates were normal at DO concentration of 5-15 mg/L.

As can be seen in Figure 3., the nitrite accumulation phenomenon occurs at the aerobic stage, Figure 5. presents the oxygen evolution during wastewater treatment process using EFBBR, and the curve is cooperated with Figure 3a.. The experiment is arranged with SBR process. DO increases by degrees in the whole aerobic stage. In zone I, the process achieve the COD elimination and ammonia transformation with nitrite accumulation, DO evolves from 0 to 3 mg/L; In zone II the nitrite accumulation continued, DO emerges flatly basically at the begin of zone II, at the end evolves continuously up to 5.6 mg/L; and in zone I II, the nitrite accumulates linearly; at the end of zone II, the nitrite accumulation closes to completely; in zone III, the nitrite accumulation is obtained maximally and DO maintain at the 5.6 mg/L level. Consequently, the nitrite accumulation phenomenon occurs during the aerobic stage using EFBBR, DO concentration is not the significant factor, but the SBR process supplies the anaerobic, aerobic and anoxic stages, the high and low DO concentration operate alternately can achieve the nitrite accumulation

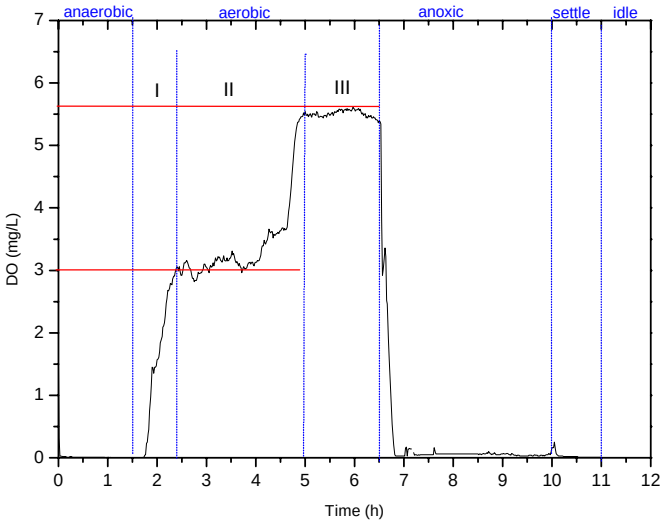


Figure 5. Oxygen evolution during the wastewater treatment process using EFBBR

3.5 Discussions of process control

The carbon oxidizing bacteria adopts the environment of carbon source sufficient

and deficient, and has developed the specific metabolism path: **famine and feast period**. While the carbon source is sufficient, the bacterium can lead to the storage of polyhydroxybutyrate (PHB) or glycogen, and not use directly in its growth; while the carbon source is lacks, the bacterium then uses PHB. The *Nitrosomonas* and carbon oxidizing bacteria have the famine feast period characteristic equally, can adapt the periodic undulation of DO. Under the low DO, the *Nitrosomonas* breathe using the limited oxygen oxidizing ammonia nitrogen (**feast period**). When SBR turns into the high DO and the low ammonia nitrogen concentration stage (**famine period**), the *Nitrosomonas* is at the endogene breath condition, its activities obtain the restoration in time. However, the *Nitrobacter* can adapt the high and low DO change alternately and disappear gradually. In this work, we discovered the famine and feast period of the nitrite oxidizing bacteria, and the satisfied results are obtained.

The nitrite accumulation is a controllable result of the process. Through online examines DO, ORP, pH, can prompt each reaction parameter and control expediently with the dynamic conditions, and all the process will carry on the direction to nitrite accumulation. This kind of control is not the hypothesis fixation reaction time, but really runs according to the changes of the original ammonia nitrogen concentration and so on, achieves the online reaction time control real-timely. So the controllable parameters in detail and the process will be realized and also waiting for in further studies.

4. Conclusions

The nitrite accumulation efficiency is obtained highly in EFBBR. Based on the different FA concentration, the high nitrite accumulation efficiency are obtained obviously, the FA is not the significant influence factor on nitrite accumulation. pH influence is complex, the nitrite accumulation realization is the integrative result of all the factors, at the pH range of 7-8 is selected in EFBBR.

The literature described that the nitrite accumulation can occur at the range of 12-14 ℃ and 30-36 ℃. In this work, the EFBBR operation without the temperature control (naturally 19-33℃) and with temperature control at the range of 20-25 ℃ (experimental condition), can realize the nitrite accumulation successfully.

Consequently, the nitrite accumulation phenomenon occurs during the aerobic stage using EFBBR, DO concentration is not the significant factor, but the SBR process supplies the anaerobic, aerobic and anoxic stages, the high and low DO concentration operate alternately can achieve the nitrite accumulation. In this work, we discovered the famine and feast period of the nitrite oxidizing bacteria, and the satisfied results are obtained.

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II.4 Biofilm Formation and Characteristics in a Novel Extra-loop Fluidized Bed bioreactor (EFBBR)

In fact, the EFBBR is a mixing system with the activate sludge and biofilm concomitantly. Biofilm formation and growth is an important factor for successful operation of the fluidized bed reactor. Several actors have been mentioned as affecting the biofilm formation and growth, namely, characteristics and concentration of wastewater, type of support media, hydrodynamics, operation conditions and nutrient addition, *etc*.. In this section, the biofilm formation and characteristics in a novel extra-loop fluidized bed bioreactor (EFBBR) were presented. The rationalization of the biofilm formation process was validated. And the correlations between structural and activity parameters have been demonstrated, including the proteins, thickness and exopolysaccarids production.

Biofilm Formation and Characteristics in a Novel Extra-loop Fluidized Bed bioreactor (EFBBR)

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Abstract: In the paper biofilm formation and characteristics in a novel extra-loop fluidized bed bioreactor (EFBBR) were presented. The results showed that: under the conditions of influent TOC 90.75~233.95 mg/L and operation period 6 h was beneficial for biofilm formation. And biofilm was steadily, whose thickness was above 300 μm which adhering the interior. When biofilm formation was obtained, it declared that the initial bacteria adhesion was important for biofilm formation. The simple methods used for the characterization of the biofilm gave the biofilm evolution: the biofilm is influenced by the exploitation conditions (cycle management). Correlations between structural and activity parameters have been demonstrated: proteins are linked with the activity and thickness is linked with exopolysaccarids production.

Keywords: extra-loop fluidized bed bioreactor (EFBBR), biofilm formation, proteins, thickness

Symbol	
δ	biofilm thickness (m)
ρ_c	mass volume of particule support (kg/m^3)
C	dissolved oxygen concentration in reactor (mg/L),
C_s	saturation concentration of dissolved oxygen (mg/L)
d_{intc}	interieur diametre of particle support (m)
h	hauteur of particle support (m)
K_{La}	transfer coefficient (s^{-1}).
M_c	mass of particles in reactor (kg)
N	number of particles in reactor
V_{bio}	volume of biofilm (m^3)
V_c	volume of particle support (m^3)
V_r	volume of reactor (m^3)
X	concentration of fixed biomass (kg/m^3 reactor)
Y	fraction of fixed biomass (mg biofilm/ g PVC)

1 Introduction

As an effective technology of biological wastewater treatments, the applications of biofilm process become wider along with the control of industrial wastewater and municipal sewage (Kimura K, et al., 2008; Robertsa JA, et al., 2000). The characteristics of biofilm wastewater treatment system were decided by the biofilm formation and mechanism. Since 1970's the reaction-diffusion model was presented, many of researchers carried continually on the biofilm formation and mechanism (Grady CPL, et al., 1999). The innovations such as growth-degradation substrate kinetics (Belkhadir R., et al., 1988a,b) and cellular automation models (Wimpenny JWT and Colasanti R, 1997) were obtained. However the models applied restrictively according to the assumptions respectively.

While focused on biofilm, the microstructure and surface morphology of biofilm are directly related with the activity of multispecies microbes and the substrate transfer in biofilm. A biofilm can be defined as a layered structure of microbial cells and cellular products, like extracellular polymers, attached to a solid surface. It can

thus be seen as the accumulation product of naturally immobilized microorganisms at an interface. The main parameters on biofilm include: density , pore distribution, porosity, specific surface area, adhesion strength, tortuosity factor, diffusion coefficients and fractal dimensions(Belkhadir R, et al., 1988). The structural and morphological characteristics of biofilm are very important for the overall performance of a biofilm reactor. And these factors strongly affect the biomass hold-up and transfer in a biofilm reactor. It has been observed as follows by using co-focal scanning microscope(Gibbs JT and Bishop PL, 1995): Heterogeneous biofilm is composed of microfloras embodied in exopolysaccharides (EPS), which are adhering to adaptive carriers, and there are varieties of voids, micropores and channels. In general, the main factors to influence microbe microstructure and morphology include species of microorganism, transfer of substrate, flowing characters of fluid, *etc*.(Eberl HJ, et al., 2000; Hinson RK, and Kocher WM,1996).

The fluidized bed is a biofilm reactor which used in wastewater treatment. Nowadays, fluidized bed biofilm reactors (FBBR) for treating industrial and municipal wastewater have been well known (Rabah FK, 2003). However many research works focused on multiple nutrient removal in biofilm systems, such as carbon, nitrogen and phosphorus removal(Chowdhury N, et al.,2008; Patel A, et al., 2006). But the microstructure and surface morphology of biofilm were presented infrequently.

Biofilm formation and growth is an important factor for successful operation of the fluidized bed reactor. Several actors have been mentioned as affecting the biofilm formation and growth, namely, characteristics and concentration of wastewater, type of support media, hydrodynamics, operation conditions and nutrient addition, *etc*. It was reported that biofilm is composed of two major components: microbial cells and products of metabolism, especially exopolymers, which may assist in binding microbial cells to surface. The microbial extracellular and cell surface polymers were important in biofilm phenomena during the initial interaction between a bacterial cell and the substrate. The slime producing would enhance the biofilm formation, especially in the nitrification process. And the microbial adhesion is promoted by the bonding action of exopolymers. Consequently, microbial exopolymers play a key role in biofilm formation and growth (Cheng SS, et al., 1997).

In this study a novel extra-loop fluidized bed bioreactor was used for treating the synthetic wastewater. The biofilm formation and characteristics were investigated, such as measurements of proteins (PN) and relationships of activities, exopolysaccharides (EPS) and thickness, PN/EPS ratio, evolutions average biofilm thickness and concentration in fixed biomass calculated according to various correlations.

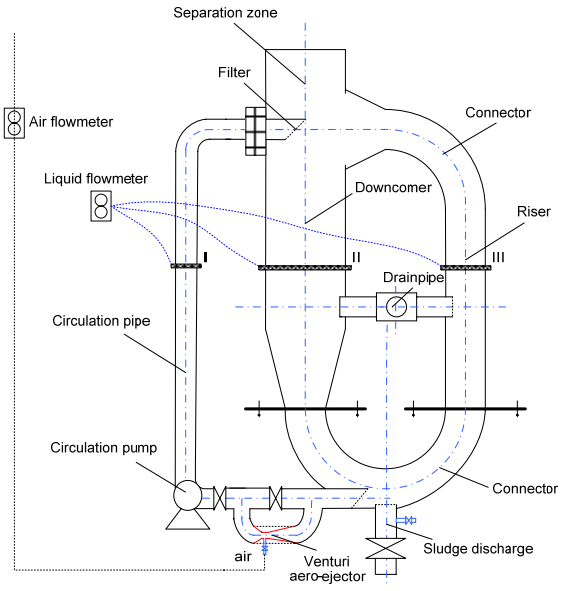
2 Materials and methods

2.1 Laboratory-scale fluidized bed

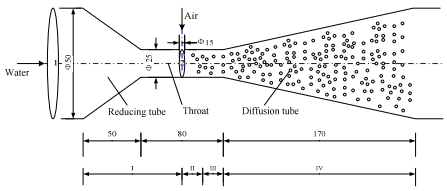
Figure 1 shows the schematic diagram of the extra-loop fluidized bed reactor, which is made of PVC. The reactor is composed of a riser and a downcomer and a circulation pipe, whose inner diameter is 100mm, 200mm and 50mm, respectively. The working height is 1.0m with the total working volume of 38L.

Table 1. Parameters of the extra-loop fluidized bed reactor (EFBBR)

Index	
Total height t of FB (m)	2.2
Effective height of riser (m)	1.0
Inner diameters of riser (m)	0.1
Effective height of downcomer (m)	0.8
Inner diameter of downer (m)	0.2
Effective volume (L)	38
Replace the volume (L)	25



(a) extra-loop fluidized bed

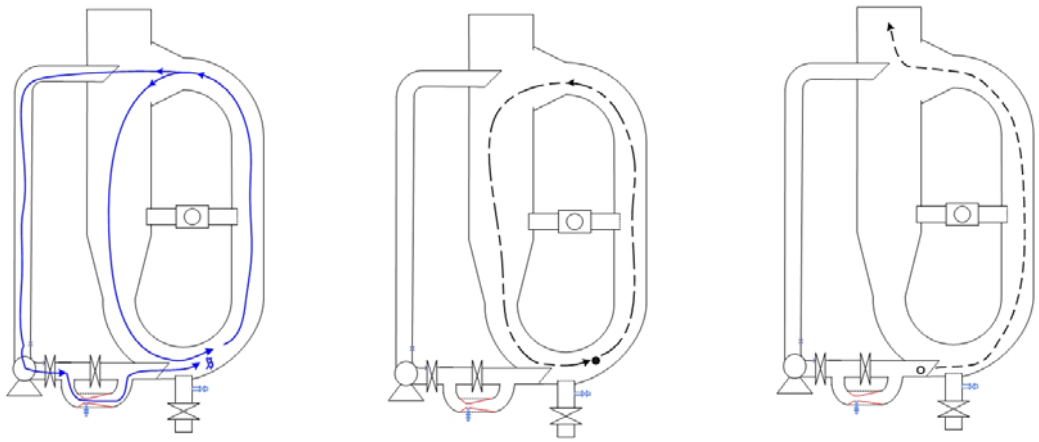


(b) Venturi aero-ejector

Figure 1. Schematic diagram of the experimental apparatus (with Venturi aero-ejector)

2.2 Operating conditions

The fluidization is realized by controlling the flow of the circulation pump. The Venturi aero-ejector is one kind of the aeration equipments whose inspiratory collection and mixing operate simultaneously. The inspiratory capability is controlled by the circulation pump and the air flowmeter. Figure 2 shows the liquid, solid and gas circulations in the fluidized bed.



(a) Liquid cycles (b) Solid cycle (c) gas cycle

Figure 2. Liquid, solid and gas circulations in the fluidized bed

- *Liquid cycles (2 cycle)*

No.1 riser → upconnector → downcomer → subconnector

No.2 riser → upconnector → circulation pipe → Venturi aero-ejector (selective) → subconnector

- *Solid cycle (1 cycle)*

riser → upconnector → downcomer → subconnector

- *Gas cycle (demi-cycle)*

Venturi aero-ejector (selective) → subconnector → riser → upconnector → separation area

Liquid cycle: When the circulation pump operates, there are two cycles in the fluidized bed. First the pump inhales water which runs through the filter from top of the bed (upconnector) to the circulation pipe. Then the water passes the Venturi aero-ejector to the riser part by the subconnector. Simultaneously the water carries out the other cycle, passing the upconnector, downcomer, subconnector orderly, and back to the riser finally.

Solid cycle: With the circulation pump in operation, the solid medium achieves its fluidization state. The solid can be fluidized in the riser and the upconnector. Due to gravity, the solid will drop from the upconnector to the downcomer and return to the bottom of the bed. Then another cycle begins continuously.

Gas cycle: Also because of the circulation operation, the Venturi aero-ejector which is installed as a bypath inbreathes the air from the feed-tube that connects with the outside atmosphere. The air will be diffused. The mixing air carries out the cycle from the bottom through the riser to the upconnector, and releases back to the atmosphere at the separation zone.

2.3 carrier

In this study the PVC tubes are used for carriers and its physical properties are showed in Table 2.

Table2. Physical properties of carrier

Type	Range of diameter(mm)	Ture density(g/mL)	Stacking density(g/mL)
PVC tube	ϕ10(s=1mm), h=10-15mm	1.2	0.387

Synthetic Wastewater

The pilot-plant was located at the ENSIL (Limoges, France). The characteristics of the synthetic wastewater are reported in Table3. Table3 clearly shows that the extra-loop fluidized bed reactor is fed by a mixture of sugars (containing the powdered milk and glucose) and salt such as NH_4Cl g/L and KH_2PO_4. Not only the powdered milk provided the basic nutritive elements which the organic matter and other microorganisms need, the glucose has provided the carbon source, the ammonium chloride has provided the nitrogen source, the sodium bicarbonate has provided the inorganic carbon source and the alkalinity, the phosphate provides the phosphorus element which the microorganism need, also increased the pH buffer capacity. According to the need, may make the adjustment. The experimental water temperature is 15-42℃.

Table 3. The characteristics of synthetic wastewater

	Parameter	Concentration (g/L)
powdered milk, glucose	COD, TOC	0.4, 0.6
NH_4Cl	NH_4-N	0.28
K_2HPO_4	Orthophosphate	0.028

2.4 Methods

1. Thickness and estimate of the fixed biomass

The fraction from biomass (mass of biomass fixed per support) and the concentration in biomass (quantity of biomass fixed per reactor volume) are distinguished.

The thickness of biofilm is measured on bioparticles thanks to a binocular magnifying glass with reversed focal distance STEMi V6 connected to Videomet software. It is carried out an average of the measurements using five bioparticles (10 measurements for each one). The volume of biofilm on a particle is then given by equation (1):

$$V_{bio} = \prod \cdot h \cdot \delta \cdot (d_{int\,c} - \delta) \qquad (1)$$

The correlations are given by Table4 which reported by Rabah FKJ and Dahab MF (2004) are used to calculate the density of the biofilm:

Table 4. Correlations for the estimate of the biofilm density starting from its thickness in FBBR

equation	Source
ρ_{bio}= 65 mg/cm^3 for 0< δ <300 μ m ρ_{bio}= 96.8-0.106 δ mg/cm^3 for 300< δ <630 μ m ρ_{bio}= 30 mg/cm^3 for δ >630 μ m	Mulcahy and La Motta (1978)
ρ_{bio}= 104.3-0.125 δ mg/cm^3 for δ <622 μ m ρ_{bio}= 30 mg/cm^3 for δ >622 μ m	Boaventura and Rodrigues (1988)
ρ_{bio}= 120(δ /180)$^{3.7}$ mg/cm^3 for δ <180 μ m ρ_{bio}= 120(δ /180)$^{-1.8}$ mg/cm^3 for δ >180 μ m	Hermanowicz and Cheng (1990)
ρ_{bio}= 191.4 - 0.224 δ mg/cm^3 for δ <593 μ m ρ_{bio}= 58.6 mg/cm^3 for δ >593 μ m	Coelhoso et al. (1992)

The number of particles in reactor is given by equation (2):

$$N = M_c / (\rho_c \cdot V_c) \qquad (2)$$

Then equation (3) gives the total concentration of biofilm in reactor:

$$X = (V_{bio} \cdot \rho_{bio} \cdot N) / V_r \qquad (3)$$

The fraction of fixed biomass is finally given by equation (4)

$$Y = (V_{bio} \cdot \rho_{bio}) / (V_r \cdot \rho_c) \quad (4)$$

This method is simple, fast and precise. However, some limits are not to neglect like the importance of the sampling of bio-particles and the effects of prospect which can harm the measuring accuracy.

2. Structure

Thirty particles support are taken and washed with distilled water in order to recover the biofilm for finally putting it in suspension in 250 mL of distilled water. This suspension is then crushed using a Ultrasonic crusher and divided to 2 samples. Measurements are carried out on these two samples. Then weigh the dry particles in order to be able to bring back the results to PVC mass.

a. Total protein

They are measured by the method of Lowry O, et al., (1951). This colorimetric proportioning is based on the resultant of two simultaneous reactions:

- standard reaction Biuret: the polypeptide molecules which contain at least four groupings C-N-OH give in alkaline medium a colored cupric complex
- the phenolic cores of tyrosin, tryptophan and with a degree less cysteine and histidine reduce the reagent of Folin (tungsto-phosphomolybdic)

The calibrated method is with known quantities of Bovine Serum Albumin (BSA). Thus, the results will be expressed out of mg BSA/ mg PVC. The slope is 0.0733 Mg BSA/mL per unit of absorptance and coefficient of correlation of 0.9986.

b. Quantity of exopolysaccharides (EPS)

Method of Dubois M, *et al.*, (1956) is used. In this method, polysaccharides are hydrolyzed by the sulphuric acid concentrated out of monosaccharides which are dehydrated into derived from furfural which reacts in their turn with phenol. The calibrated method is with known quantities of glucose. Also, the results are expressed out of mg of glucose by mg PVC). The slope is of 51.52 mg/L of glucose per unit of absorptance and the coefficient of correlation of 0.9995.

3. Measure activity by respirometry

a. Experimental device

The test respirometric is carried out in a reactor whose effective volume is 800 mL equipped with a magnetic stirrer. Agitation is adjusted so as not to bring of oxygen to medium while ensuring the mass transfers in reactor. The measurement of oxygen concentration is carried out by a probe Orbisphere Model 3600 diving in reactor and connected to a system of data-processing acquisition of data. The frequency of acquisition is measured every 30 seconds.

b. Principe of respirometric measurement

The speed of oxygen uptake by biomass (OUR: Oxygen Uptake Rate) is calculated by carrying out a mass balance on the oxygen dissolved in reactor (equation (5)):

$$\frac{dC}{dt} = K_{La}(C_s - C) - OUR \qquad (5)$$

OUR (mg/L/s) is divided into two components

- OURend: speed of endogenous oxygen uptake due to the degradation of substrates by self-oxidation of the biomass
- OURexo: speed of exogenic oxygen uptake corresponding to the degradation of substrates quickly biodegradable

Then Equation (6) is given:

$$\frac{dC}{dt} = K_{La}(C_s - C) - OUR_{end} - OUR_{exo} \qquad (6)$$

For exogenic breathing, the activity is distinguished from the autotrophic bacteria (nitrifying) and heterotrophic to lead thus to equation (7):

$$\frac{dC}{dt} = K_{La}(C_s - C) - OUR_{end} - OUR_{exoA} - OUR_{exoH} \qquad (7)$$

c. Course of a test

To take approximately 50 g bioparticles in pilot whom one places in reactor of respirometry. And supplement to 800 mL with tap water, and then launch agitation

and ventilation. After stabilization of the probe (about 20 minutes), it can launch the acquisition of the data during approximately 5 minutes. Then ventilation is cut until obtaining a dissolved oxygen concentration of 4.5 mg/L. Then evaluate the speed of oxygen uptake in absence of substrate (OURend). Then it can be carried out a reventilation until saturation to estimate the oxygen concentration at saturation (Cs) and the coefficient of transfer (K_{La}).

The second part proceeds in three times:

- Firstly, sodium acetate 5mL with 8 g/L is injected at the same time as the cut of ventilation. One can then calculate the speed of consumption exogenic of the oxygen dissolved by the heterotrophic bacteria (OURexoH).
- Once concentration of 4.5 mg/L reached, reaction medium during approximately 4h in order to be sure that all the carbonaceous substrate was consumed
- Secondly, add 4 mL of ammonium chloride to 4 g/L at the same time as the cut of ventilation. It can calculate the speed of consumption exogenic of dissolved oxygen by the autotrophic bacteria (OURexoA)
- Finally, the speed of consumption is obtained.

The first limit of respirometric method in this case is the time of analysis. Indeed, considering the small quantities of biomass brought into action, times of oxygen uptake make that measurement lasts at least 24 hours. Therefore, the computed values are not really instantaneous of the activity of biofilm within the pilot.

3 Results and discussions

3.1 Formation

The pilot plant was seeded simultaneously with the PVC tubes as carrier and the suspended nitrifying sludge (2000-3000 mg/L MLVSS) from the Wastewater Treatment Plant of Limoges. The synthetic wastewater containing the nutrients such as ammonium chloride, bicarbonate and phosphate, was one-off fed into the reactor. The experimental run was conducted with constant aerated gas by Ventrui

aero-ejector. First start-up conditions include: normal temperature (about 20℃), aeration flow 120 L/h, influent TOC 90.75~233.95 mg/L, operation period 12 h. During the continuous 11 days experimental runs, sludge expanded and qualities effluent were dissatisfactory, a few sludge escaped following on the heels of effluent. The color of carrier surface was not changed. By microscopical exam procedure, it was not founded that the microorganism adhering to carrier. Figure 3 depicts the influent and effluent concentrations of TOC versus the operation days. TOC removal efficiencies were up to 60%. Obviously, the biofilm of carrier have not effected of on nutrients removal, contrarily the activated sludge. Because of 12 h operation period, it is beneficial for activated sludge growth and reproduction, thereby sludge captured the nutrients which should be fed to microorganism of carrier surface, and thus biofilm formation was difficult. Moreover sludge expanded also restrained biofilm formation. Based on activated sludge played dominant function in reactor, even a few microorganisms could adhere above the carrier, biofilm formation cannot achieve using the weak nutrients.

Thus change the operation conditions, operation period was shortened to 6 h. The start-up process renewed. After 7 days operation, the color of carrier changed significantly and the adhesion phenomenon carried on carrier surface. By microscopical exam procedure, microorganisms acculturated and cumulated on carrier surface (see figure 4), biofilm was buff and clarity. During the experiment, sludge was not expanded, the concentration of sludge maintain steadily. Figure 5 shows biofilm formation versus the operation days.

At the later experiment, biofilm formation was steadily, the thickness was above 300 μm which adhering the interior. Because of PVC tube structure, biofilm formation carried on stronger the interior than exterior. When biofilm formation was obtained, the operation period backed to 12 h, biofilm did not fall off. It declared that the initial bacteria adhesion was important for biofilm formation, the exoteric infection was weak when biofilm achieved. Thereinafter studies were under different condition according to the necessaries.

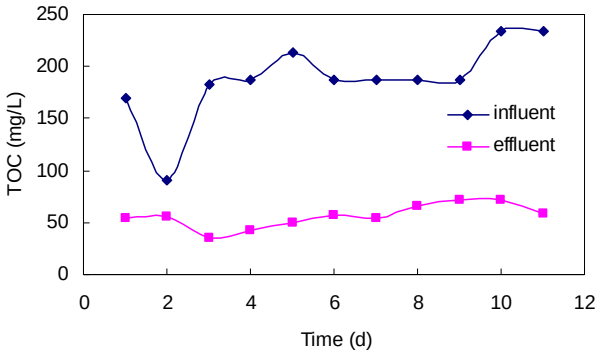


Figure 3. Influent and effluent concentrations of TOC versus the operation days

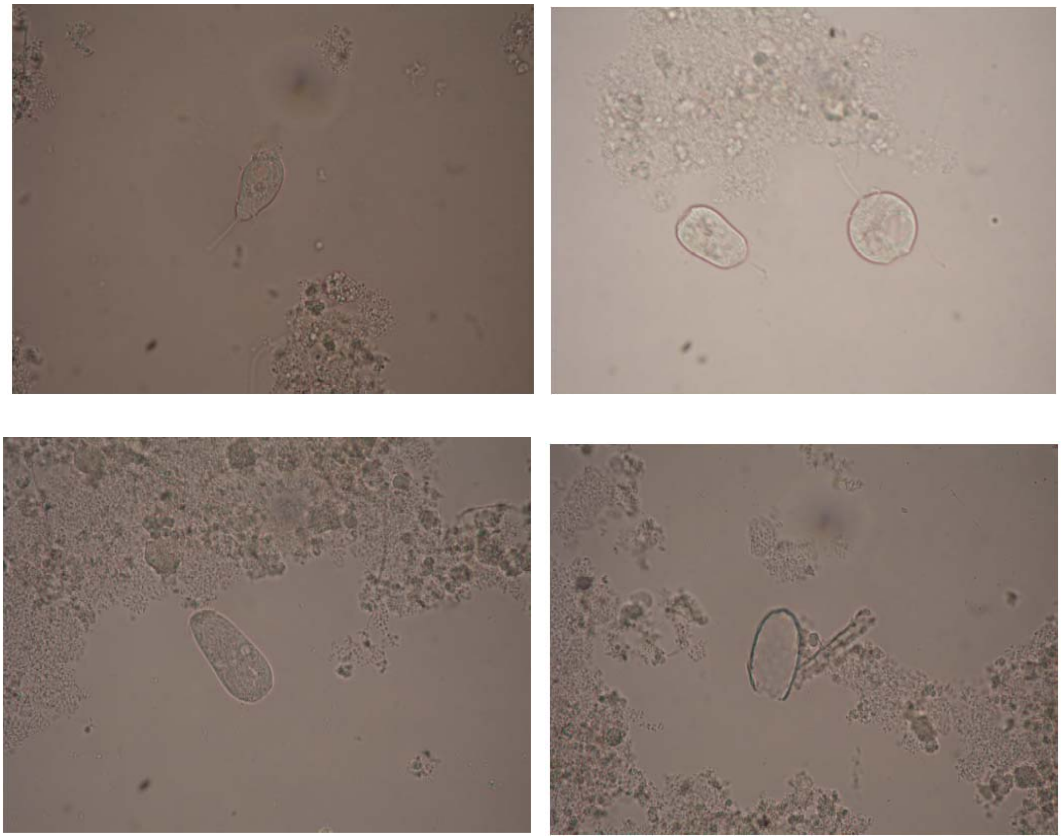


Figure 4. Types of microorganisms

(a) naked PVC tube (b) 7 d

(c) 14 d (d) 21 d

(e) > 30d (f) > 30 d profile

Figure 5. Biofilm formation versus the operation days.

3.2 Characteristics of boifilm

Three phases are to be distinguished during 90 days studies. From 0 to 12 days, the phases are as follows: 2h of anaerobic followed by 9h of aerobic then one hour of rest. The end of this first phase is marked by an incident: The bubbles of the consecutive pilot to the accidental draining of sludge. Then the reactor is maintained

under the same conditions until 43 day, date from the implementation of the complete cycle describes previously.

3.2.1 Specific components and relationships to thickness and activities.

Measurements of proteins (PN) and relationships of activities

The quantity of total proteins within the biofilm (Figure 6) evolves constantly with the course the various production runs from the pilot: after a strong growth during the first days of exploitation, it fell after the incident of exploitation of 12 day before increasing again during the production run in aerobe. The exploitation by complete cycles as from 43 day involves a strong reduction in this quantity of proteins. After 70 days, the beginning of stabilization is observed.

Similarly, the constant evolution of the various activities is measured by respirometry within the biofilm. Heterotrophic speeds specific endogenic and exogenic evolve as well: the major reduction at the beginning (0 to 36 days) is undoubtedly due to the incident of exploitation of 12day while the implementation of the complete cycles at 43day causes their reduction then a beginning of stabilization.

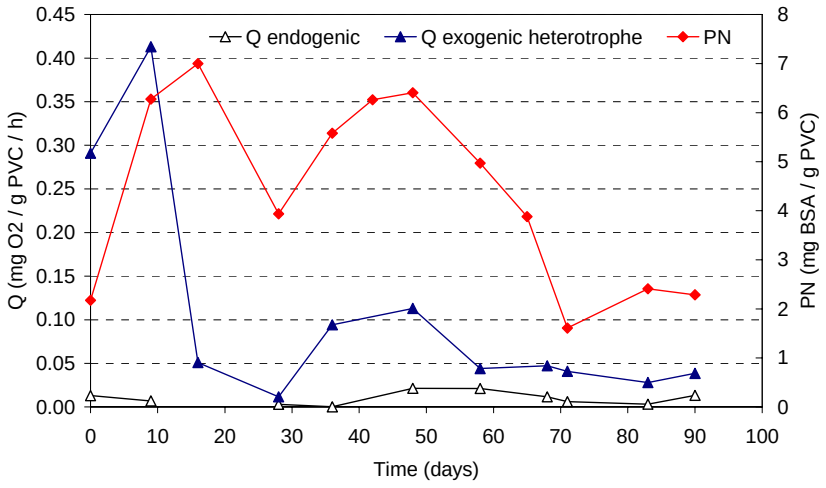


Figure 6. Evolution of the quantity of proteins and the respirometric activities

Exopolysaccharides (EPS) and thickness

The EPS are responsible at the same time for the adhesion and cohesion of the cells. The secretion of EPS in great quantities by biofilm is a phenomenon associated

with the mechanical stress to which the biofilm is subjected. This stress (caused by frictions between particles, bubbles of air…) an increased secretion of these EPS causes. Moreover, it can find that during the first phases of the biofilm formation, there is a strong production of exopolysaccharides, what supports the initial adhesion of bacteria.

As described on Figure 7., EPS evolve constantly during the exploitation of pilot. Their production does not seem affected by the incident of exploitation of 12 day. Against, their quantity falls abruptly starting from the implementation of complete cycles. The beginning of stabilization is then observed. If the latter is confirmed thereafter, the peak of secretion of EPS could be associated the overproduction related to the initial adhesion of biofilm.

The biofilm thickness increases constantly until the implementation of complete cycles. From this moment, it can observe then a major reduction average thickness. Obviously, besides it can find the important detachment of biofilm.

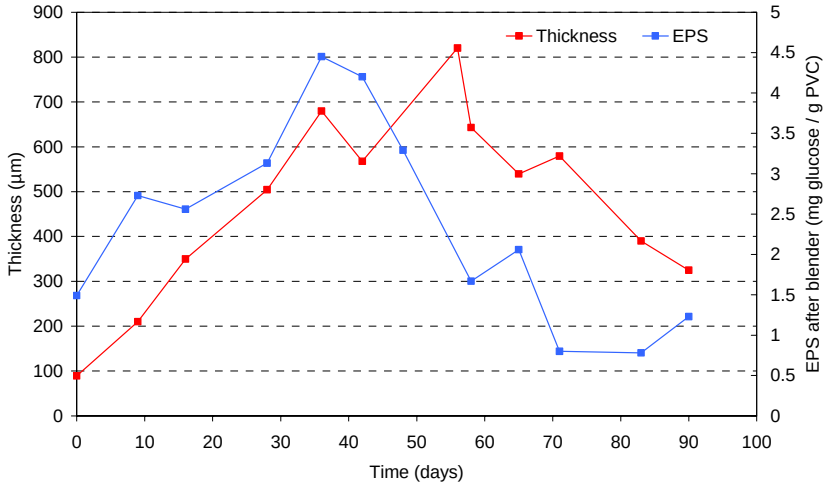


Figure 7. Evolution of the EPS and thickness of the biofilm

The biofilm thickness used as indicator of the evolution of the biofilm in many studies concerning the biofilm in engines EFBBR, is not a sufficient parameter to estimate the viability of biofilm. Indeed, as Figure 8., the evolution thickness is especially related to the quantity of EPS which surrounds the micro-organisms. However, the EPS intrinsically do not indicate the concentration of active biomass. The thickness is, like EPS, an indicator of the forces of shearing (friction of the air, shock between particles and against the wall of the reactor) to which the biofilm is subjected.

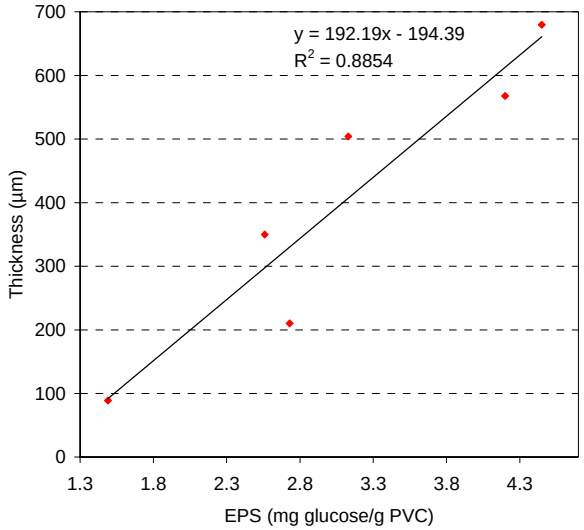


Figure 8. Relation between the thickness of biofilm and quantity of EPS

PN/EPS

Considering the results, the PN/EPS can be interpreted like the proportion of active biomass compared to the inert extra cellular of biofilm. Figure 9. gives the evolution of ratio during the exploitation of pilot. The first peak observed corresponds to the first consecutive peak of activity to the starting of reactor (Figure 6.), EPS being then in constant growth (Figure 9.). The incidents of exploitation of 12 day fact quickly of reduce the PN/EPS which takes again its growth to reach a new peak between 55 and 60 days. It can observe the fall a last peak (mainly of with the strong reduction in EPS) between 80 and 85 days.

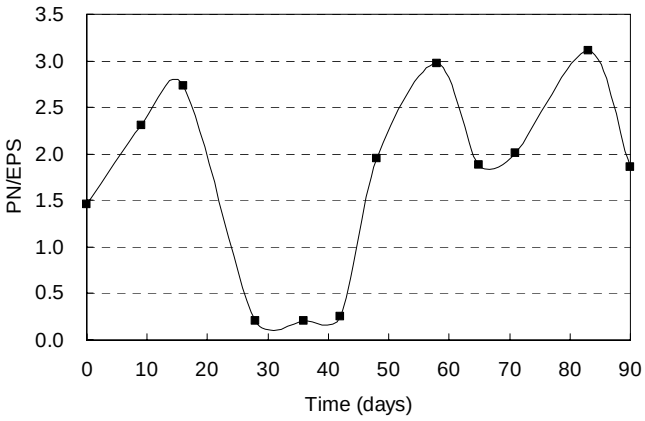


Figure 9. Evolution of PN/EPS during the exploitation of the engine

3.2.2 Estimate of biomass fixed starting from thickness

Based on the various correlations suggested by Rabah and Dahab, calculations were obtained very divergently, the results in terms of quantity of biomass fixed in reactor (Figure 10.). In all the cases, the concentration of fixed biomass is not proportional to thickness and concentration can be constant in the variations thickness.

However, these correlations being based on the decrease of the density of biofilm with the thickness, the evolutions are similar in particular for those Coelhoso et al. (1992), Mulcahy and La Motta (1978). and Boaventura and Rodrigues (1988). The first gives the highest results while the two others give intermediate results. For these three cases, after one period of initial growth, the concentration stabilizes as from the day a 15 then light peak to the maximum the thickness at 57day. The correlation of Hermanowicz and Cheng (1990) gives an evolution a little different with one period from more reduced growth (10 day) then a clear reduction 57 day before a new increase. These results confirm the fact that the thickness of biofilm is not the parameter determining the quantity of biomass really present.

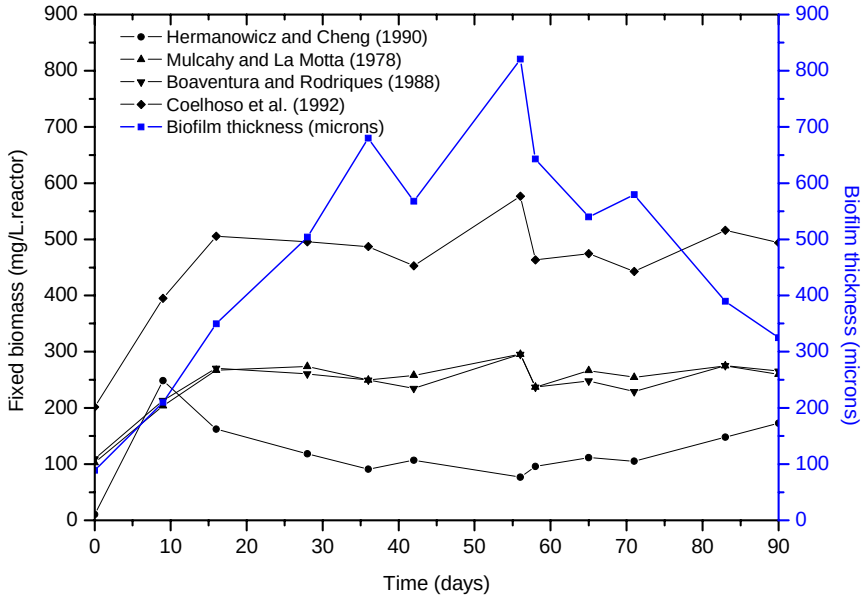


Figure 10. Evolutions average thickness of biofilm and concentration in fixed biomass calculated according to various correlations

4 Conclusions:

In a novel fluidized bed bioreactor, under the conditions of influent TOC 90.75-233.95 mg/L and operation period 6 h was beneficial for biofilm formation. And biofilm formation was steadily, the thickness was above 300 μm which adhering the interior. Because of PVC tube structure, biofilm formation carried on stronger the interior than exterior. When biofilm formation was obtained, it declared that the initial bacteria adhesion was important for biofilm formation.

The simple methods used for the characterization of the biofilm gave the biofilm evolution: the biofilm is influenced by the exploitation conditions (cycle management). Correlations between structural and activity parameters have been demonstrated: proteins are linked with the activity and thickness is linked with exopolysaccarids production.

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II. 5 Discussion of Results and Modelization

II. 5.1 Introduction

As an effective technology of biological wastewater treatments, the applications of activated sludge system and biofilm process become wider along with the control of industrial wastewater and municipal sewage (Joseph AS, et al., 2003). These treatments processes are based on the use of microorganisms, immobilized or not. Nowadays a great interest is conceded to biofilm processes, which prove to be economic and efficient. The existing biofilm processes can use three kinds of microbial aggregates: static biofilms (e.g. in trickling filters), flocs (e.g. in activated sludge processes) and particulate biofilms (in biofilm airlift suspension reactors; biofilm fluidized bed reactors). Fluidized bed bioreactor (FBBR) seems to be the best one and present many advantages relating to hydrodynamics and mass transfer phenomena (Toumi LB, et al., 2008).

Mathematical models are developed as well, such as Activated Sludge Model (ASM) (Henze M, et al., 2000), and biofilm kinetics (Bruce E R and Mccarty PL, 1980). However using ASM in biofilm processes, the results are not satisfactory, thus modeling of biofilm are innovated. Kinetics model of FBBR are presented as well. Asif M and Abasaeed AE (1997) studied on a heterogeneous model describing the glucose isomerization process in an immobilized enzyme fluidized-bed bioreactor. It was found an excellent agreement between model predictions and experimental data for two isomerases (PG-GI Complex and Sweetase) obtained from the literature. Tsuneda S. et al., (2002) performed on a completely mixed three-phase FBBR used in treating simulated domestic wastewater. The data obtained were fitted to five different kinetic rate equations. The kinetic parameters of each model were obtained using a Gauss-Newton nonlinear regression analysis method. As a result, although various types of conventional biokinetic models such as Monod, Haldane and Andrew types were examined, all the theoretical substrate response curves underestimated time constants compared to the actual substrate response plots. At present, many research works using biofilm kinetics were reported (Mccarty P and Meyer T, 2005; Béteau JF, et al., 2005; Khiari B, et al., 2008). Therefore, successful application of fluidized bed reactors lead several researchers to propose models that could describe the biological mechanisms with realistic accuracy. But, up-to-date, the complexity of various

interactions between microorganisms, mass transfer phenomena and hydrodynamics occurring in these kinds of systems, let proposed models open to discussion since they are established on number of simplifications and assumptions.

During the last thirty years, extensive research on biological wastewater treatability in SBR has been carried out. However, most of this effort focused on the experimental aspects of design and operation and only few papers presented mathematical expressions for the SBR system (Nakhla GF, et al, 1997). Compared with the continuous flow activated sludge systems, the mathematical description of SBR is not fully developed. However the mathematical expressions that partially describe the SBR operation have been reported since last 1970s. Dennis and Irvine (1979) developed substrate mass balance equations for the fill and react periods, and later Irvine and Ketchum (1989) presented mathematical expressions for bacterial growth and substrate utilization during the react period using Monod kinetics. Nakazawa and Tanaka (1991) developed the mathematical model of SBR based on the continuous full-mixed activated sludge system. Since IAWQ recommended ASM, the researchers carried out the SBR mathematical simulation with ASM. Oles and Wilderer (1991) described the NH_3 and NO_x evolution during the biological process using ASM1. Bernner (2000) established the model of N and P transformation in a SBR.

However, the real biological system is the complex ecosystem, it is impossible that the activated sludge or biofilm exists solely. And the mathematical model considers the system incompletely. In this study, a kinetic model of organic degradation in an extra-loop fluidized bed bioreactor was attempted based on test for PVC carriers and a feed synthetic wastewater. The experiment measured the biofilm density and the maximum specific rate of substrate utilization. And from the results, the diffusion coefficient within the biofilm and that on the biofilm surface was determined as well. The model was established and validates its validity over the range of the test conditions.

II.5.2 Model developments

II.5.2.1 The coexistence system of the activated sludge and biofilm

In fact, the EFBBR is the coexistent system with the activated sludge and biofilm. The activated sludge grows and renews in the system and the biofilm formation and accumulation carries out in the system as well. The research demonstrated that the biofilm formation is the result of the physical, chemical and biological process (Liu. Y et al., 2000). Figure 1. presented the biofilm formation process on carrier. The organic matter transfers from the liquid phase to the carrier's surface; the portion is adsorbed and modified the carrier's surface (Figure 1.a). The suspended microorganisms are transferred to the modified carrier's surface; some parts which adhered on the carrier parse again after the physical, chemical and biological process, some parts are not parsed and adhered on the carrier (Figure 1.b). The adhered cells grow with incepting and consuming the substrate and nutrition in the water; some production released out of the cell, the exopolymers can combine the biofilm firmly, hence the biofilm formation achieved and the substrate is consumed simultaneously (Figure 1.c). The accreted cells or the free cell which produced can be released into the water at a certain extent (Figure 1.d).

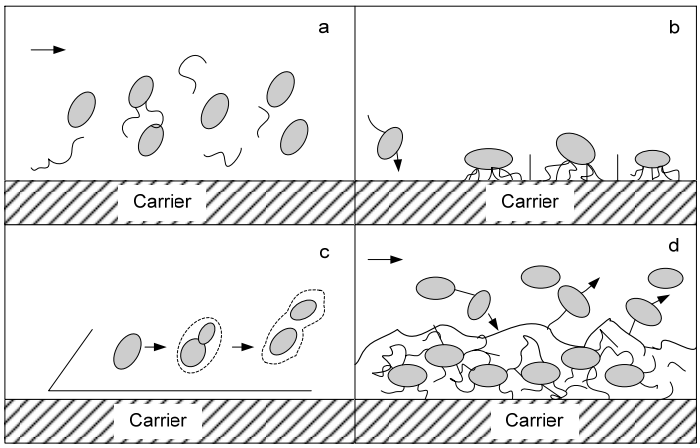

Figure 1. The biofilm formation on carrier

II.5.2.2 Mathematical model

Hu LM and Chai LH (2005) suggested the CSTR biofilm model (the activated sludge and biofilm system in fact) and assumed the simplification system. Some reasonable considerations or the simplification to the biofilm wastewater treatment system were obtained: neglect biofilm's three-dimensional space structure; the biofilm is infinite thin, and has not affected to the fluid environment; Considered the

sole soluble substrate which is the food origin of the suspended microorganism and cohered microorganism; and supposes the soluble substrate for the sole restrictive growth factor; Based on the dynamic operation of the biofilm reactor, the suspended and cohered microorganism can transfer each other, this kind of transformation processes can effect on the removal as well.

The research indicated that in the assured system, the suspended microorganism density has represented contact frequency between the microorganism and the carrier. Generally, the microorganism and carrier contact probability along with its markup when the suspended microorganism density increases. The literature had reported that it has the proportional relationship between the cohered microorganism density and the suspended microorganism's density.

In summary, the biofilm formation and dynamics process mathematical model can be adopted following supposition to establish, and carries on the theoretical analysis and the simulation. In the reactor the carrier surface has the limited quantity to be possible to breed the spot surely, therefore the cohered microorganism has a maximum area density; the suspended microorganism can be adsorbed surely the carrier surface according to its density and the score of the free breed point on carrier in proportion; the cohered microorganisms fall off and enter the fluid in proportion to its area density; the sub-cells of the cohered microorganisms compete mutually the growth space of the carrier: The sub-cells of the score G can find the point of attachment, and the 1-G sub-cells cannot find the point, only can enter the fluid.

Because the full saturated carrier surface provides the very few growth opportunity to the sub-cell, therefore the supposition of decreasing function G=G(W) is reasonable. The growth of the suspend microorganism and cohered microorganism are applicable with Monod equation and the probability function can be written as following:

$$G(W) = \frac{1 - W}{1.1 - W} \tag{1}$$

$$W = \frac{X_b}{X_{bm}} \tag{2}$$

Where,

G(W): decreasing function of carrier surface occupancy percentage
W: cohered microorganism occupancy percentage on carrier
X_b: cohered microorganism concentration on carrier, mg/dm^3
X_{bm}: maximum cohered microorganism concentration on carrier, mg/dm^3

Based on the above suppositions, the mathematical model of the CSTR reactor was recommended by Hu and Chai (2005) and expressed as:

$$\begin{aligned}
\frac{dS}{dt} &= D(S_0 - S) - Y_a^{-1}\mu_{ma}\frac{X_a S}{K_{Sa}+S} - Y_b^{-1}\mu_{mb}\frac{X_b S}{K_{Sb}+S} \\
\frac{dX_a}{dt} &= X_a(\mu_{ma}\frac{S}{K_{Sa}+S} - D - k_a) + \beta X_b + X_b\mu_{mb}\frac{S}{K_{Sa}+S}(1-G(W)) - \alpha X_a(1-W) \\
\frac{dX_b}{dt} &= X_b(\mu_{mb}\frac{S}{K_{Sa}+S}G(W) - \beta - k_b) + \alpha X_a(1-W)
\end{aligned} \tag{3}$$

Where:

dS/dt: consume rate of the substrate, mg/L h
dX_a/dt: consume rate of the suspended microorganism, mg/L h
dX_b/dt: consume rate of the cohered microorganism, mg/L h
S: substrate concentration in reactor, mg/L
Y_a: yield coefficient of the suspended microorganism
Y_b: yield coefficient of the cohered microorganism
X_a: suspended microorganism concentration in reactor, mg/L
F: flow velocity, m^3/h
V: reactor volume, m^3
D: dilution coefficient, D=F/V, h^{-1}
β: fall off rate of the cohered microorganism, h^{-1}
α: adhere rate of the suspended microorganism, h^{-1}
μ_{ma}: maximum specific consume rate of the suspended microorganism, h^{-1}
μ_{mb}: maximum specific consume rate of the cohered microorganism, h^{-1}
k_a: decay rate of the suspended microorganism, h^{-1}
k_b: decay rate of the cohered microorganism, h^{-1}
k_{sa}: saturation coefficient of the suspended microorganism, mg/L
k_{sb}: saturation coefficient of the cohered microorganism, mg/L

II.5.2.3 Mathematical model analysis and simplification

Equation (3) can be applied in the continuous biological treatment process with the activated sludge and biofilm coexistent system. Certainly, equation (3) can be restored as single microorganism system, such as the activated sludge system and biofilm process.

However, for all the SBR process, the model has to be innovated and simplified. In equation (3) D is the dilution coefficient, The feed stage of the SBR process can be employed as well because of the reactor volume change along with the feed.

In SBR process, equation (3) would be modified with omitting the D, so the equation is simplified and expressed as:

$$\begin{aligned}
\frac{dS}{dt} &= -(Y_a^{-1}\mu_{ma}\frac{X_aS}{K_{Sa}+S} + Y_b^{-1}\mu_{mb}\frac{X_bS}{K_{Sb}+S}) \\
\frac{dX_a}{dt} &= X_a(\mu_{ma}\frac{S}{K_{Sa}+S} - k_a) + \beta X_b + X_b\mu_{mb}\frac{S}{K_{Sa}+S}(1-G(W)) - \alpha X_a(1-W) \\
\frac{dX_b}{dt} &= X_b(\mu_{mb}\frac{S}{K_{Sa}+S}G(W) - \beta - k_b) + \alpha X_a(1-W)
\end{aligned} \qquad (4)$$

Equation (4) present the substrate and microorganism (the activated sludge and biofilm) normal SBR process. It can be simplified farther so as to fit in with the stead-state system. Therefore, assume G(W)=1, it means that the carrier surface occupancy percentage is 100%, on carrier there is the biofilm only. The biofilm can fall off and the suspended microorganism can adhere, but a stead-state balance is existed. Consequently, equation (4) would be modified more, is evaluated as:

$$\begin{aligned}
\frac{dS}{dt} &= -(Y_a^{-1}\mu_{ma}\frac{X_aS}{K_{Sa}+S} + Y_b^{-1}\mu_{mb}\frac{X_bS}{K_{Sb}+S}) \\
\frac{dX_a}{dt} &= X_a(\mu_{ma}\frac{S}{K_{Sa}+S} - k_a) + \beta X_b - \alpha X_a(1-W) \\
\frac{dX_b}{dt} &= X_b(\mu_{mb}\frac{S}{K_{Sa}+S} - \beta - k_b) + \alpha X_a(1-W)
\end{aligned} \qquad (5)$$

Equation (5) is the simplified mathematical model of SBR for the stead-state of the activated sludge and biofilm coexistent environment.

II.5.3 Parameters calculation

However, the actual activated sludge and biofilm coexistent system is too complex to discuss difficult respectively. Because the biofilm formation using the inoculated activated sludge, the characteristics of the biofilm can be seen as the same as the suspended sludge. Thus, the performance of the activate sludge and biofilm is the same type of the microorganism.

However, the calculated results show the microorganism including the activated sludge and biofilm; in actual reactor the both carrier on their function respectively. In fact, the microorganism exist as the biofilm formation adhering on the carrier surface in biofilm reactor, the nutrient in water must transfer to the biofilm surface and interior and eliminated by the microorganism. The transfer is contained the reaction-diffusion mode. Hence, the kinetics of biofilm reaction system has the relations with the biological reaction and the diffusion process, and the diffusion process limit the nutrient removal mostly. Under the diffusion condition, the substrate which on the biofilm surface is eliminated following:

$$r_A = k_A S \tag{8}$$

Where,

r_A: reaction rate per unit time and unit biofilm area, g/m^2 h;

k_A: rate coefficient with the area, m/d

From equation (8), it is showed that the substrate eliminated following the first-order reaction law.

For the thick biofilm, equation (8) can be rewritten as:

$$r_A = \sqrt{D_f k_{Vf} S} \tag{9}$$

Where,

D_f: diffusion coefficient, m^2/h

k_{vf}: first-order reaction constant, h^{-1}

The D_f can be calculated with the dry biofilm density (Rittman BE, and McCarty PL, 1980),

$$\frac{D_f}{D_w} = 1 - \frac{0.43\rho_f^{0.92}}{11.19 + 0.27\rho_f^{0.99}} \tag{10}$$

The dry biofilm density is measured as about 500mg/L in EFFBR, so D_f/D_w is obtained with 0.98. The diffusion of the glucose is reported by Fan LS (1990) such as Dw=0.667×10^{-9} m^2/s, so D_f is 2.35×10^{-5} m^2/h.

Assumed the activated sludge and biofilm effect on the nutrient removal simultaneously with same rate. In EFBBR, the activated sludge is 2.404g/L and the

biofilm is about 500 mg/L, so S used in equation (9) is 17.2% of total S. Using the carrier surface area (600g PVC tubes with total surface area is 0.157 m^2), and the biofilm density, from the equation (9) k_{vf} is obtained as 0.212 h^{-1}.

Connected equation (5)(6)(9), the mathematical model of EFBBR with SBR process can be expressed as:

$$\frac{dS}{dt} = -(\frac{\mu_{ma} X_a S_a}{K_{sa} + S_a} + A\sqrt{D_f k_{Vf}} S_b) \qquad (10)$$

Where,

A: biofilm surface area, m^2

$S=S_a+S_b$: relation to the concentration of the activated sludge and biofilm, mg/L

II.5.4 Analysis of model error

In fact, the actual biological system is the complex biogeocenose, the activated sludge and biofilm coexist and bring into play the different role in nutrient removal. The mathematical model is established based on the assumed conditions, and explain the dynamic process in principle only. The errors incorporate as follows:

The EFBBR is a CSTR reactor, but its fluid state is not strict full-mixed, the different fluid states are appeared in the different positions, and the substrate distributing asymmetrically. Its structure is complex as well, the model can not express whose functions in the operation.

The carrier is not strict full sphere, and its fluid state is complicated.

The operation circumstantiality is fluctuant at certain extent, and is not really stead-state normally.

The nutrient elimination is been regarded as First-order reaction law, but the factual reaction is including physical, chemical and biological process, using first-order reaction law characterized approximately.

Those coefficients are related with temperature, the EFBBR operates at the wide range correspondingly, the mathematical model is not demonstrated either.

The biofilm thickness is changed according to the operation conditions, and its density is the function of the thickness.

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Conclusion générale

L'étude proposée dans ce mémoire a consisté à évaluer et à optimiser un nouveau bioréacteur de type lit fluidisé en boucle fonctionnant en discontinu (EFBBR). Le réacteur est composé de deux boucles : une boucle constituant la zone de fluidification couplée à une zone de sédimentation, plus large, et une seconde boucle sur laquelle est connectée une pompe ayant pour finalité la mise en circulation dans le réacteur et, au travers d'un aéro-éjecteur, l'aération de l'effluent. La hauteur du réacteur est de 1m pour un volume utile de 38 L. La fluidification est contrôlée par le débit dans la boucle de pompage. L'aéro-éjecteur est de type Venturi ; il permet la maîtrise de l'aération par la régulation de la dépression sur le col du Venturi et un contrôle du débit d'air. Le système ainsi défini permet de maîtriser les flux de liquide, de solide et de gaz dans la zone de fluidification.

Les caractéristiques hydrodynamiques et du transfert d'oxygène ont été déterminés pour différentes configurations du réacteur. Les résultats montrent que le temps de mélange hydraulique est diminué lorsque la vitesse du fluide dans le réacteur augmente. Le nombre de Peclet caractéristique du réacteur est environ de 0,2 pour un nombre équivalent de réacteurs en série n de 2.5 à 3. L'hydrodynamique du réacteur peut être approchée par la configuration d'un réacteur parfaitement agité. Lorsque le débit d'aération augmente pour un même débit dans la boucle de mise en circulation (capacité d'aération) le temps de mélange hydraulique est réduit. Durant les trois phases du procédé (alimentation anoxique, fluidisation, décantation), le temps de mélange hydraulique dans le réacteur n'est pratiquement pas réduit par l'augmentation conjointe de la charge en solide et de l'aération.

Les études montrent que les paramètres essentiels de l'hydrodynamique sont la vitesse du fluide, la capacité d'aération et la présence de la phase solide. Suite à une augmentation de la vitesse dans la boucle de pompage (u1) le transfert gazeux augmente rapidement selon une relation du type :

$$Q_g = 190.35\{(\rho \cdot \frac{u_1^2}{2})[(\frac{S_1}{S_2})^2 - 1]\} - 95.088$$

Le coefficient de transfert K_{La} augmente d'une part avec l'accroissement de la charge

en air mais également, pour un même ratio gaz/liquide, lorsque la perte de charge est importante. La charge en solide a une influence complexe sur le K_{La}. Celle si a des conséquences non significatives pour les charges inférieures à 1000g mais lorsque la charge en solide augmente avec des valeurs supérieures à 1000g, le coefficient de transfert chute. Dans des conditions de ratio gaz/liquide de 0,8 à 5,2%, le K_{La} a une valeur de 0,62 à 1,37 10^{-2} s^{-1}.

Le bioréacteur séquentiel à lit fluidisé a été mis en œuvre pour le traitement d'eau reconstitué dans un premier temps avec les conditions de cycle suivantes : 1,5h en anaérobie, 5h en aérobie, 3,5h en anoxie, 2h de sédimentation et repos endogène. De bons résultats épuratoires sont obtenus avec une bonne qualité de l'effluent sur les paramètres suivants : COT, COD, NH_4-N, PO_4-P ainsi que sur l'élimination du phosphore total (PT). Le système permet une bonne réduction de la matière carbonée, de l'azote et du phosphore tout en s'adaptant aux variations de charges. Les résultats montrent que durant la période d'expérimentation l'influence de la concentration initiale en carbone (DCO) est faible. Le rapport C/N a également peu d'influence sur le rendement d'élimination de la DCO, celui-ci restant proche ce 90%. Pour un rapport C/N de 33,4, la DCO est pratiquement totalement éliminée avec plus de 90% de rendement. Ces conclusions sont en accord avec le travail de Punrattanasin (1997). Cependant, quand le rapport C/P est de 10,4 l'élimination de la DCO chute à 32%. Dans une certaine mesure la température influence peu la biodégradation de la matière organique carbonée. Les performances du EFBBR en nitrification-dénitrification peuvent être excellentes. Durant toute la période testée, l'élimination de l'ammoniaque est supérieure à 95% avec des concentrations dans l'effluent à traiter de 13.8, 34.9 ou 44.6 mg/L en azote ammoniacal (NH_4-N).

L'effet de la concentration initiale en NH_4-N a été étudié sur la nitrification que l'on sépare traditionnellement en phénomène de nitritation et la nitratation. Seule la nitritation intervient pendant la phase aérobie et la denitrification démarre naturellement à partir des nitrites durant la phase anoxique.

Pour un rapport C/N de 33,2, il y production de NO_2-N et de NO_3-N, alors que pour un rapport C/N=10.4, les nitrites et nitrates ne sont pratiquement pas observés. Il apparaît que le EFBBR permet dans certaines conditions la réduction directe de l'azote ammoniacal.

Les performances du bioréacteur pour l'élimination du phosphore sont satisfaisantes. À la fin de l'étape aérobie, l'accumulation des nitrates et nitrites est maximale (respectivement 25,02 - 47,95 mg/L et 0,40 - 2,97 mg/L - écarts pour les expériences réalisées). Durant la phase d'anoxie, la concentration en phosphore devient nulle. Le EFBBR apparaît comme un nouveau procédé efficace pour la nitrification-dénitrification et l'élimination simultanée du phosphore. Dans ce travail, pour un rapport azote total/DCO compris entre 0,0805 et 0,139, le phosphore est totalement éliminé avec une influence réduite de la température.

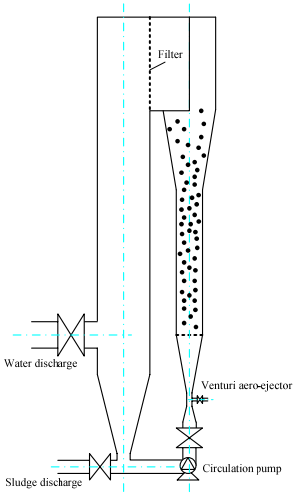
L'utilisation du bioreacteur à lit fluidisé avec des concentrations de 91 à 234 mg/L en COT dans l'effluent, a permis la formation d'un biofilm. d'une épaisseur d'environ 300 μm. A cause de la structure des garnissages en PVC le développement du biofilm est supérieur à l'intérieur des tubes. Les phénomènes d'adhésion étant essentiels dans la formation du biofilm, des méthodes simples utilisées pour la caractérisation du biofilm ont permis de suivre le développement de celui-ci et montrer l'importance des conditions d'exploitation de l'unité (gestion des cycles). Des corrélations entre la structure et les paramètres d'activité ont été observées, les protéines étant reliés à l'activité et l'épaisseur du biofilm fonction de la production exopolysaccharides.

L'accumulation de nitrites est fortement observée dans le bioréacteur EFBBR. L'étude de leur accumulation en fonction de la concentration en ammoniaque disponible montre que les plus forts taux d'accumulation en nitrites ne sont pas reliés à la concentration en ammoniaque. L'influence du pH est difficile à interpréter. L'accumulation des nitrites est le résultat de l'intégration de plusieurs facteurs. La littérature rapporte que l'accumulation de nitrites est favorisée (par rapport à l'accumulation des nitrates) dans des plages de température de 12-14℃ et 30-36℃. Cela résulte de l'inhibition préférentielle des bactéries responsables de la nitritation et de la nitratation. Dans ce travail, les différentes expérimentations sont réalisées soit sans contrôle de la température (19-33℃) soit dans des conditions expérimentales contrôlées (20-25℃) avec dans les deux cas une accumulation de nitrites. Comme l'accumulation des nitrites est observée durant l'étape aérobie, la concentration en oxygène dissous n'est pas la cause de l'absence d'oxydation des nitrites en nitrates. L'alternance de phases en anaérobie et aérobie dans le SBR avec des concentrations

forte puis faible en oxygène semble le facteur favorable au phénomène. Les bactéries propres à l'oxydation en nitrite semblent se développer favorablement dans ce cycle de carence provisoire en nutriment.

Les perspectives à ce travail sont de plusieurs ordres:

- Pilote: fonctionnement de ce pilote pourra être amélioré ar son automatisation. L'alternance de phases pourrait être asservie à l'évolution de la concentration en oxygène et/ou du pH et ainsi optimiser la durée global des cycles. L'alimentation et la vidange seraient également asservies à ces capteurs. Un nouveau design de réacteur, plus fonctionnel est proposé figure suivante



- La connaissance des phénomènes de shunt des nitrates par l'exploration et la comparaison des mécanismes de nitrification / dénitrification. Cette connaissance pourrait être apportée par une approche microbiologique de caractérisation des biomasses actives.

- Le biofilm: le garnissage utilisé n'a pas été optimisé par rapport à sa colonisation par le biofilm. Une recherche des relations support / bioadhésion en fonction des forces de cisaillement inhérentes au fonctionnement de notre pilotes pourrait améliorer la proportion de biomasse fixée et donc la productivité du réacteur. De nouvelles méthodes de caractérisation de la croissance du biofilm pourrait être appliquées et corrélées avec l'activité épuratoire du système.

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Annexes

Publishes during Ph.D. study period:

Xu G.-d, Lu Y.-sh., et al., (2005). Treatment of industrial wastewater in a new bi-external recycling biological fluidized bed. FUWWS, Xi'an, China, 18-20 May

Xu G.d, Lu Y.-sh, Zhang Zh.-y., (2005). Study on the hydrodynamic properties of sequencing batch biological fluidized bed with double outside circulating. *Journal of Qiqihar University*. 2(1):1-4,11 (in Chinese)

Xu G.-d., Lu Y.-sh., Bian H.-s, Zhang Zh.-Y., (2006). Wastewater treatment apparatus of bi-external recycling biological fluidized bed. China. ZL 200420107837.8., Licensed Bulletin Number: CN 2760018Y, Licensed Bulletin Date: 22, Feb. 2006

Lu Y., Laurent J., Dagot C., Baudu M. Traitement d'eau usée par réacteur biologique séquentiel à lit fluidise. Journées thématiques Biofilms 2006. BRGM Orléans, 14-15 Juin

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Partial experimental data:

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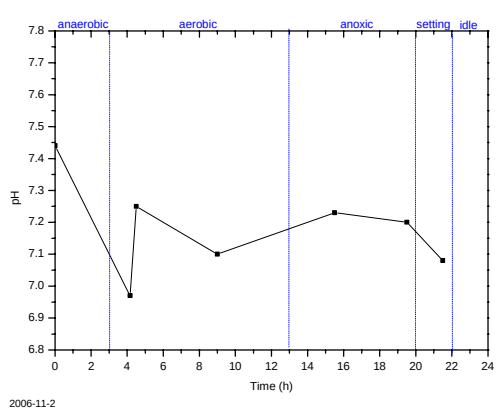
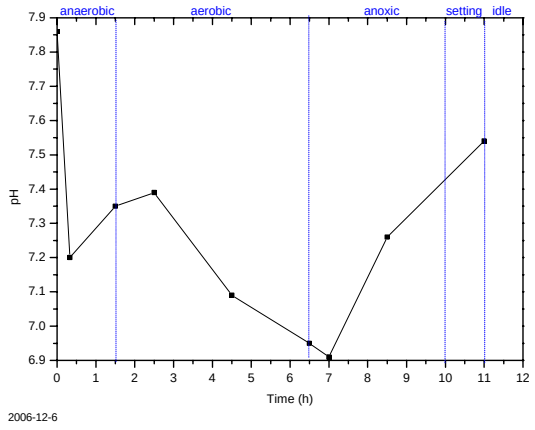
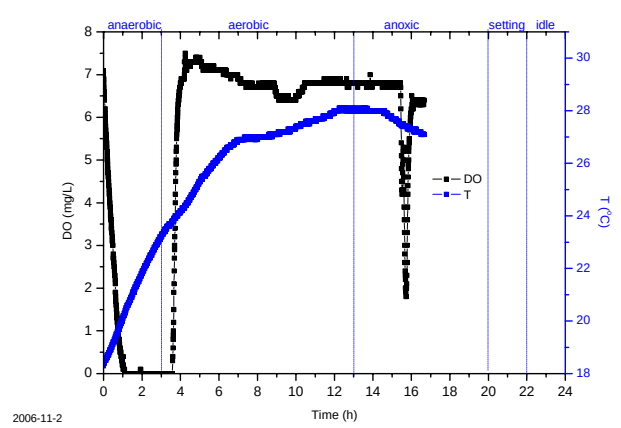
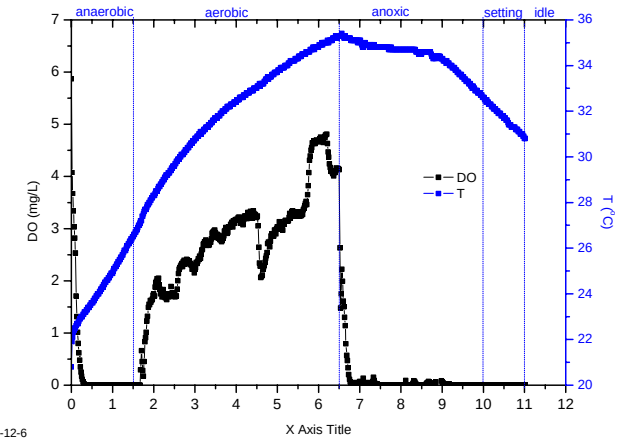
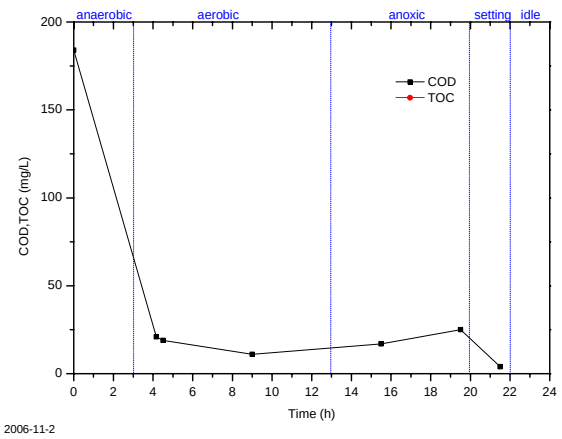
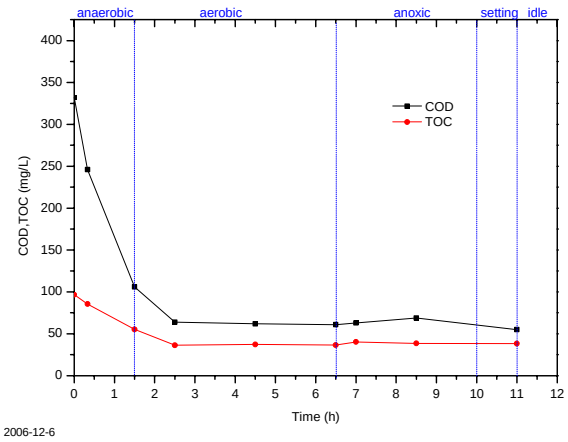
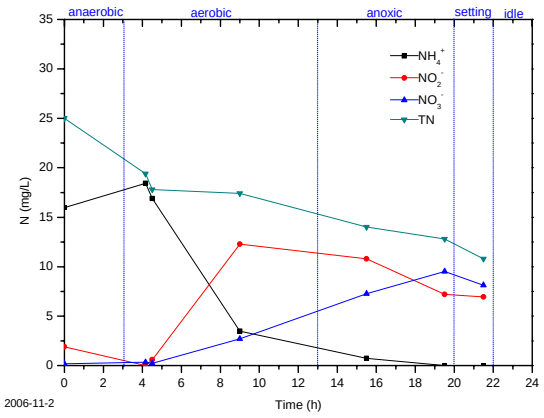
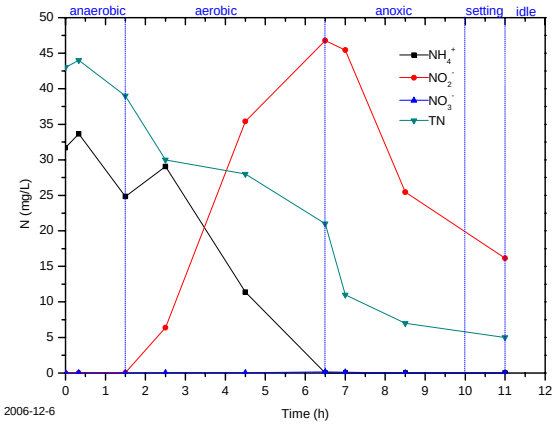
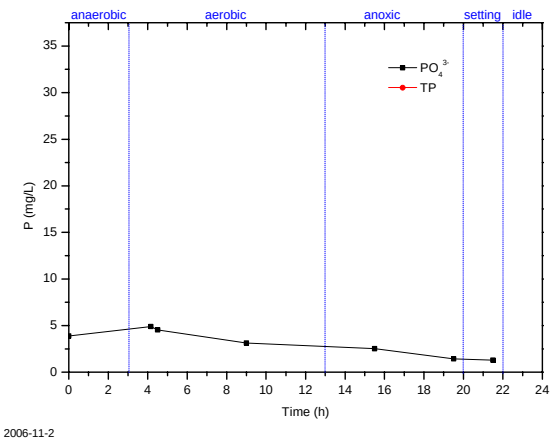
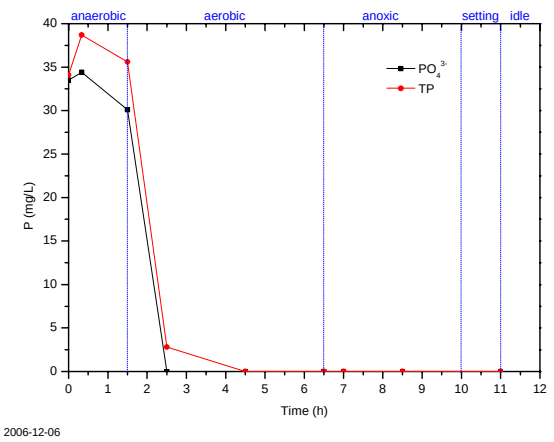
pH			
DO T			
C			
N			
P			

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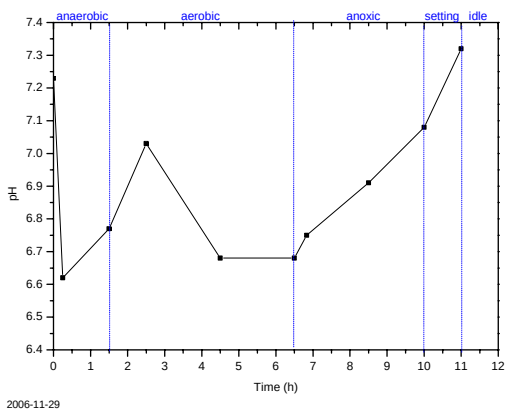
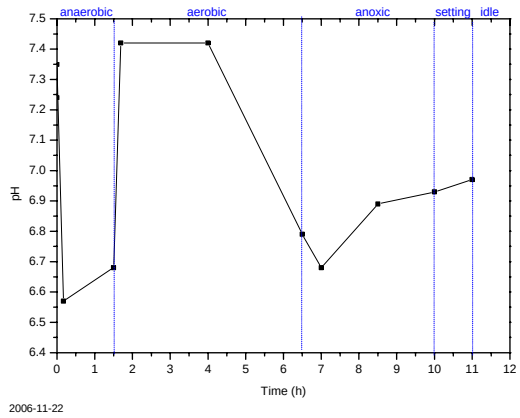
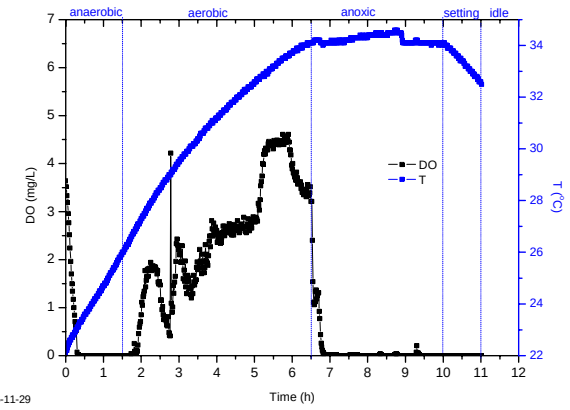
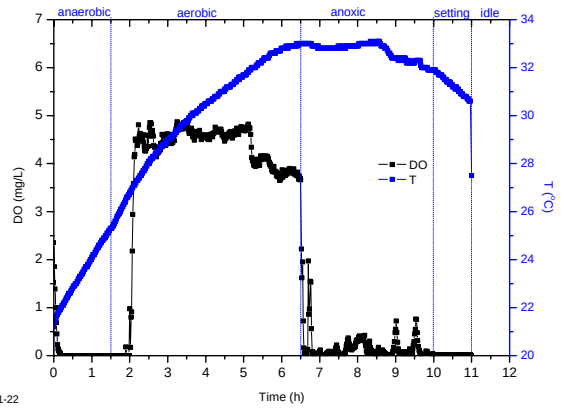
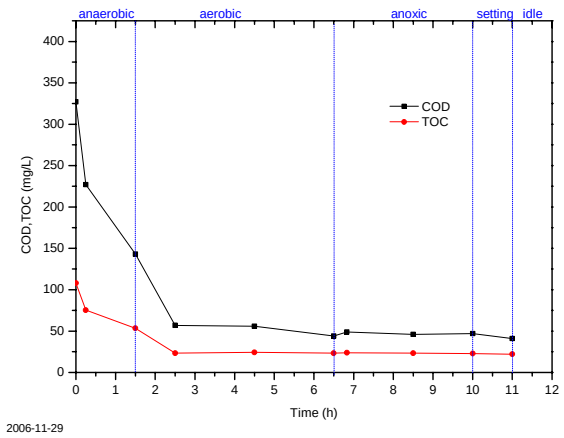
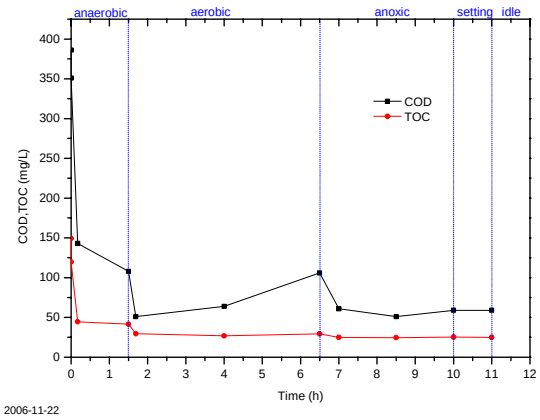
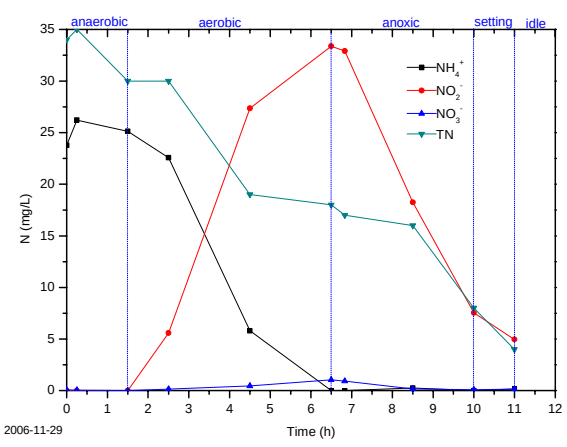
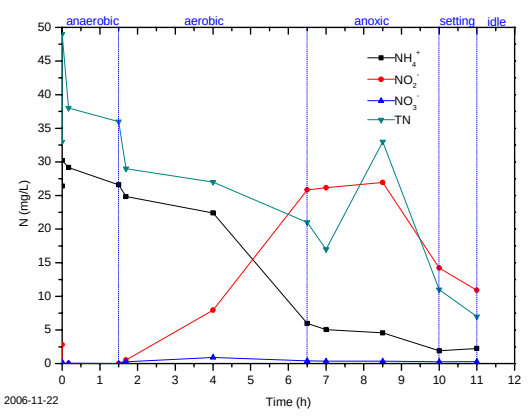
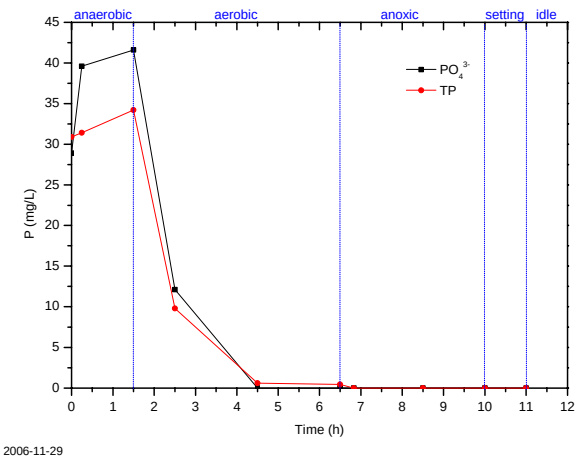
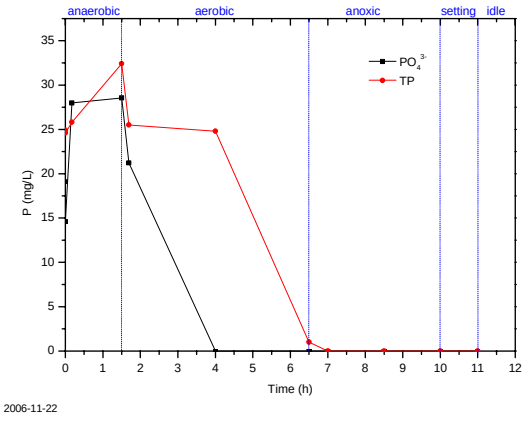
pH			
DO T			
C			
N			
P			

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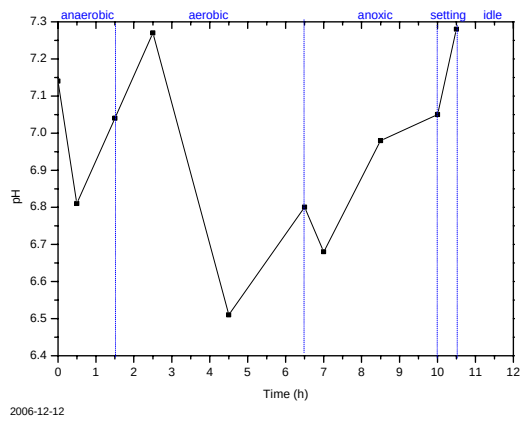
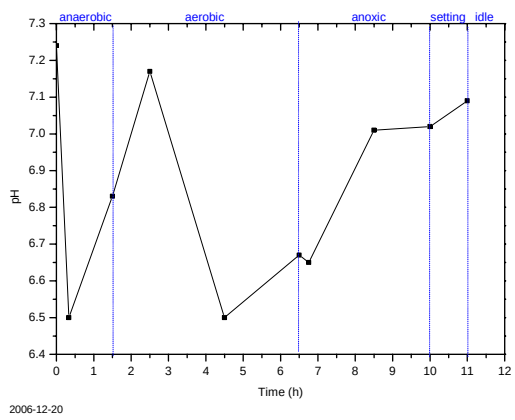
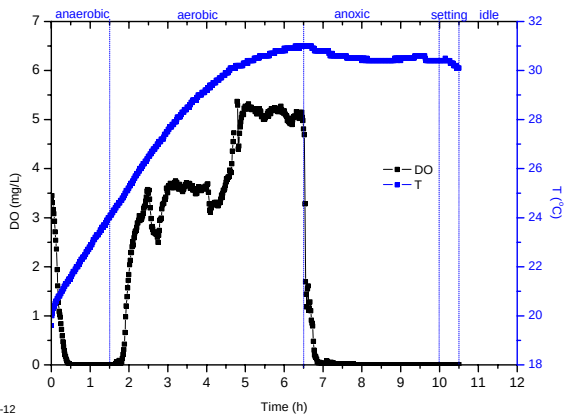
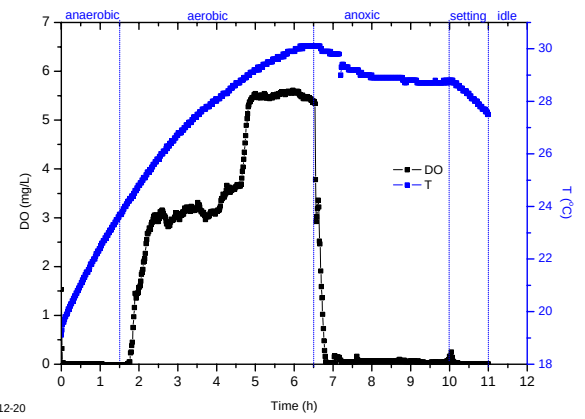
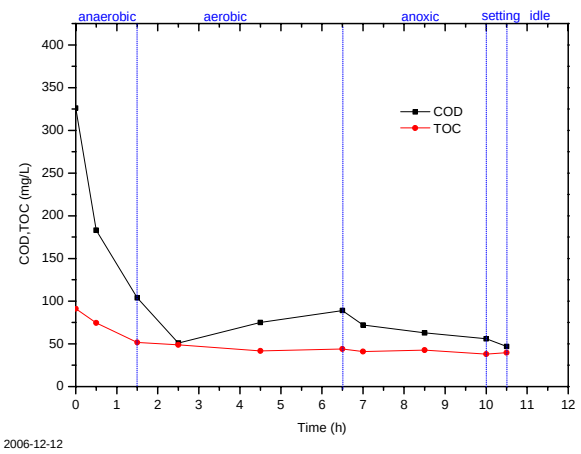
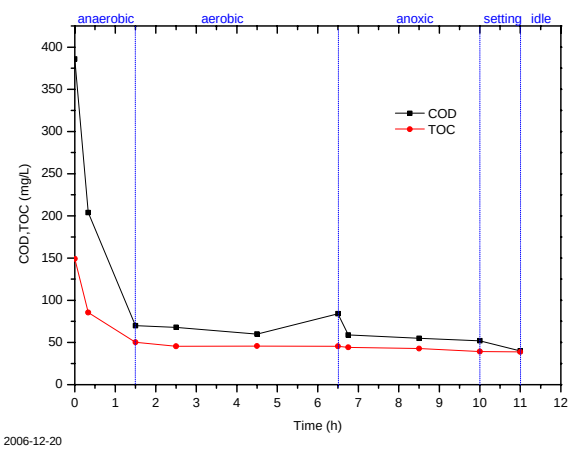
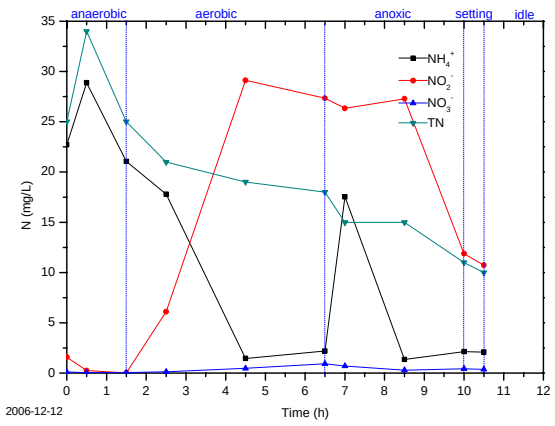
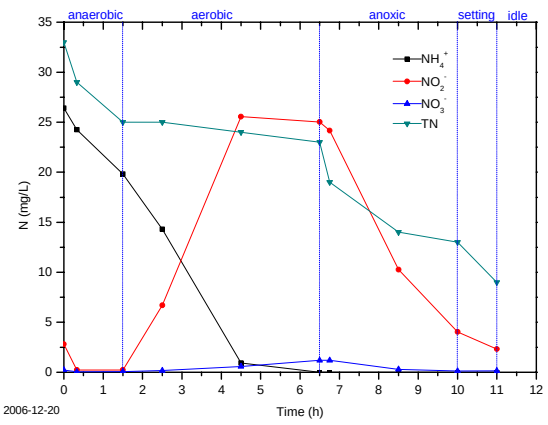
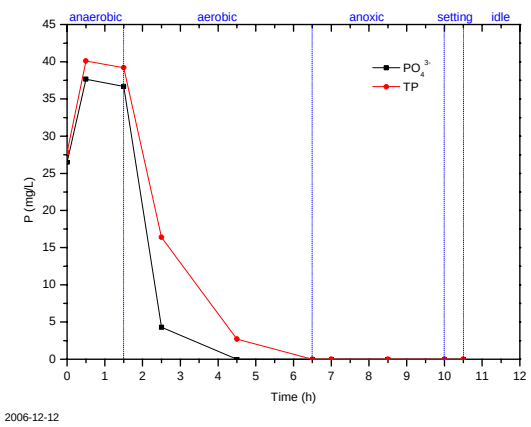
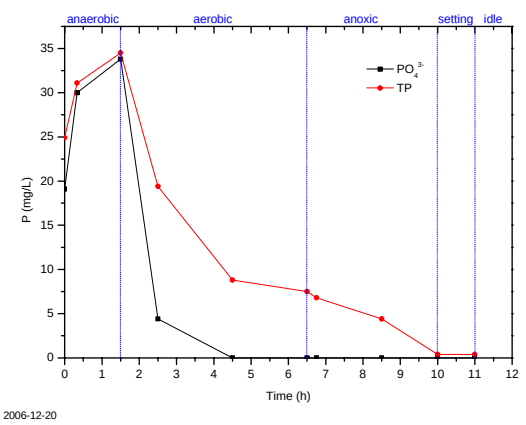
pH			
DO T			
C			
N			
P			

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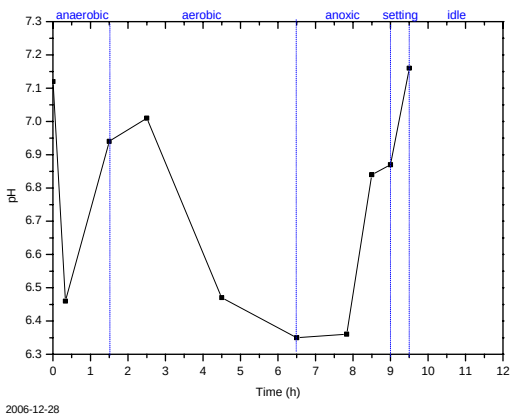
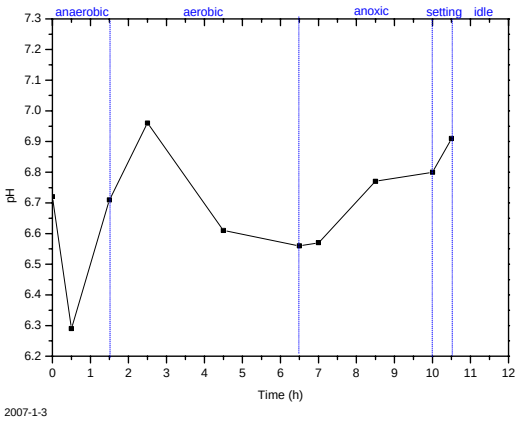
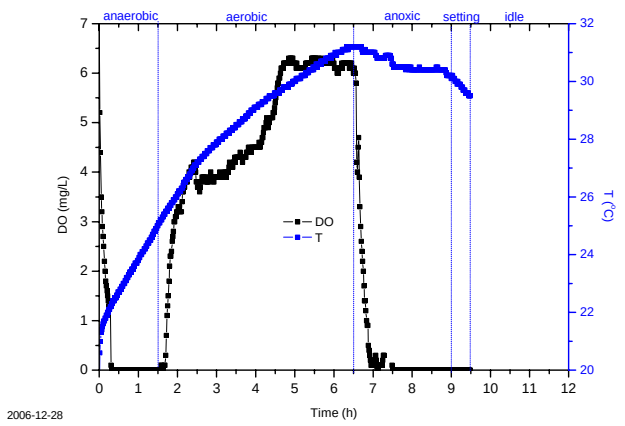
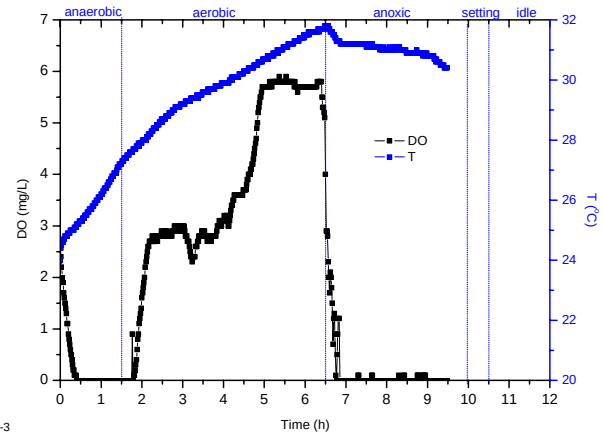
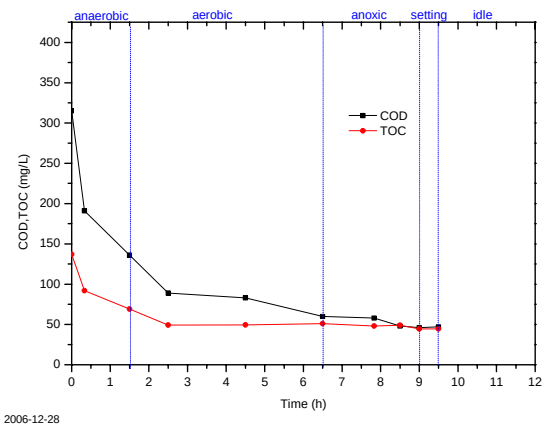
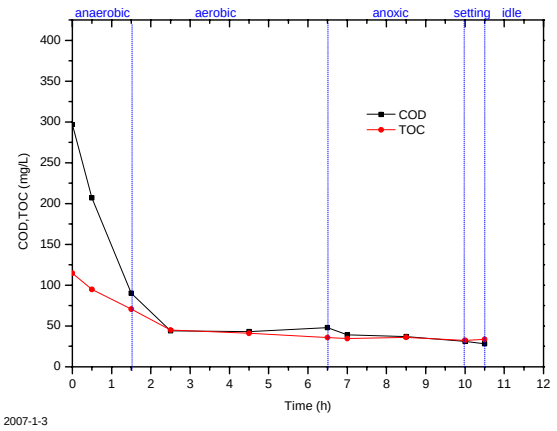
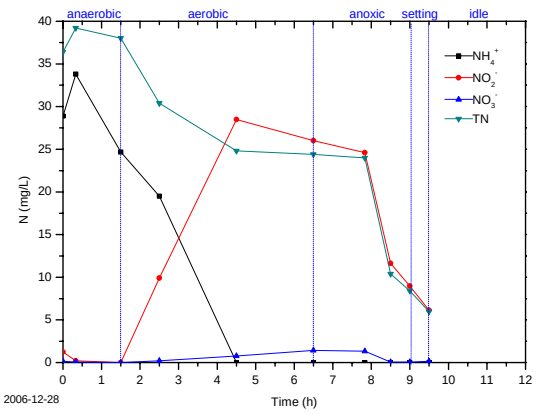
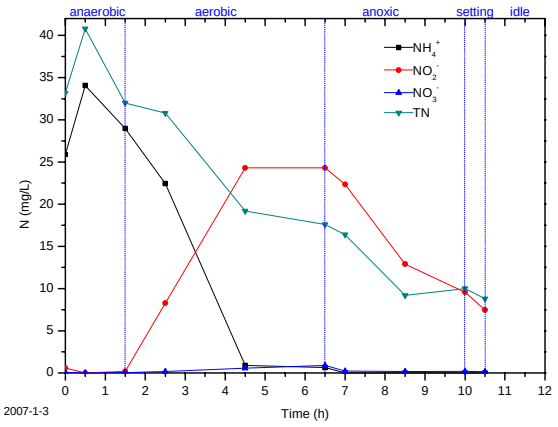
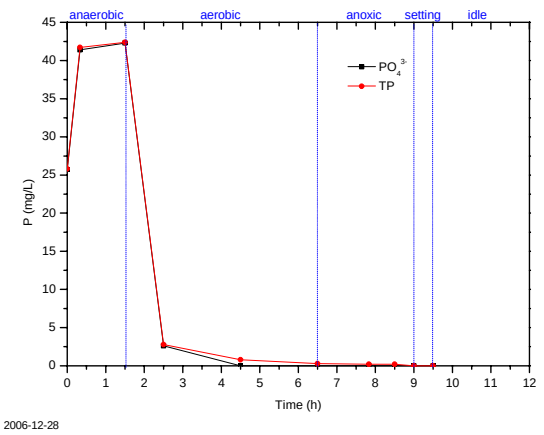
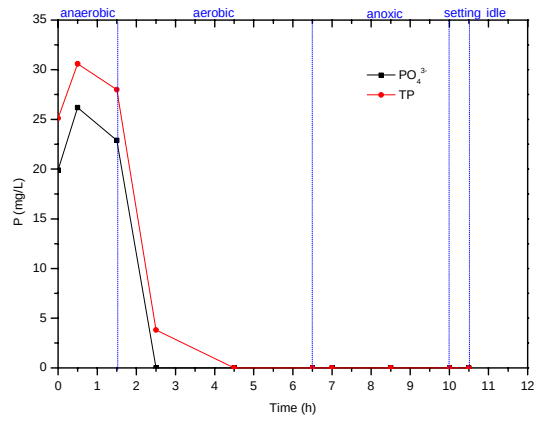
pH			
DO T			
C			
N			
P			

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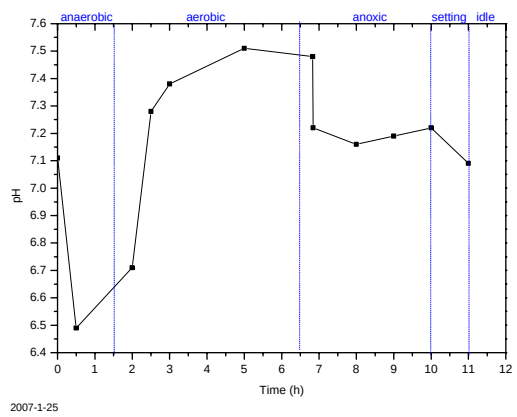
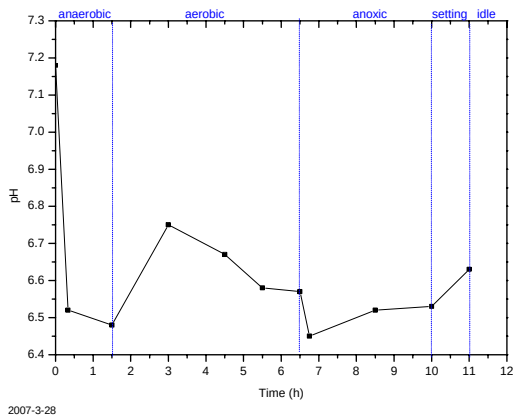
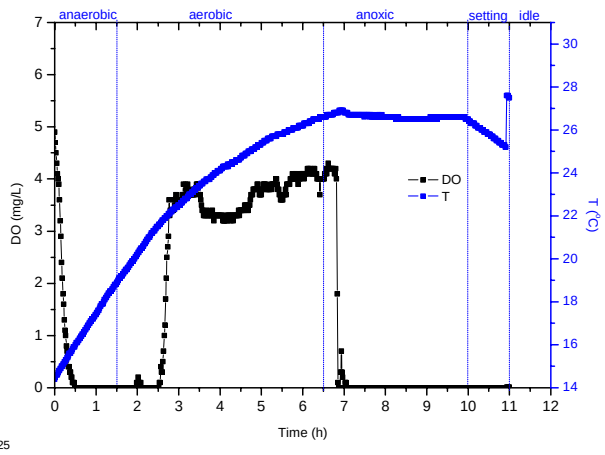
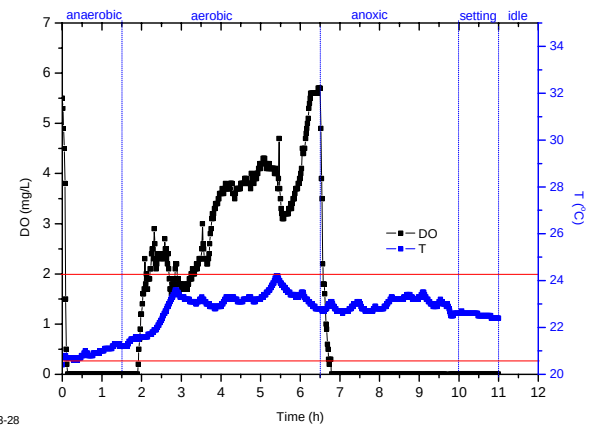
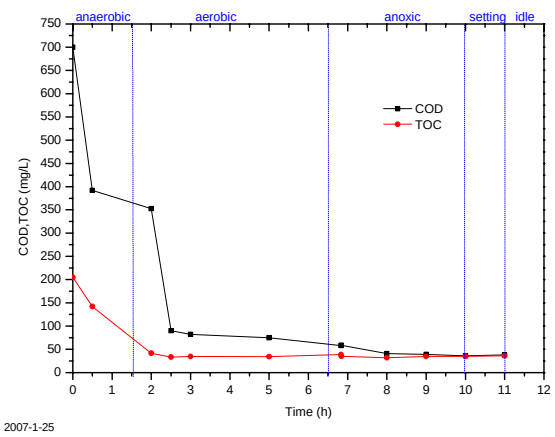
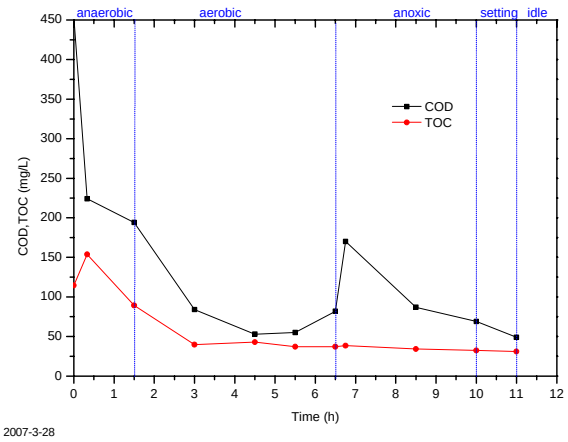
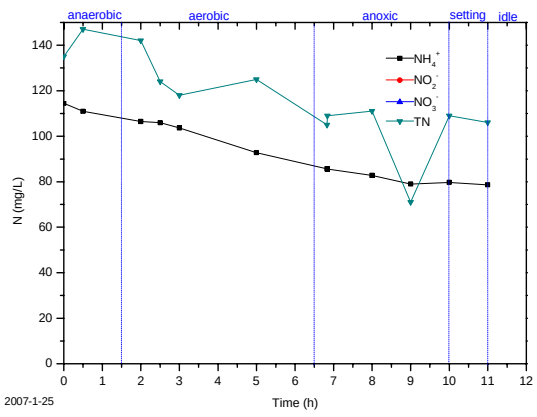
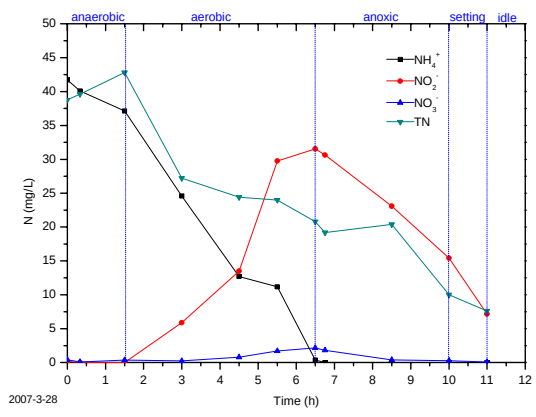
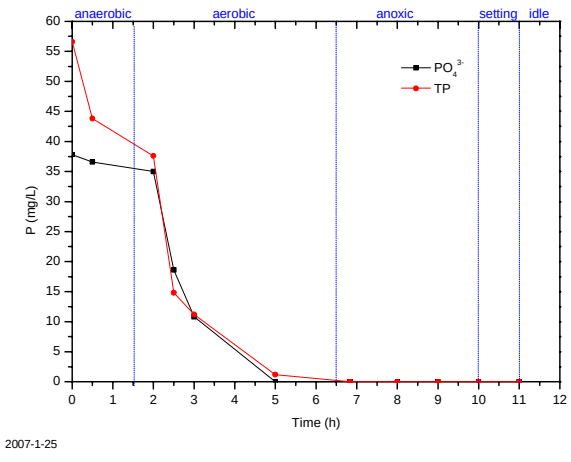
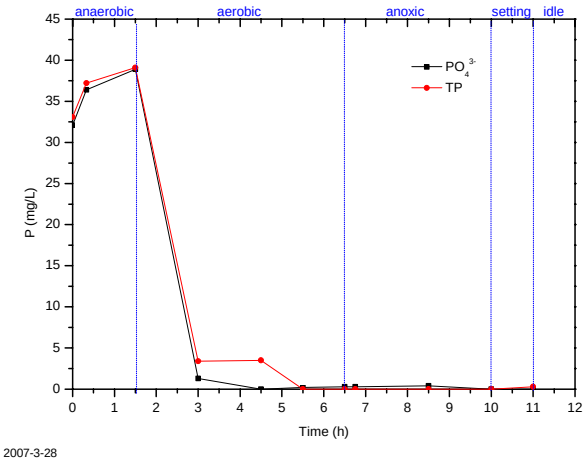
pH			
DO T			
C			
N			
P			

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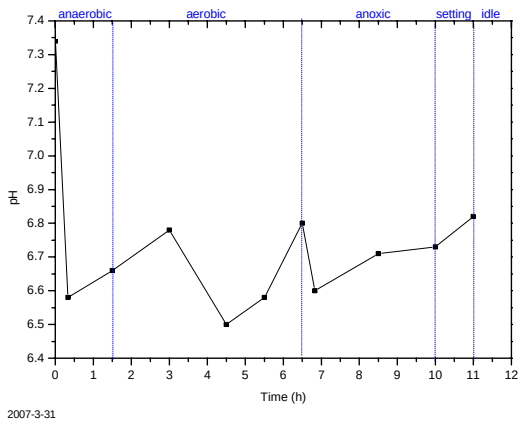
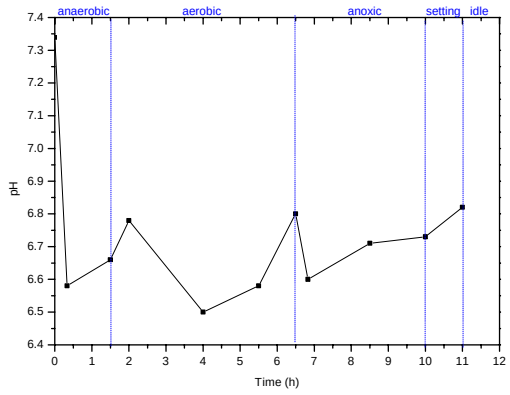
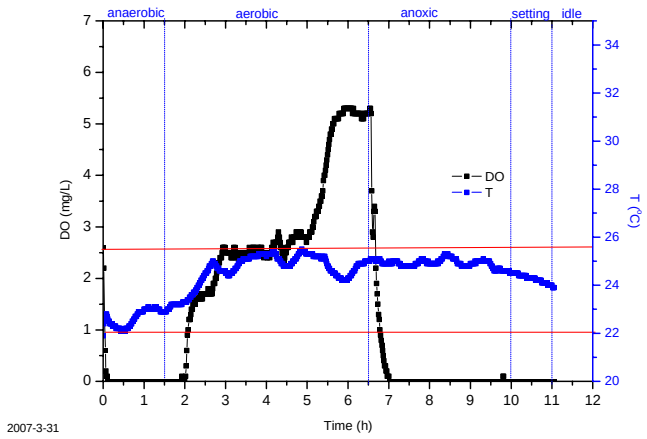
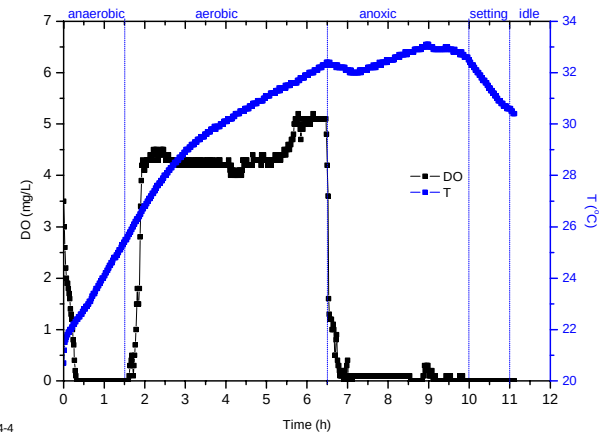
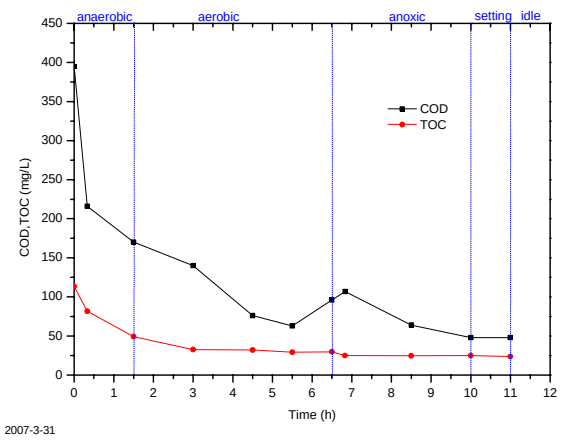
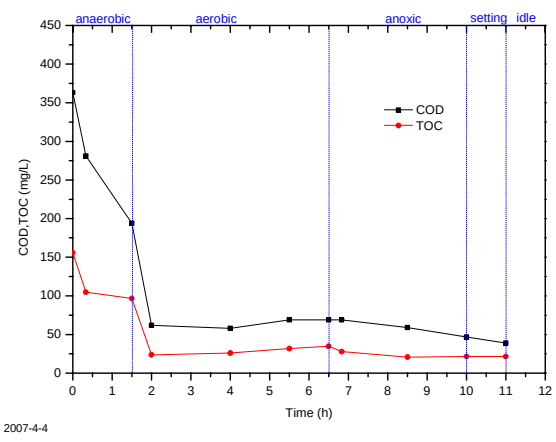
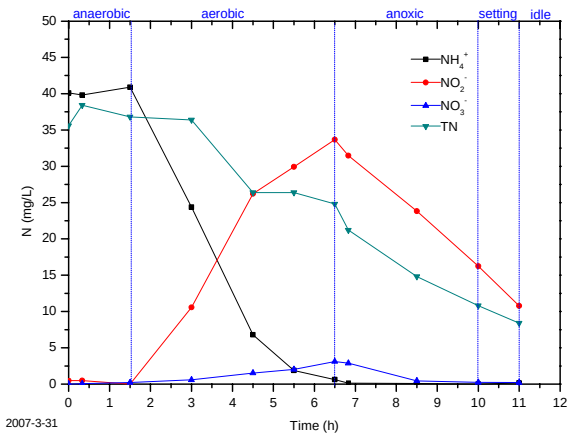
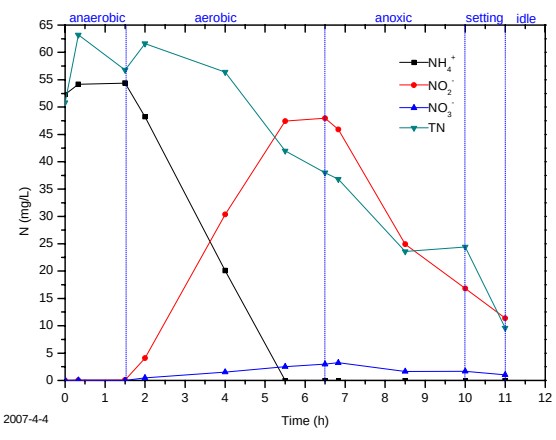
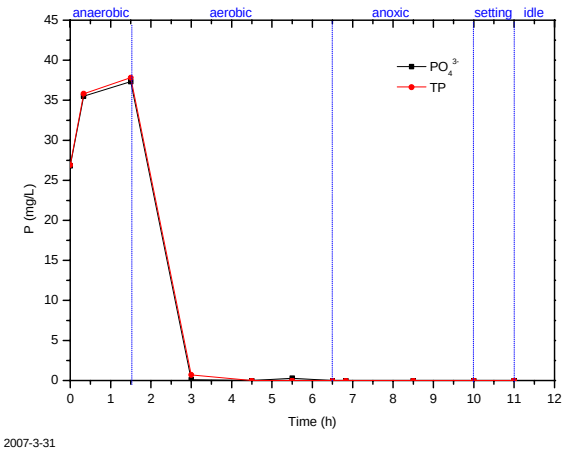
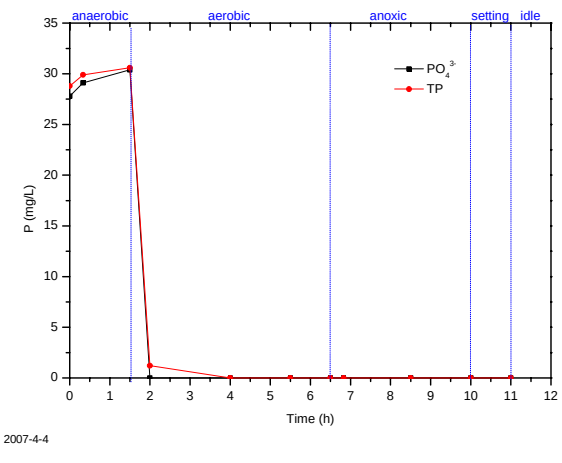
pH			
DO T			
C			
N			
P			

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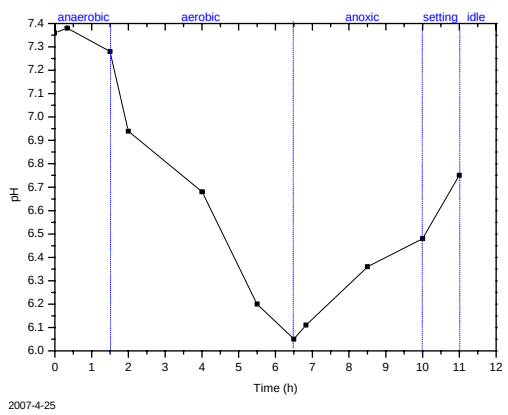
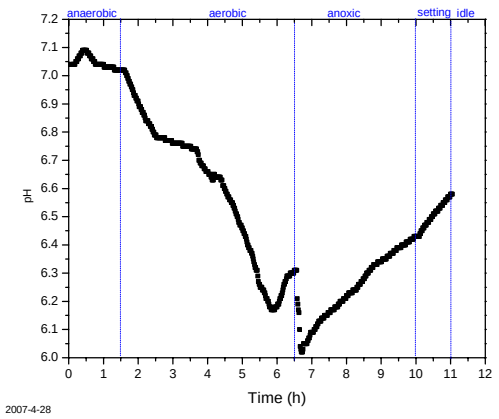
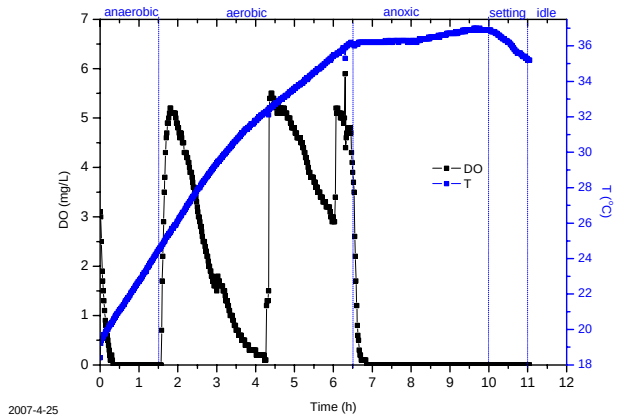
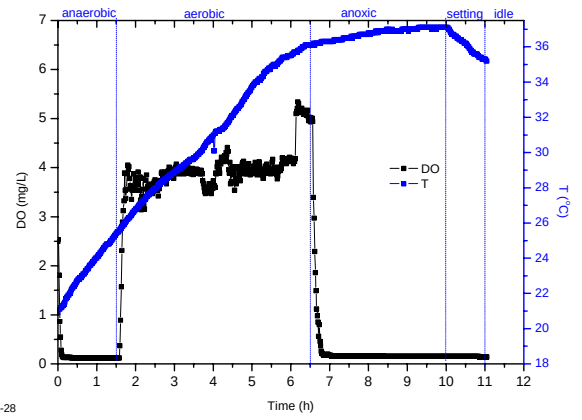
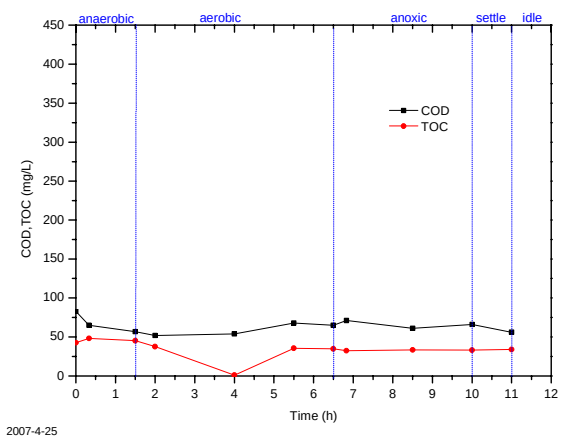
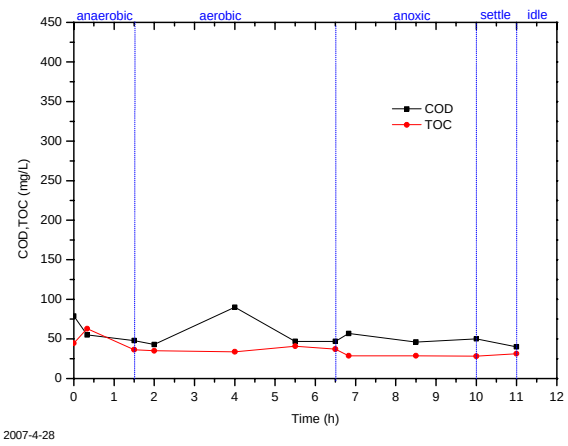
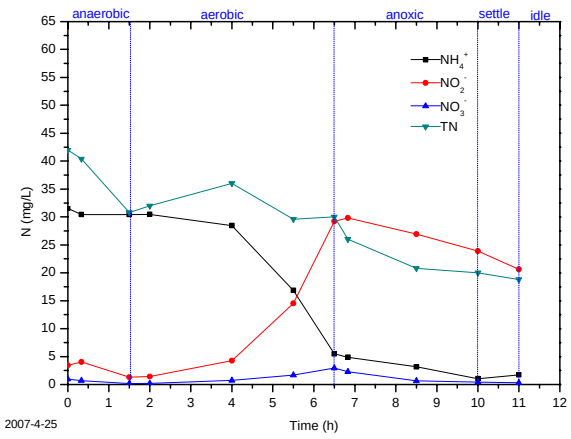
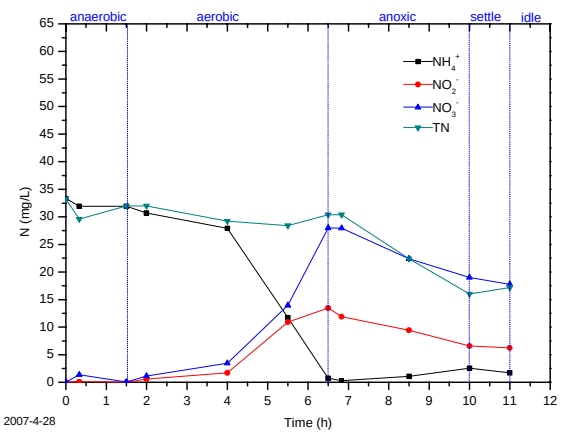
pH			
DO T			
C			
N			
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