東海大學環境科學與工程系碩士班

碩士論文

利用 Hydroxylamine 鑑定及模式模擬同時硝化脫硝反應程序

Application hydroxylamine to identify and model simultaneous nitrification and denitrification (SND) process

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題目：利用 NH_2OH 鑑定及模式模擬同時硝化脫硝反應程序

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論文口試委員審定書

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經本委員會審議，認為符合碩士資格標準。

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中華民國 101 年 7 月 23 日

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摘要

本研究利用實驗設方法 (DOE)，找出製作多孔性載體之最佳配比。利用回收污泥製作的生物載體應用於循序批分式反應槽中(SBBR)，將兩個系統(20%及 40%) 載體添加比例的水質分析數據進行比較，並利用中間產物羥胺(Hydroxylamine，NH_2OH) 鑑定及模式模擬同時硝化脫硝反應程序 (SND)。由實驗結果得知，製作生物載體之最佳配比為污泥 5: 紅土 4: 化學添加劑 1。其抗壓強度為 35.3 ± 3.5 kgf/cm^2，外部比表面積 2.6 ± 0.1cm^2/g，密度 1.8 ± 0.4 g/cm^3 及吸水率 45.2 ± 5.8 %。透過羥胺(Hydroxylamine，NH_2OH)鑑定 SND 反應程序，當反應槽系統中較高的氨氮量轉換為亞硝酸鹽時，NH_2OH 生成量會隨之增加，即可增加反應槽硝化率及提升反應槽 SND 的總去除率。每克的氨氮分別生成 7.61×10^{-7} 的 NH_2OH 及 5.61×10^{-7} 的 NO_2^-。此外，SBBR- 40% 載體添加比例之反應槽系統(K_{SND} 8.6)之去除效率較 SBBR- 20% (K_{SND} 8.3)為佳。整體的結果顯示，添加較高比例的生物載體，有利於更多生物量生長，增加反應槽系統中生物量濃度，並可提升整體之去除效率。

關鍵字: 廢棄活性污泥 (WAS)，同時硝化脫硝 (SND) ，實驗設計方法 (DOE)，羥胺 (Hydroxylamine，NH_2OH)， SND 總去除效率 (K_{SND})

Abstract

This study applying design of experiment (DOE) method to obtain the optimal formula to assembly the pellets rebuild the WAS into porous immobilized pellets, which can both reduce the organic and nutrient substance in wastewaters. Two different carrier ratio (20% and 40%) pellets added to SBBR systems, then, applying NH_2OH to identify the model for simultaneous nitrification and denitrification (SND) process. The results indicate WAS content pellets, can obtain an optimal formula sludge 5: laterite 4: chemical additive: 1. The pellet has the compressive strength: 35.3 ± 3.5 kgf/cm^2, specific external surface area of 2.6 ± 0.1cm^2/g, bulk density: 1.8 ± 0.4 g/cm^3 and water absorption: 45.2 ± 5.8%. And then reused the pellet in sequencing batch biofilm reactor (SBBR) and can enhance wastewater treatment performance significantly. Results shows that the higher hydroxylamine (NH_2OH) released, the more ammonium be converted into nitrite, and the total SND removal efficiency also can upgrade due to the high K_N in the system based upon the NH_2OH released from the system. In the first part of SND process, it is found a NH_2OH and NO_2^- release rate of 7.61×10^{-7} and 5.61×10^{-7} g/g MLSSd· NH_4^+-N. Furthermore, the SND efficiency for the

SBBR-40% ratio system (K_{SND} 8.6) were better than that of the SBBR 20% system (K_{SND} 8.3). The overall results suggested the higher carrier filling ratio, the more biomass can be retained in the reactors, and can increase biomass concentration in reactors with corresponding higher specific removal efficiencies.

Keywords: waste activated sludge (WAS), simultaneous nitrification and denitrification (SND), design of experimental (DOE), hydroxylamine (NH_2OH), total SND removal efficiency (K_{SND})

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Abbreviation

Abbr.	Description	Unit
BNR	Biological nutrient removal	--
COD	Chemical oxygen demand	mg/L
DO	Dissolved oxygen	mg/L
E^0	Standard ORP for the given oxidation reduction process	mV
F	Faraday constant	--
K_N	Nitrification rate	mg-NH_4^+-N/L-hr
K_{DN}	Denitrification rate	mg-NO_3^--N/L-hr
MDL	Method detection limit	mg/L
MLSS	Mixed liquid suspended solids	mg/L
ND	Not detectable	--
ORP	Oxidation-Reduction Potential	mV
R	Gas constant	9.314 $Jmol^{-1}K^{-1}$
SBR	Sequencing batch reactor	--
SBBR	Sequencing batch biofilm reactor	--
SEM	Scanning Electron Microscope	--
WAS	Waste activated sludge	--
E_{SND}	SND efficiency	%
DOE	Design of experiment	--
F/M		Kg COD/ kg MLSS- day
C/N	Carbon nitrogen rate	--

CHAPTER 1 INTRODUCTION

Background information

The activated sludge process is currently one of the most popular and efficient biological wastewater treatment systems in Taiwan, but this method will generate a large number of wasted activated sludge (WAS) and indirectly create a waste disposal problem. There are many ways to deal with WAS. Such as landfill, compost, and incineration. The large amount of domestic WAS is still booming and will cause trouble in Taiwan.

However, based on considerations of cost and equipment, waste sludge is commonly send to sanitary landfilling (Chu *et al.*, 2002). Currently, the cost of disposing the wasted sludge has been hiked with the multiples folds in recent years, are reaching $3,000 /ton. Normally, the biological wastewater sludge is the residue of microbial metabolism. The influent wastewater containing carbon, nitrogen, phosphorus and trace minerals become a source of nutrition of the biological growth and metabolisms. The excess sludge would be generated, celled WAS. The WAS itself contains many rich minerals, it can be recycled to reapply to biological treatment and convert into resources. In this study, waste activated sludge was sintered to made biofilm carrier and applied to biofilm wastewater treatment system. The current situation of land scarcity and strict environmental regulations has seriously limited the expansion of activated sludge process in the developed nations (Cheeseman *et al.,* 2003). Therefore, the current concept and practice are to develop an effective process for minimizing and reusing WAS in order to achieve resource recovery.

There are many reports about recovering WAS by sinter method to make bricks, lightweight aggregates, ceramics and carrier (Kim *et al.,* 2003; Joan *et al.*, 2011). The sintering theory is melting the bonding of particles in a mass of powders by molecular or atomic attraction in the solid state. By application of heat causing strengthening of the powder mass and possibly resulting in densification and recrystallisation by transport of materials (Upadhyaya, 2001). The basic factors impact the sintering includes: chemical composition, particle size distribution, forming pressure, temperature and sintering time (Yang, 2001).

The design of experiment (DOE) is a method to conduct minimal tests to find out the critical elements that affect the results and can reduce the cost and time of trial and error (Ivanova & Malone, 1999; Joaquim *et al.,* 2001). Hence, this approach had been used to gain an optimal formula to assemble the porous WAS pellets with the requirement characteristics of enough porousity and compressive strength to reuse as immobilized material.

The sequencing biofilm batch reactor (SBBR) system has simple, stable and reliable characteristics, which has many advantages as compared with the activated sludge growth system. In such a compact treatment system can save the required space of treatment plant, and meet the local land limitation, avoiding sludge bulking problems, lower in the amount of waste sludge, and high performance. It can increase the biomass in reactor and conduct simultaneous nitrification and denitrification (SND) effectively (Wu and Jin, 2011). This study will apply the rebuilt WAS pellets to immobilized SBBR system and remove ammonia from wastewater. The trace inorganic substance in the reused WAS pellets can also provide extra nutrients for the biofilm attached on the surface of the immobilized cells. It even provides simultaneous nitrification and denitrification (SND) efficiency with real time aeration programmable control system. Therefore, the advanced nutrient removal can be performed simultaneously by nitrification and denitrification processes in the immobilized system. The addition of porous pellets in the oxic-anoxic process accelerates the overall treatment efficiency since it combines the advantage of both activated sludge and attached biofilm. This study analysis the mid product- hydroxylamine and can identify the mechanism of nitrification and denitrification (SND).

Objective of research

This study utilized the WAS, laterite and chemical additions to make porous pellets then reuse them in the SBBR system to remove nutrient from synthesis high nitrogen wastewaters. This study had attempted to apply the various pellets ratio to increase the biological nutrient removal (BNR) efficiency.

The objectives of this study included:

1. To find out the optimal formula of rebuild the WAS pellets.
2. Apply the NH_2OH to identify and model SND process.
3. Compared with two volume pellet ratios for the SBBR systems.
4. To develop a model for SBBR/ SND system.

CHAPTER 2 LITERATURE REVIEW

2.1 Wasted Activated Sludge (WAS)

Many physical and chemical methods remove excess nutrients (such as nitrogen, phosphorus) in wastewater were applied. Among all, the activated sludge process (ASP) is still one of the most popular biological wastewater treatment systems. Currently, there are many wastewater treatment plants under designing and constructing in Taiwan area. Those plants are belonging to secondary treatment process, i.e., which still treating wastewater by using ASP mainly. Normally, those secondary treatment processes usually generate excess amount of WAS (Wojciechowska, 2005). The commonly waste sludge disposed by landfill, compost and incineration. Traditionally, there are two major WAS disposal processes i.e., landfill and incineration in the developed countries. Landfill needs large area of land to carry it out, which is not suitable to the overcrowded Taiwan. The incineration can significantly reduce the volume of WAS, but it needs the supplementary fuel to make sure the WAS can burn completely (Dewil *et al.*, 2005). The concept of sustainable use of resources for Taiwan's high population density environment is necessary and need paid much attention. In order to reduce environmental loading and effective use of land, therefore the reuse of WAS is extremely significant at this point.

2.1.1 Characteristics of Wasted Activated Sludge (WAS)

Lin (2006) indicated sludge contents 50% ash. The high content of ash could be reused and its low heavy metal content, which was positively help for the material sintering. The sludge characteristics of the wastewater treatment plant were varied by raw water quality, coagulant type and operation mode. The sludge pressure filter was the most efficient mechanical dewatering tool and can obtain the water content below 60%. The water content of the other dewatering machine was higher 80% - 85%, which had to apply additional drying equipment to reduce the water content. Those were poor efficiency and energy consumption. The WAS main components include suspended solids, Fe-Al hydroxide, coagulant, water and small amount of organic matter. The chemical composition based mainly SiO_2, SiO_2 in the raw water comes from mineral sands, while Al_2O_3, Fe_2O_3 mainly from clay minerals and aluminum coagulation dosing system or ferric coagulant, other chemical substances including K_2O , MgO, Na_2O, and other types of sulfur salts. Taiwan sewer sludge composition analysis shows that under a fixed water source, its chemical composition remains stable all the time (Chen, 2006).

2.1.2 Recycling Wasted Activated Sludge

Many treatment processes explored to the dispose sludge, such as incineration, sanitary landfill and compost. Theoretically, the sludge recycling technology mainly includes following four types:

1. Energy: Fuel made of sludge to produce heat and electricity.
2. Resources of material: Adsorbent for adsorption of organic and inorganic concrete.
3. Material: Prepare concrete lightweight aggregate.
4. Usage of farm and land: Prepare compost and soil conditioner.

Before sludge reused, it has to be pre-treated to stabilize, disinfect and reduce waste volume. Many studies dealing with how to recycle WAS, use in the building industry or in the agriculture industry, made lightweight aggregate, clay ceramics or biological treatment process carrier (Huang *et al.*, 2001; Kim *et al.*, 2003; Qi *et al.*, 2010; Joan *et al.*, 2011).

Some investigations related to the WAS minimization and reutilization were shown in Table 2-1. This study attempts to use the WAS as the main material to bake porous media and reuse them in a biological process as immobilized cell and to reduce nutrients in wastewater. The reused porous media in bioreactor can enhance the wastewater removal efficiency by increasing the biomass in a sequencing biofilm batch reactor (SBBR).

Table 2-1 Application of wasted activated sludge (WAS)

References	The aspect of reutilization
This study, 2012	Biofilm carriers
Huang, 2010	Biofilm carriers
Su, 2008	Immobilized pellets, Air diffuser
Chung, 2007	Immobilized pellets
Qi *et al.*, 2010	Lightweight ceramic
Cheeseman and Virdi, 2005	Lightweight aggregate
Wang *et al.*, 2009	Lightweight aggregate
Xu *et al.*, 2008	Ceramic
Chiou *et al.*, 2006	Ceramic
Cheeseman *et al.*, 2003	Ceramic
Kim *et al.*, 2003	Micro-media
Gulnaz *et al.*, 2006	Adsorbent for dye

2.2 The WAS sintering theory

2.2.1 Mechanism of forming

The forming mechanisms of powder particles (Chang, 1999) are：

1. Packing: Forming the initial effect of particles with sliding, resulting in the accumulation of particles rearrange, reduce the gap between the powder.
2. Plastic deformation：As stress increases, the particle deformation to makes the density upgrade between the powders.
3. Brittle fracture：After shaping, the large pore reused, the particle will fill the small pore in it.

Bhatty and Redit, (1989) pointed out that, after the forming of the powder media can provide better jobs and the density of the specimen, and granular forming high of sintered specimens than the entire sintered pellets. Mainly due to the test the body of the pore size distribution with consistency, resulting in even its foam. Sintered powder sample will have a high strength, density particle due to the homongeous disperse in the reaction.

2.2.2 Mechanism of Sintering

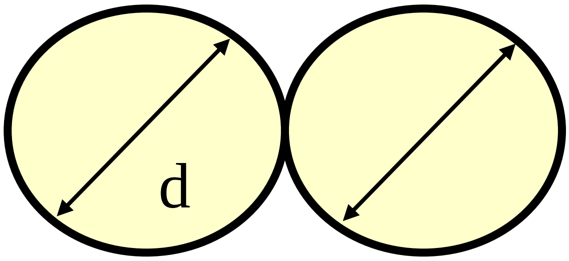
The sintering reaction was heated under the melting point of the material, and rearrange the internal structure of materials up to high intensity, high-density sintered body (Li *et al.*, 2009).

1. Solid-state sintering: applied surface diffusion, lattice diffusion, boundary diffusion or solid material with the surrounding atmosphere was reaction of the mass transfer.
2. Sintering by viscous flow: Sintering was caused by the flow of non-crystalline material, viscous flow sintering mechanism of sintering as the main environment in silicate (Skrifivars, 1994).
3. Liquid phase sintering: applied the melting and solid precipitation to increasing particle size and density.

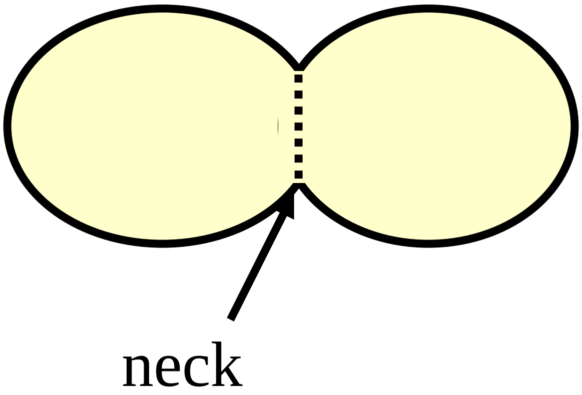
The factors of affect baking were sintering temperature, the time of heating, chemical composition, forming pressure and size distribution.

German (1996) was built the sintering model, which divided into four steps and shows in Figure 2-1. The reaction was started the point contact, and then the neck growth. The new grain boundary was formed between the particles. Finally, two particles were merged to be a single particle.

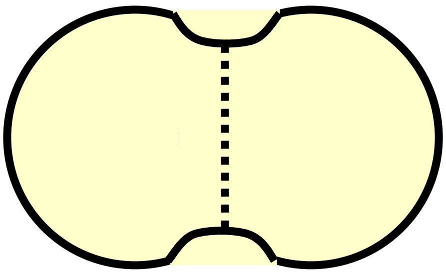
Initial point contact



1. Early stage neck growth



2. Last stage neck growth



3. Terminal condition fully coalesced spheres

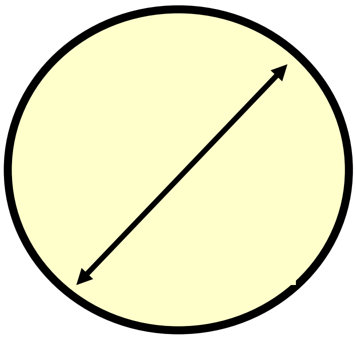


Figure 2-1The granule agglutination response schematic drawing (German, 1996).

Material without viscosity and gas production conditions, the material had to use additives to make the above two points occurs. But the heated gases may not be enough, or not a swelling effect. Table 2-2 shown the various types of chemical composition and temperature of escaping gases list.

Table 2.2 Various types and temperature of overflowed gases with all kinds of chemical compounds.

Chemical equation	Reaction temperature (^{o}C)
$FeS_2 + O_2 \rightarrow FeS + SO_2\uparrow$	350 ～ 450
$4FeS + 7O_2 \rightarrow 2Fe_2O_3 + 4SO_2\uparrow$	500 ～ 800
$Fe_2(SO_4)_3 \rightarrow Fe_2O_3 + 3SO_3\uparrow$	560 ～ 775
$MgCO_3 \rightarrow MgO + CO_2\uparrow$	400 ～ 900
$Na_2CO_3 \rightarrow Na_2O + CO_2\uparrow$	>400
$CaCO_3 \rightarrow CaO + CO_2\uparrow$	600 ～ 1,050
$CaSO_4 \rightarrow CaO + SO_3\uparrow$	1,250 ～ 1,300
$6Fe_2O_3 \rightarrow 4Fe_3O_4 + O_2\uparrow$	1,000 ～ 1,550

2.3 Mechanism of immobilized system

2.3.1 Attached biofilm on the biofilm carriers

There are different ways for selection has wastewater biological treatment by the characteristic wastewater, categories of removal substances and treatment level. The microbial growth can be divided into suspended-growth and attached-growth systems. The suspended-growth is the microbial remains suspended such as activated sludge. Attached-growth, called biofilm, is microbial which attach on the inert medium to form the local high-density biological treatment system and decomposing pollutants, such as trickling filters (TF) and rotating biological contactors (RBCs). In this study, the rebuilt WAS pellets were utilized as bio-carriers in the activated sludge reactor. The immobilized system in the bioreactor is composed of support material and attached growth biomass. Figure 2-2 shows the formation of immobilized system which is complex as a result of a combination of many factors, such as bacterial growth, substrate consumption, attachment, external-internal mass transfer of substrates and products, cell death, shear loss (biofilm loss because of erosion), sloughing (fragments disrupting from the biofilm), structure of the support material, competition between bacterial species, and effects of predators (Wijffels and Tramper, 1995).

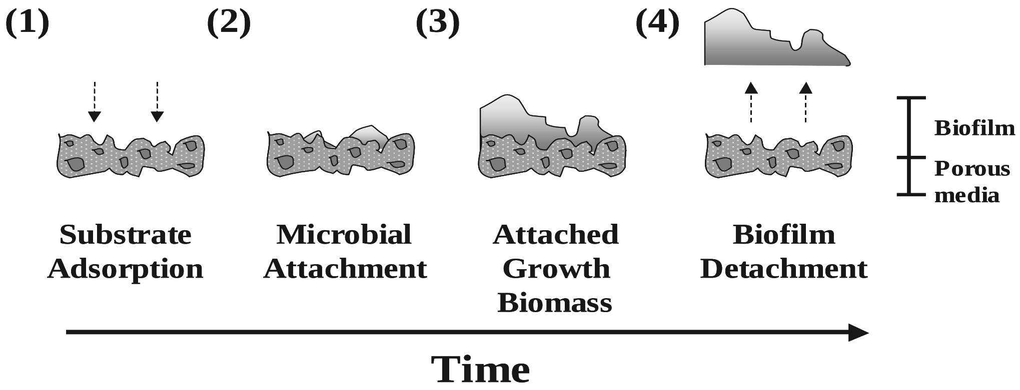


Figure 2-2 Schematic presentation of the formation of a biofilm (Wijffels and Tramper, 1995).

The biofilm formation process included as follows:

(1) Substrate adsorption: Substrate adsorbed into the support material.

(2) Microbial attachment: Microbial in the bulk were attached onto the surface of support material (bio-carriers).

(3) Attached growth Biomass: Substrate utilized with the attached growth biomass. The biofilm thickness can be increased and become matured gradually.

(4) Biofilm detachment: When the biofilm become matured for a long time, the biofilm was peeled out owing to the inner starvation zone formed.

The immobilized system compared with traditional activated sludge system has main advantages as follows (Daniel *et al.*, 2009; Chiu *et al.*, 2007):

1. Without the need for external carbon source dosage.
2. Has a higher load capacity.
3. Lower sensitivity to toxicity effects, as well as to other adverse environmental conditions.
4. Reduce operating costs and expenses.
5. Elimination of long sludge-settling periods.

2.3.2 The biofilm system

Biofilm reactors take advantage of various biomass to remove nitrogen and phosphorus in a single bioreactor (Fu *et al.*, 2010; Zhang *et al.*, 2009). Figure 2-3 shows the biofilm can be aerobic on the surface, anoxic in the middle and anaerobic at the point of attachment to the pellet. The concentration gradients of dissolved oxygen (DO) and organic substrate are similar, being highest at the external surface of the biofilm and lowest at the surface of pellet (Semmens *et al.*, 2003). The diffusion reaction theory shows that the growth rate of biofilm is dependent on substrate loading rate applied to the biofilm system. Therefore, the substrate loading rate may represent the capability of biofilm growth, and can be regarded as the growth force of biofilm culture (Liu *et al.*, 2003).

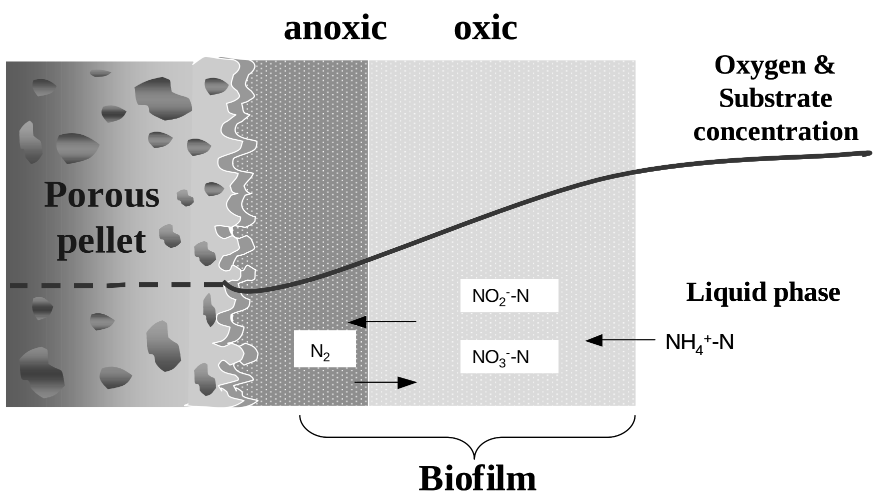


Figure 2-3 Diagram of oxygen and mass transfer of immobilized system under nitrogen removal reaction (Semmens *et al.*, 2003).

2.4 Biological nutrient removal (BNR)

The microbial decomposed and oxidized organic pollutants of wastewater affected by the following conditions; (1) maintain the F/M in the aeration tank; (2) maintain the DO; (3) separate from the sludge sedimentation tank should be concentrated higher than activated sludge concentration in aeration tank; (4) removal SS and the proliferation of microbial decomposition of BOD, treated water should be discharged to maintain a sludge retention time.

2.4.1 Nitrification

Normally, the nitrogen compound removal can be divided into two processes, nitrification and denitrification (Ahn, 2006). Nitrification is converting ammonia nitrogen to nitrite or nitrate nitrogen. The reaction is shown as:

$$NH_4^+ + \frac{2}{3}O_2 \rightarrow NO_2^- + 2H^+ + H_2O \quad Eq.(2-1)$$

and

$$2NO_2^- + O_2 \rightarrow 2NO_3^- \quad Eq.(2-2)$$

The overall nitrification combined Eqs. (2-1) and (2-2) into Eq. (2-3) and shown as:

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O \text{..........} Eq.(2-3)$$

Traditionally, nitrification requires oxygen as electron acceptor and under aerobic condition with the autotrophic bacteria, e.g. *Nitrosomonas* and *Nitrobacter* (Siripong and Rittmann, 2007; Michaud *et al.*, 2006). There are some parameters which will inhibit nitrification, i.e., pH, DO, temperature, etc. When nitrification proceeded, the alkalinity was consumed by hydrogen ion released and brought the pH down. The optimal pH values are between 7.5 to 8.5 (Guo *et al.*, 2009). The sludge retention time (SRT) is also an important parameter for nitrification. The nitrification reaction system was longer, more complicate than carton removal process (Hung, 2008).

2.4.2 Denitrification

Generally, ammonia nitrogen in aerobic condition is converted to nitrite and nitrate nitrogen by nitrification process. Denitrification can convert with nitrate (NO_3^-) and nitrite (NO_2^-) into nitrogen gas. Those two nitrogen compounds in drinking water will cause public health problems, i.e., blue baby syndrome in infants and cancer in human beings (Terada *et al.*, 2007).

In traditional denitrification phase, the denitrifiers need organic matters and carry out denitrification process under anoxic environment. In anoxic conditions, denitrifiers can use nitrite and nitrate instead of oxygen as the terminal electron acceptors. The organic matters work as electron donors for anoxic denitrifiers at the same time. If the organic matter is not sufficient as electron donors, the denitrification will be inhibited. Therefore, it must added extra carbon source to enhance denitrification process.

$$NO_3^- \rightarrow NO_2^- \rightarrow N_2O_{(g)} \rightarrow N_2 \quad \text{..........} \quad Eq.(2-4)$$

2.4.3 Simultaneous nitrification and denitrification (SND)

Many studies showed the nitrification and denitrification can occur in the same reactor at the same time, which is defined as simultaneous nitrification and denitrification (SND) (Ding *et al.*, 2011; Guo *et al.*, 2009; Chiu *et al.*, 2007; Zhu *et al.*, 2007; Zeng *et al.*, 2003).

The SND process can divide into two categories; pure-culture and mixed-culture systems. Pure-culture system implies the SND reactor has only one bacterium which can achieve nitrification and denitrification consecutively. Some bacteria can accomplish this process like *Nitrosomonas europaea* and *Paracoccus* denitrificans (Stüven and Bock, 2001). Although the pure-culture have a good performance in nitrogen compounds removal, but pure-culture is strictly limited to use in the small-scale and is difficult to apply in the field. Therefore, mixed-culture system is focused on improving the field SND treatment process. Two parameters: dissolved oxygen and carbon source, need to be considered in mixed-culture system. The dissolved oxygen limitation is 0.5 to 2.0 mg/L for SND process (Chu *et al.*, 2006; Chiu *et al.*, 2007). Due to the rate of nitrification is much faster than that of denitrification, therefore, a balance controlled reaction system will insure the consecutively processes work smoothly. Low DO condition can decrease nitrification reaction rate and inhibit it close to that of denitrification process. Nitrification in SND can consume 8.64 g-$CaCO_3$/g-NH_4^+-N alkalinity in the reactor; while the denitrification reaction will produce 3.6 g-$CaCO_3$/g-NO_3^--N alkalinity and maintain pH in the solution. Therefore, the biological system will not require extra alkalinity to adjust pH value during the overall denitrification stage.

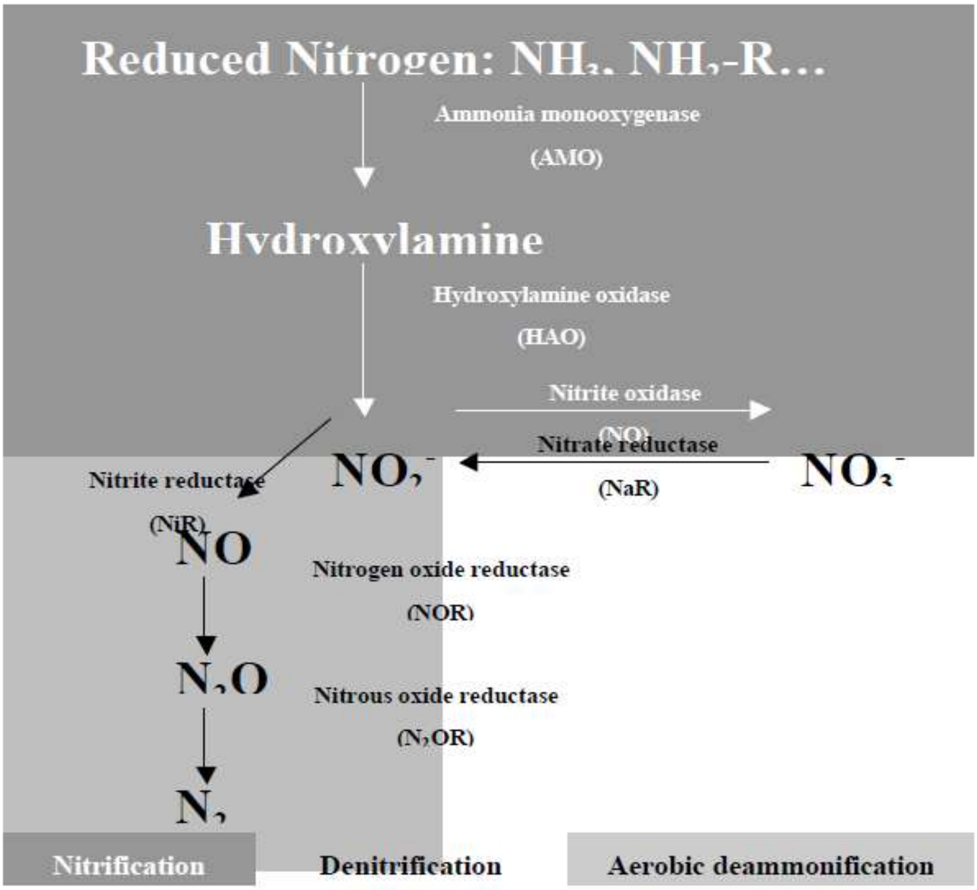


Figure 2-4 Flow chart of conventional nitrification/denitrification and one-step SND via nitrite pathway (Tsao, 2001).

2.5 Sequencing batch biofilm reactor (SBBR)

The sequencing batch reactor (SBR) is considered as an attractive method of treatment because it has good performance for the removal of nitrogen, phosphorus, and COD. Recently, the sequencing batch biofilm reactor (SBBR) system has attracted great attention due to its ability to take advantages of both a biofilm reactor and a SBR (Ding *et al.,* 2011). The SBBR, which uses alternating anoxic and aerobic conditions, has been proven feasible for nitrogen and phosphorus removal (Fu *et al.,* 2010). Furthermore, the SBBR offers an anoxic microzone in the inner layers of the biofilm due to a dissolved oxygen (DO) gradient during the aeration phase (Choi *et al.,* 2008). Therefore, simultaneous nitrification and denitrification (SND) could be achieved, with nitrification on the surface of the biofilm and denitrification in the inner layers (Cassidy *et al.,* 2000). Li *et al.,* (2003) indicated the SBBR can govern the biomass level and enhance removal efficiency by biofilm. The SBBR system has many advantages, currently, is commonly applied in biological treatment (Wu and Jin, 2011).

The SBBR system includes advantages following: Can be improved biomass concentration in reactors with corresponding higher specific removal efficiencies.

1. The biofilm can bear a great potential for the simultaneous remove of organic carbon and nutrients.
2. Reduce the amount of excess sludge production and shorten reaction time.
3. Up-grading of existing wastewater treatment plants at a minimum cost.
4. The greater volumetric loads and higher stability.

Table 2-3 showed the treatment performance by using the SBR and the SBBR systems from references. There are different kinds of wastewater treated by using SBR and SBBR systems to provide a satisfactory effluent water quality.

Table 2-3 The treatment performance by using SBR and SBBR systems from references.

Reactor	Wastewater source	Removal efficiency	Authors
SBBR	Synthetic (municipal)	COD : 92.5% NH_4^+-N: 95.8% TP: 97.5%	Wu and Jin, 2011
SBBR	Synthetic (municipal)	COD : 94.3% NH_4^+-N:80% TP: 97.5%	Jin *et al.*, 2011
SBBR	Synthetic (domestic)	COD :96% NH_4^+-N:99% TP:100%	Ding *et al.*, 2011
SBBR	Synthetic (domestic)	COD :> 99% NH_4^+-N:> 98% PO_4^{3-}-P:> 90%	Kishida *et al.*, 2006
SBR	Synthetic (municipal)	COD :86.6-95% NH_4^+-N:96-98.4%	Katarzyna Bernat *et al.*, 2011
SBR	Synthetic (swine wastewater)	COD : 82% NH_4^+-N: 100% PO_4^{3-}-P: 20.1%	Won and Ra, 2011
SBR	Synthetic (municipal)	COD : 89% TN: 88% TP: 93%	Ge *et al.*, 2010
SBR	Synthetic (industrial)	COD : 94-98% NH_4^+-N: 93-95% PO_4^{3-}-P: 90-94%	Tanwar *et al.*, 2008

2.6 Nernst Equation

The biological nitrogen removal, i.e., nitrification and denitrification, processes is an oxidation-reduction reactions during which electron are transferred from the reducing agent to oxidizing agent until the reaction reaches equilibrium. The electrochemical potential between the reducing and the oxidizing agents is known as the oxidation-reduction potential (ORP), which measures the net potential of the system (Weissenbacher *et al.*, 2007). Both conventional nitrification /denitrification and SND reaction are oxidation. Using real-time control not only improve effluent quality but also reduce the energy consumption during the wastewater treatment process. There are many studies point out that the measured on-line ORP can provide better control of the reaction status in the bioreactor (Won and Ra, 2011; Gao *et al., 2*009). Using the ORP measurement as the on-line control of the biological nitrification/denitrification process depends on the detection of an obvious change of the measured system ORP. The measured ORP value in biological system is correlated to the concentration changing of the reductive and the oxidative species represented in a Nernst equation (Chiang *et al.*, 2006).

The general Nernst equation is shown in Eq. (2-5):

$$E = E^{0} + (RT / nF)\ln([Oxi]/[Red]) \text{...} Eq.(2-5)$$

Where:

E = ORP (mV)

E^0= standard ORP for the given oxidation-reduction process (mV)

R= gas constant (8.314 $Jmol^{-1}K^{-1}$)

T= absolute temperature (K)

N= number of electrons transferred in the reaction

F= Faraday constant (96,500 $Cmol^{-1}$)

[Oxi] = Concentration of oxidizing agent

[Red] = Concentration of reducing agent

Chang *et al.* (2004) used on-line measured data (e.g. ORP) and nitrogen compounds (e.g. ammonia, nitrite and nitrate) in the reactor to substitute terms in Nernst equation. Deduced Nernst equation can be used to understand the nitrification and denitrificaion conditions in reactior. ORP value of any degree conversion of reactants to products in reactor can be precisely calculated. Thus, on-line control strategy can effectively utilize in a SBR system.

2.7 Design of Experiments (DOE)

MINITAB® 14 is a statistical software used to analysis the optimal analysis of operation factors (Gunawan*et al.*, 2005). Choose the major factors and after the test, a response surface and contour plot was obtained, which will display the optimal operation zone for the following study.

In order to correlate the dependent variables and independent variables with the minimum possible number of experiments, a central composite design for two factors has been used. The total number of experiments (N) required for two independent variables was determined by *Eq. (3-6)* (Lu *et al.*, 2008).

$$N = 2^K + 2K + n_c \text{……………………………………………………} Eq.\ (3\text{-}6)$$

Where K represents the number of independent variables, in the present study, K=2 and n_c is the center point. The data were analyzed using MINITAB® 14 statistical software. Three replications of center point were selected for center composition design and totally, 11 experiments were predicted by the software.

CHAPTER 3 MATERIAL AND METHODS

3.1 Experimental design and flow chart

The flow chart of this study was divided into four parts (Figure 3-1).

Part (A): Rebuilt the WAS pellets as a biofilm carrier.

Part (B): Develop the SBBR system.

Part (C): Apply the NH_2OH to identify SND process.

Part (D): The Nernst equation with the SND process.s

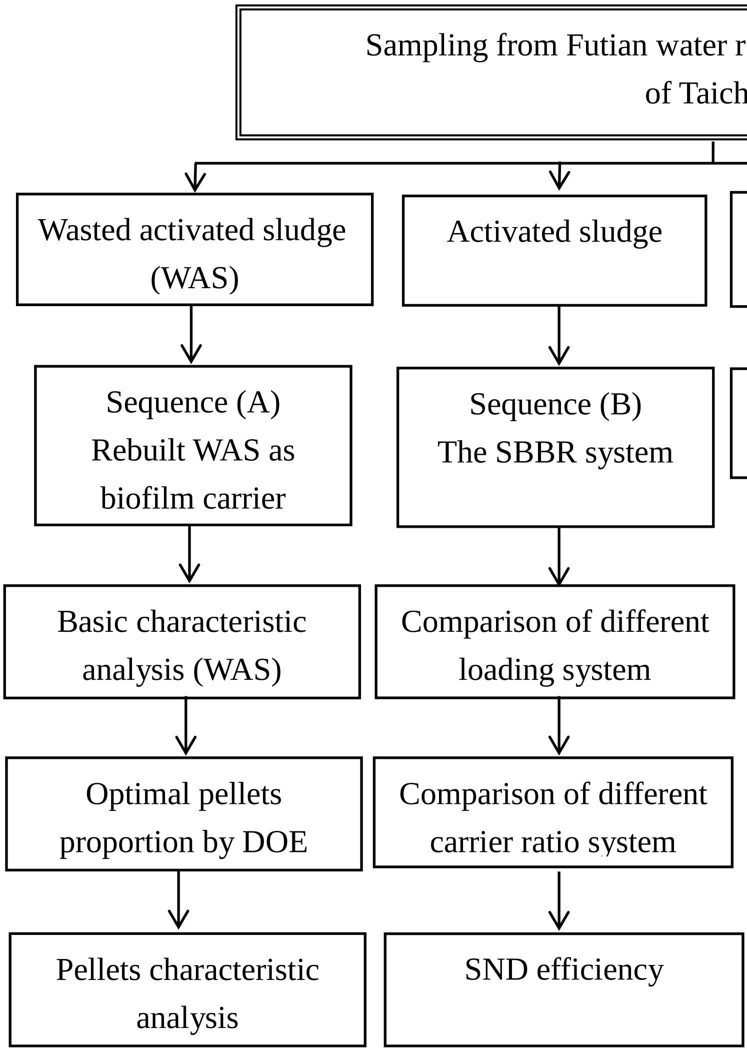


Figure 3-1 The flow chart of this study included three parts. Part (A): Rebuilt the WAS pellets as a biofilm carrier. Part (B): Develop the SBBR system. Part (C): Apply the NH_2OH to identify SND process. Part (D): The Nernst equation with the SND process.

3.2 Rebuilt WAS as biofilm carrier

3.2.1 Characteristic and sources of WAS

The WAS was collected from Futian water resource recycling center of Taichung City. It treats 55,000 CMD domestic wastewater from downtown Taichung City (Tsai, 2007) and septic sewer treatment center of Taichung City and produced 327tons dry sludge cake daily. The wasted sludge collect from digestion sludge, which has a 80% of moisture. The WAS was dried at 105^{o}C for two days before conducting rebuild pellets process. The ash content is measured after baked under 800℃ for three hours (NIEA R205.01C). The formula of the moisture, ash and flammable contents in WAS are shown in *Eqs.* (3-1), (3-2) and (3-3).

Moisture content ≒ $(W_1-W_2) / W_1 \times 100\%$ ……..…..…..*Eq.(3-1)*

Ash content ≒ $W_3 / W_1 \times 100\%$.................................*Eq.(3-2)*

Flammable content ≒ 100% - Moisture content % - Ash content % ..*Eq.(3-3)*

W_1 ≒ weight of sample before burned in oven (25 ^{o}C)

W_2 ≒ weight of sample dried by 105 ^{o}C

W_3 ≒ weight of sample baked by 800 ^{o}C

3.2.2 The procedure of manufacture the WAS pellets

The process of rebuild the WAS to the biofilm carrier was to mix the WAS, laterite and chemical additive and leave it on the 105°C oven drying for three days. The laterite was help the pellets to shape and the chemical additive is to generate foam agent and can increase the hardness. The dried WAS and laterite was milled by ball mill machine ground into powder then sifts to the grind size of the powder close to 15 μm (Figure 4-1). The fine size of powder can enhance the pellet structure strength after sintered. The mix formula of WAS and laterite was design by MINITAB®, DOE method, which test every design proportion then try and error to find out the optimal formula. Thereafter, the pellets were baked in an programmable oven under the temperature raised from 200℃ to the final temperature of 900℃. The overall time to bake the pellets is 6 hours (360min). After baking, those pellets were cooled down to the room temperature (25℃). After many trial tests, this study obtained the optimal formula ratio of WAS: laterite: chemical additive is 5: 4: 1, i.e., the sludge proportion of 50% and their diameters were between 12-15 mm (Figure 4-4). The method of manufacture the biofilm carrier pellets is shown in Figure 3-2.

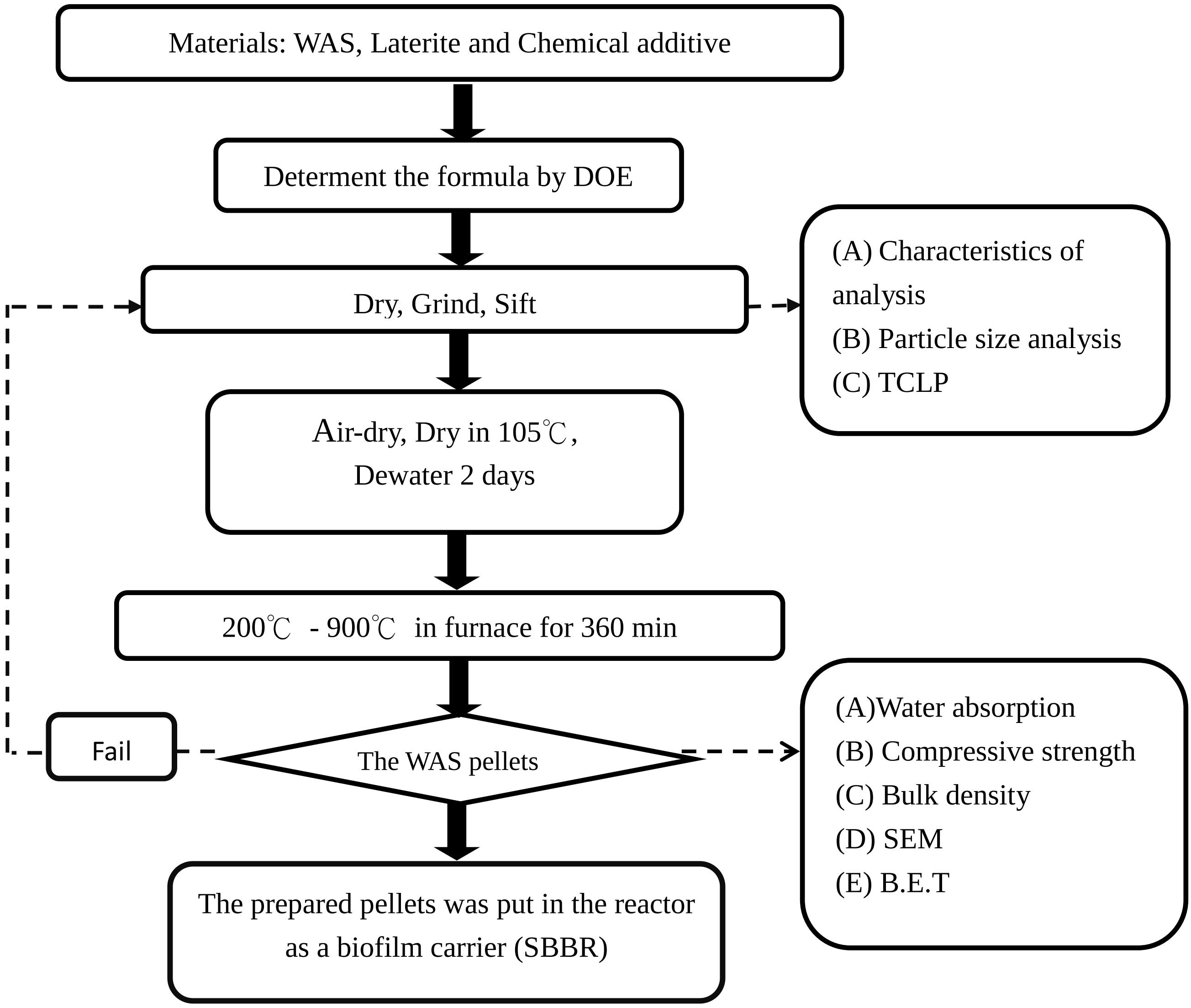


Figure 3-2 The flowchart showing a method of manufacture the WAS biofilm carrier pellet.

3.3 The WAS sampling and basic characteristics analysis

3.3.1 Water absorption

In physical characteristics of the porous carrier, the water absorption is measured by the reference density measurement (Cheeseman *et al.*, 2003). The water absorption testing was following the Chinese National Standard (CNS-487). The sample was immersed in 23^{o}C water for 24 hours, and then removes out of the water. Dried the surface water of sample, measured the sample weight that was the weight of the water saturation.

water absorption (%) $\fallingdotseq (W_s - W_d) / W_d \times 100\ \%$…………..….*Eq. (3-4)*

Where:

W_s : the weight of dry surface and water saturation (g)

W_d : the weight of dry sample (g)

3.3.2 Compressive strength

Strength of various materials measured by the compressive strength, which testing method is adopted Chinese National Standard (CNS1010 R3032). The sample was prepare to made into a 3cm x 3cm cubes and testing the value of uniaxial compressive stress.

3.3.3 Bulk density

According the Archimedes principle, obtained after the sample volume, and then divided by the weight of sample.

Volume: V_S (cm^3) = $V_W - (W_b - W_a) / \rho_W$…………..……..*Eq. (3-5)*

Bulk density: ρ_S ($g \cdot cm^{-3}$) = W_S / V_S…………….……..……*Eq. (3-6)*

Where:

W_S: Weight of dry sample, (g)

W_a: Weight of graduated cylinder + $W_{S,}$ (g)

W_b: Weight of quantitatively to the 100ml water + W_a, (g)

V_W: Volume of quantitatively water, (cm^3)

ρ_S: Density of water ($g \cdot cm^{-3}$)

3.3.4 Specific external surface area

The easiest method for the determination of the specific external surface area, a_s, is the counting-weighing method. Hence, a representative sample of dry particles is counted after the weighing (Andreasen, 1928). Using the particle density, the volume of the average spheres having the same volume, d_v, is calculated. The specific external surface area is related to d_v by this expression:

$$a_s = \frac{6}{\rho_p d_v} \qquad \text{Eq. (3-7)}$$

Where:

a_s: Specific external surface area, (m^2/g)

ρ_p: Particle density, (g/cm^3)

d_v: equivalent diameter from the same volume, (cm^3).

3.3.5 Toxicity characteristics leaching procedure (TCLP)

The WAS from the domestic wastewater plant may contain trace heavy metals, therefore, before rebuilt pellets and WAS must be free from toxicity as determined by using the leaching test. Five toxic heavy metals (Cu, Pb, Cr, Zn and Cd) were analyzed and all were found below the restriction (NIEA R201.14C, 2004).

Table 3-1 The Regulation of heavy metal concentration of leaching.

Element	Regulation of TCLP from HM (mg/L)*
Cu	15
Pb	5
Cr	10
Zn	25
Cd	0.5

*Heavy metals regulation was obtained from Waste Material Cleanup, EPA, Taiwan, 2004.

3.4 The sequencing batch biofilm reactor (SBBR) system

3.4.1 Experiment setup

Figure 3-3 shows two pilot-scale sequencing batch biofilm reactors with 20% and 40% of pellets in the reactor to conduct SND reaction. This study used the type specification of experiment setup shown in Table 3-2, which includes the basic setup of bioreactor, real-time monitor and computerized monitoring system.

The rectangular biological reactor was made by acrylic fiber glass with the height of 45.0 cm and the inside, width and length of 25.0 cm and 25.0 cm, respectively. The effective working volume was 25 L.

The mixer (Oriental Motor, Japan) operated 150 rpm, and aeration pump maximum air flow rate is 12 L/min. The real-time monitor of pH meter (SUNTEX PC-310, Taiwan, R.O.C.) is adjusted by using the pH 4.0 and pH 7.0 standard solutions, ORP meter (SUNTEX PC-310, Taiwan, R.O.C.) is adjusted by using the zero-point (0 mV) and 220 mV standard solutions, DO meter (SUNTEX DC-5100, Taiwan, R.O.C.) adjusted by using internal aero-correction process. The computerized monitoring system used to Lab VIEW, includes monitor software and AD/DA card. The whole system is installed in a temperature controlled cabinet.

Table 3-2 The type specification of experiment setup.

Item	Standard	Type
Biological reactor	45×25×25 cm The effective working volume was 25 L	Made by acrylic fiber glass
Mixer	Operated at 150 rpm	Oriental Motor, Japan
Aeration pump	Maximum air flow rate is 12 L/min	Serial No. 1030114, Medo Co., Japan
pH	0.00~14.00 pH	SUNTEX PC-310, Taiwan, R.O.C
ORP	±1999 mV	SUNTEX PC-310, Taiwan, R.O.C.
DO	0.00~60.00mg/L	SUNTEX DC-5100
Computer	P II 266 computer	Windows 2000
LabVIEW		LabVIEW 5.1
AD/DA card		AT-MIO-16E-10

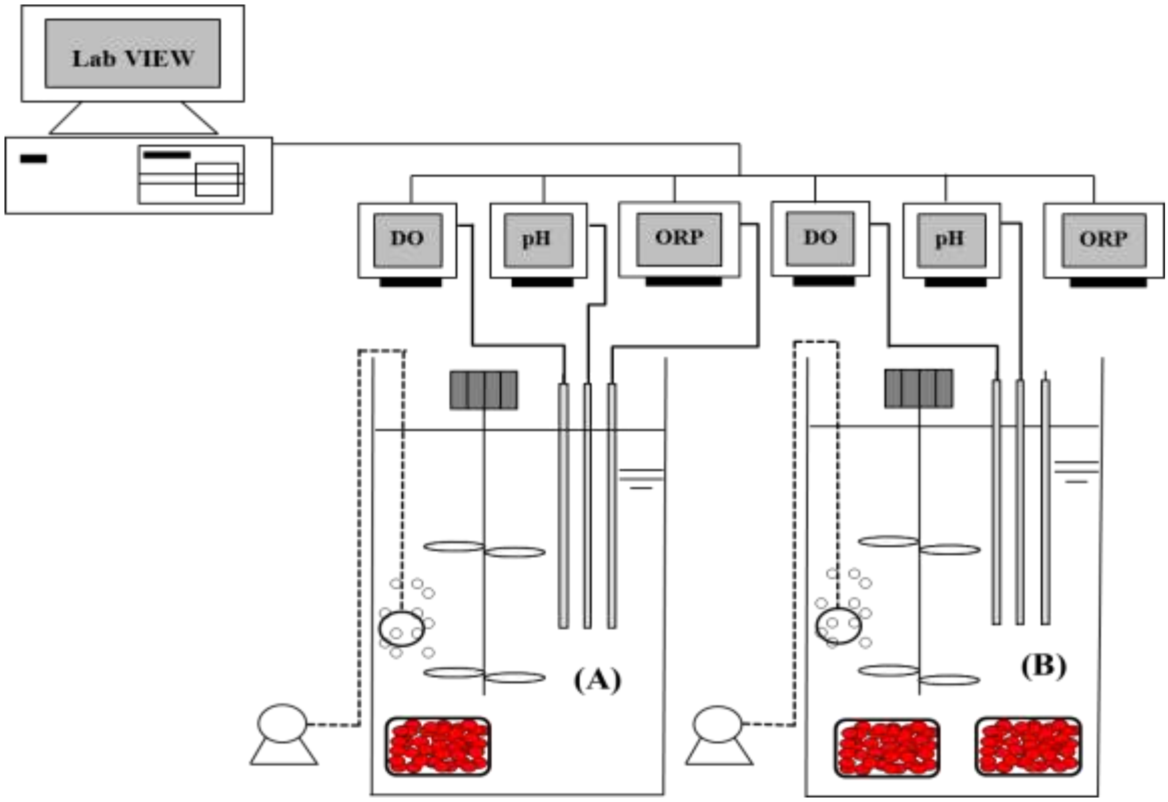
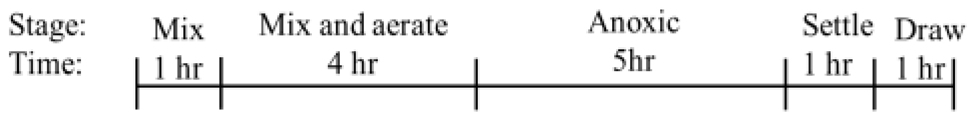


Figure 3-3 Schematic diagram of the SBBR system with 20% (A) and 40% (B) of pellets in the reactor to conduct SND reaction. All connected with on-line DO, pH and ORP sensor to a Lab VIEW system in a personal computer.

3.4.2 Experiment operation

This study conducted the nitrification and denitrification reactions by adjusting different levels of airflow in the systems. In order to achieve the SND reaction, the airflow was controlled under low level, i.e., low DO case with air 1.0 L/min with DO: 0.3-0.5 mg/L (Wang, 2008). The SBBR systems were operated with a cycle time of 12 hours in an air conditioned room (with temperature under 25±2℃). The operation cycle of each period in SBRB systems are shown in Figure 3-4. In the cyclical operation stages of cultured the sludge is (a); the first stage, the reactors only mixed without aerated (1 hour). In the second stage, the reactors mixed and aerated (4 hours), then in the third stage, the reactors only mixed (5 hours). Finally, in the fourth stage, the reactors were settling (1 hour), then, the supernatant was drawn (1 hour). After cultured the sludge, the cyclical operation stages was switching to only mixed and aeration without the anoxic stage shows in Figure 3-4 (b). The daily effluent samples were analyzed right after filtered by a 0.45 μm glass fiber membrane.

(a) The cyclical operations stage of cultured the sludge in the systems.



(b)The cyclical operation stage of SND process in the systems.

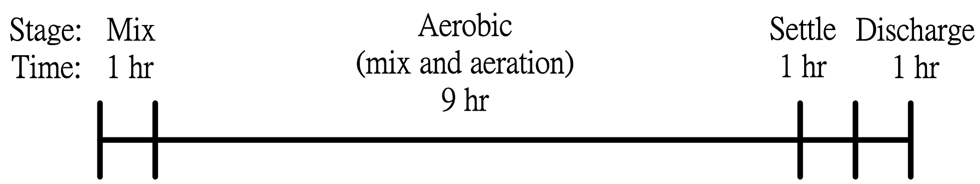


Figure 3-4 Operation cycle in (a) The operation stage of cultured sludge.
(b) The operation stage of SND process.

3.4.3 Composition of the synthetic wastewater

The formula of the stock synthetic wastewater is shown in Table 3-3. The synthetic wastewater contains carbon source (glucose), nitrogen source (urea), phosphate buffer (KH_2PO_4) and trace nutrients. The general nutrients include acetic acid, glucose, urea, ammonium chloride and phosphate. The organic and inorganic nitrogen in the synthetic wastewater are urea and ammonium chloride. The milk powder in the formula contains protein, lactose, mineral and fat. The stock synthetic wastewater is maintained in a 4℃ refrigerator to avoid degradation. The characteristics of the influent synthetic wastewater are shown in Table 3-4. The high nutrient contented synthetic wastewater with the average ratios of COD: NH_4^+-N: PO_4^{3-}-P (100: 12.6: 2.2) is used in this study.

Table 3-3 The composition of the stock synthetic wastewater in this study*

Content	Doses (in 3 L distilled water)
KH_2PO_4	20 g
Glucose: Peptone	18 g: 9 g
Urea	60 g
NH_4Cl	125 g
whole milk powder	150 g
low-fat milk powder	122 g
$FeCl_3$ (10%)	2 mL
CH_3COOH (99.8%)	58 mL
$NaHCO_3$	256 g

* (Su, 2008; Huang, 2010).

Table 3-4 The water quality of influent synthetic wastewater.

Components	Concentration (mg/L)		
	Loading I	Loading II	Loading III
COD	520 ± 18.9**	672 ± 14.5**	753± 13.2**
NH_4^+-N	70 ± 4.2**	80 ± 3.1**	92 ± 2.3**
NO_x-N	N. D. *	N. D. *	N. D. *
PO_4^{3-}-P	11± 0.3**	15 ± 2.5**	17 ± 1.6**
COD: NH_4^+-N: PO_4^{3-}-P	100: 13.4: 2.1	100: 12.2: 2.2	100: 12.2: 2.3

*N. D. : Not detected

**n = 3

3.5 The methods of analysis

3.5.1 Water quality analysis

The analysis method in this study is listed in Table 3-5. The major parameters were analyzed according to Ion Chromatography (IC) and Standard Method (NIEA W415.52B, 2005). Before conduct analysis, the samples were pre- filtered with 0.45μm glass fiber membrane to prevent jamming. Hydroxylamine (NH_2OH) was determined by calorimetrical method (Peng, 2002), which is shown in Figure3-5. First of all, 2 mL sample was filtered with 0.45μm membrane, then adding 1 ml 1% alcoholic 8-hydroxyquinolin (32502, R.D.H., Germany) and 1 ml 2N Na_2CO_3 (A356892, Merk, Germany). After mixing, obtained indoxine of indigo product then placed samples for 2 hours in room temperature. Sample was measured with a spectrophotometer (U-2000, HITACHI, Japan) with absorbance of UV light at 705 nm. Then the formulate of calibration curve was obtained. The hydroxylamine standard solution (379921, Aldrich, USA, 99.9999%) was adjusted between 0.0 to 1.0 mg/L of hydroxylamine and with a linear regression $R^2 > 0.995$.

Table 3-5 The analytic methods and instruments used in this study

Item	The Analysis Method and Instrument
COD	Methods 5220B*
NH_4^+-N	Ion Chromatography, IC
NO_2^--N	Ion Chromatography, IC
NO_3^--N	Ion Chromatography, IC
PO_4^{3-}	Ion Chromatography, IC
NH_2OH	Peng, 2002
pH	pH meter, Method 4500-H^+B* (SUNTEX PC-310)
ORP	ORP meter, Method 2580B*(SUNTEX PC-310)
DO	DO meter, Method 4500-O G* (SUNTEX DC-5100)
Temp	Temperature meter, NIEA W217.50A
MLSS	Method 2540 D*

* Standard Methods for the Examination of Water and Wastewater 21st Edition (APHA *et al.*, 2005)

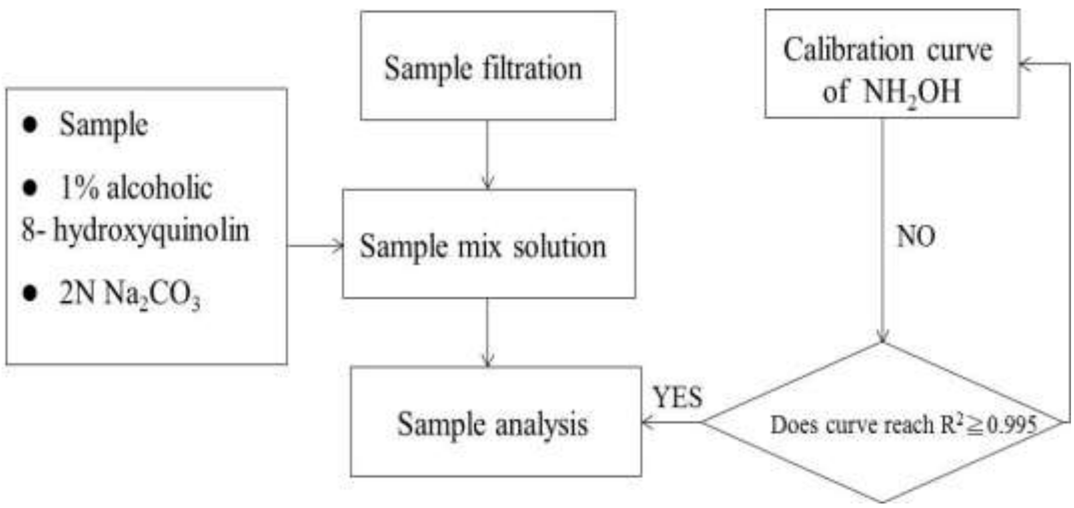


Figure 3-5 Flow chart of the NH_2OH analysis (Peng, 2002).

3.5.2 Field Emission Gun Scanning Electron Microscopy (FESEM)

FESEM analysis, which was a type of electron microscope, it images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography. Field Emission Gun Scanning Electron Microscope and Energy Dispersive Spectrometer (ESEM), JEOL JSM-6700F (Japan) in National Chung Hsing University, was used to observe the micro morphologies and structure of original.

3.5.3 The particle size analysis

The laser particle size analyzer (LS), BECKMAN COULTER LS230 (USA) in Cheng Kung University, according to ISO 13320 provides guidance on instrument qualification and size distribution measurement of particles in many two-phase systems (e.g. powders, sprays, aerosols, suspensions, through the analysis of their light-scattering properties.

It does not address the specific requirements of particle size measurement of specific materials. The laser particle size analyzer is applicable to particle sizes ranging from approximately 0.1 μm to 3 mm.

3.5.4 The B.E.T analysis

The (B.E.T), BECKMAN COULTER SA3100 (USA) in National Cheng Kung University, according to ISO 9277 specifies the determination of the overall specific external and internal surface area of disperse (e.g. nano-powders) or porous solids by measuring the amount of physically adsorbed gas according to the Brunauer, Emmett and Teller (BET) method.

CHAPTER 4　RESULTS AND DISCUSSION

4.1 The basic characteristic of the domestic waste activated sludge

The basic physical characteristic of domestic WAS, obtained from the Futian water resource recycling center of Taichung City, results were shown in Tables 4-1.　After drying at 105℃ for 2 days, the WAS has 0.06 % moisture content, 44.62 % flammable content and 55.29 % ash content while the laterite has 0.08 % moisture content, 4.87% flammable content and 95.05 % ash content.

Before the recovery of sludge is used, it is necessary to test the toxicity characteristic leaching procedure (TCLP) from NIEA.　The dehydrated sludge and laterite following wastewater treatment is used in this study, and the TCLP test results were shown in Table 4-2, and the result was lower than the standard in law (NIEA, 2004), the raw material can be made as carrier.

Table 4-1 The basic characteristics of the wasted activated sludge and laterite sample (after 105℃ treatment for 2 days) of Futian water resource recycling center of Taichung city and Tunghai University.

Basic characteristic	**Dry WAS**
Moisture content, %	0.06± 0.03*
Flammable content, %	44.62 ± 0.87*
Ash content**, %	55.29 ± 0.65*
pH	4.78 ± 0.16*

Basic characteristic	**Laterite**
Moisture content, %	0.08 ± 0.05*
Flammable content, %	4.87 ± 0.31*
Ash content**, %	95.05 ± 0.27 *
pH	5.12 ± 0.05*

*n=3

**800^{o}C, 3hr

Table 4-2 The TCLP tests for heavy metal concentration of Futian WAS and laterite.

Element	Concentration of WAS (mg/L)	Concentration of laterite (mg/L)	Regulation of TCLP from HM (mg/L)***
Cu	0.117*	0.016*	15
Pb	0.018*	0.007*	5
Cr	0.002*	0.002*	10
Zn	3.25*	0.063*	25
Cd	ND**	ND**	0.5

*n=3

**ND: None detected

***Heavy metals regulation was obtained from Waste Material Cleanup, NIEA, Taiwan, 2004.

The raw material was grounded into powder by the ball mill (BM-072, Hong –Yu Instrument, Taiwan) machine. Figure 4-1 shows the particle size distribution, and the peaks were located mainly in the 15μm. Basically, the finer the internal particle the sintered pellet will be more rigid.

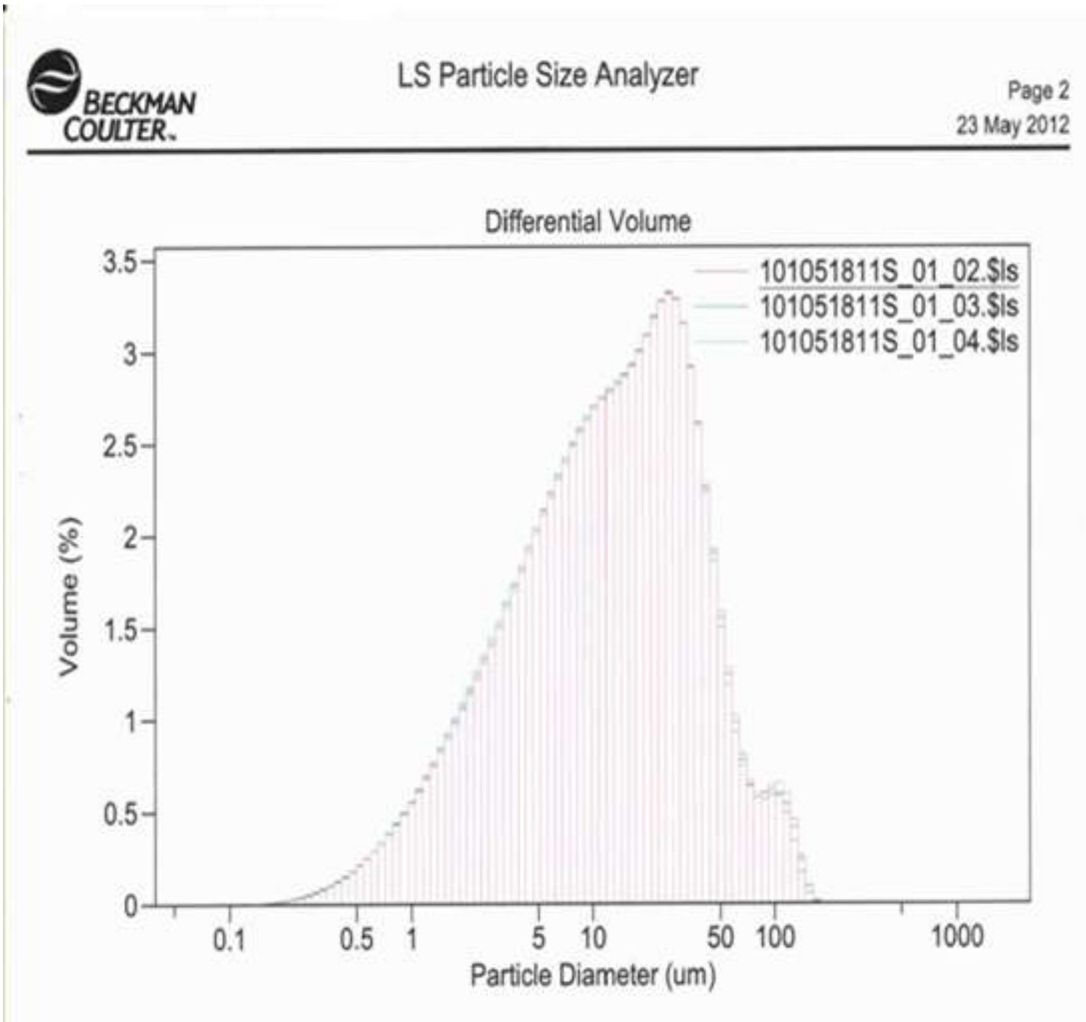


Figure 4-1 The particles size distribution analysis of the WAS powder after grounded by the ball mill machine. The peak of WAS is 15μm.

4.2 The characteristic of the biofilm carrier pellets

The purpose of this study is to build WAS pellets for immobilized media and to enhance nitrogen removal efficiency. Theoretically, a good biomass immobilized pellets has the following properties:

1. High surface and internal area.
2. High water absorption.
3. High strong compression.

The surface area can provide the supporter for biomass while the water absorption can penetrate easily the substance from water into internal pellets. There are microbials which are parts of hydrophilics in wastewater. The adsorbed rate of biofilm can be increased due to hydrophilics porosity carrier has stability in which biofilm was adsorbed (Ding *et al.*, 2011). The basic characteristics of the porous WAS pellets was shown in Table 4-3, a 50% of WAS was used following the best formula. Specific external surface area under the optimal ratio of rebuilt WAS pellets and other references are shown in Table 4-3. The compressive strength of this study: 35.3±3.5 Kgf/cm^2 is significantly higher than Huang's previous work: 11.3±2.5 Kgf/cm^2, and is strong enough and with sufficient porosity. According to the regulation of general waste recycle and disposal, the values must be exceed the standard industrial waste compressive strength of 10 kgf/cm^2 (NIEA, 2003). In this study, the biofilm carrier compressive strength was found 35.3 ± 3.5 kgf/cm^2 and it was higher than the standard regulation in order to prove the biofilm carrier maintain durability. The plot of DOE by MINITAB® was shows on Figures 4-2 and 4-3. Figure 4-2 show the 50% WAS in carrier has the highest surface area (2.6 m^2/g) and has the best compressive strength (35.3 Kgf/cm^2) in this study (showed in Figure 4-3). The rebuild of biofilm carrier were made by a mix of the WAS, laterite and chemical additive, then used the DOE method, after repeated trial, the optimal formula ratios of 5:4:1.

Table 4-3 The comparison the basic characteristics of the porous WAS pellets in this study and other references.

Pellets	**Water absorption (%)**	**Compressive strength (Kgf/cm^2)**	**Bulk density (g/cm^3)**	**Specific external surface area (m^2/g)**
This study	45.2±5.8*	35.3±3.5*	1.8±0.4*	2.6±0.1*
Huang, 2010	41.7±2.5*	11.3±2.5*	1.5±0.0*	2.2±0.1*
Su, 2008	32.9	36.7	7.1	
Chen, 2007	60.49	2.44	0.67	

*n = 3

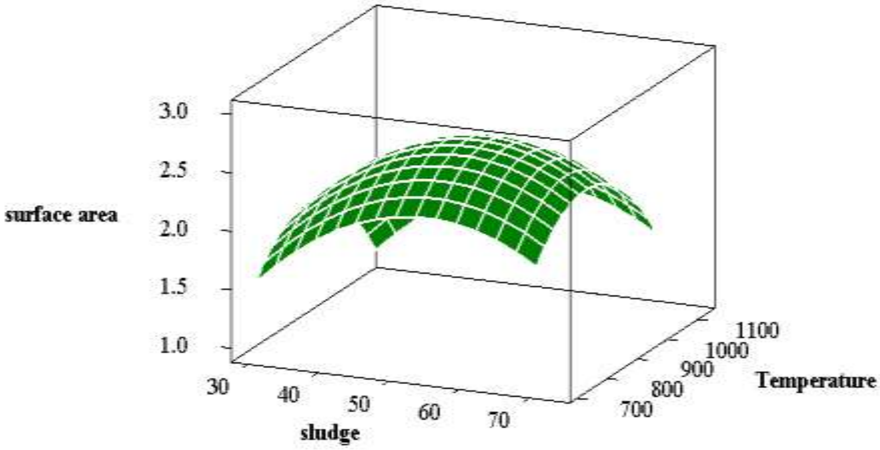


Figure 4-2 Surface plot of surface area (m^2/g), dry sludge (%) and temperature (℃) from DOE analysis.

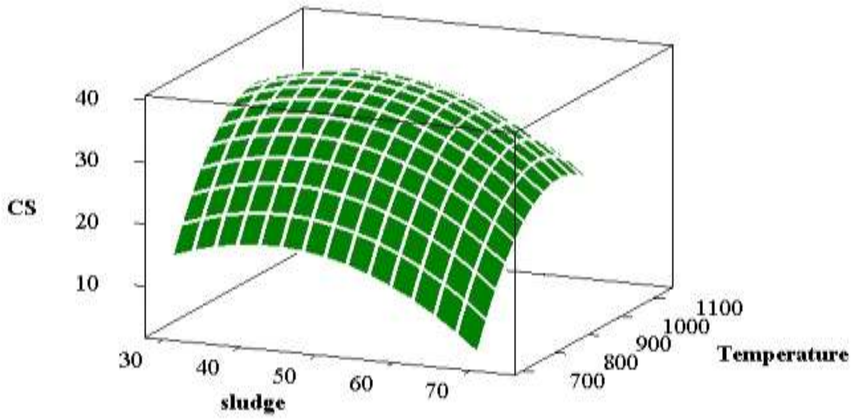


Figure 4-3 Surface plot of compressive strength (CS) (Kgf/cm^2), dry sludge (%) and temperature (℃) from DOE analysis.

4.2.1 The TCLP test

In order to achieve the purpose of waste recycling and reuse, after obtaining the optimal ratio of pellets, the toxicity characteristic leaching procedure (TCLP) test was conducted to detect the potential of toxic heavy metals leached. After the TCLP test (Table 4-4), the heavy metal concentrations were measured by flame atomic absorption spectrometer and the leached toxic heavy metals were far below the Taiwan's limitations (NIEA, 2004).

Table 4-4 The TCLP test for heavy metal concentration of the porous WAS pallets.

Element	Concentration of pellet samples (mg/L)	Regulation of TCLP from HM (mg/L)***
Cu	0.164*	15
Pb	0.138*	5
Cr	0.012*	10
Zn	0.115*	25
Cd	ND**	0.5

*n=3

**ND: Not detected

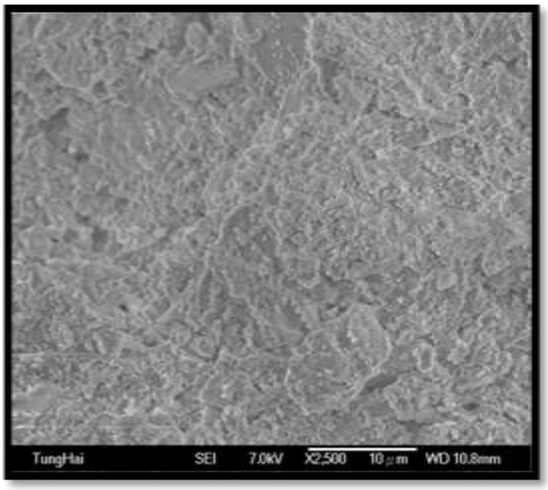
***Heavy metals regulation was obtained from Waste Material Cleanup, Taiwan, NIEA, 2004.

4.2.2 The pellets surface image and composition

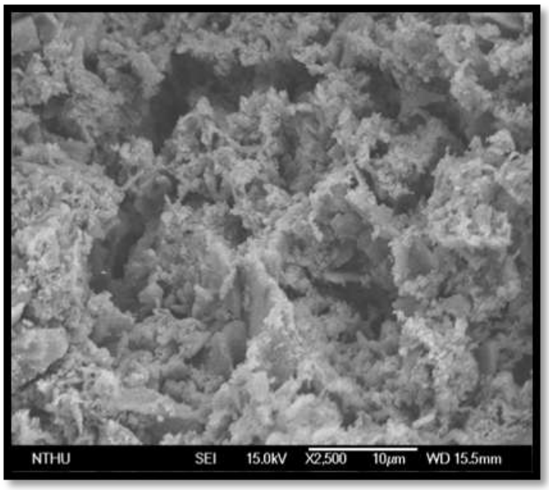
Figure 4-4 shows the biofilm carrier used in this study of SBBB system. Figure 4-4 (a) show the previous study (Huang, 2010), and Figure 4-4 (b) was made by this study. In this study, the bulk density 1.8±0.4 g/cm^3 and compressive strength 35.3±3.5 Kgf/cm^2, and compared to previous study (Huang, 2010) with the compressive strength of 11.3±2.5 Kgf/cm^2. This work enhances the compressive strength of carrier and increase the durability. The external of rebuilt WAS pellets, which the average diameters are between 12 to 15 mm. Figure 4-5 shows the SEM image of the rebuilt WAS porous pellets surface area. And compared to previous studies of particles, the result in this study contains more porosity. Figure 4-5 (c) show the porous particles, it was proved that the biofilm carrier would provide the where is conductive to microbial growth and enough attached area.

(a) Huang, 2010	(b) This study, 2012

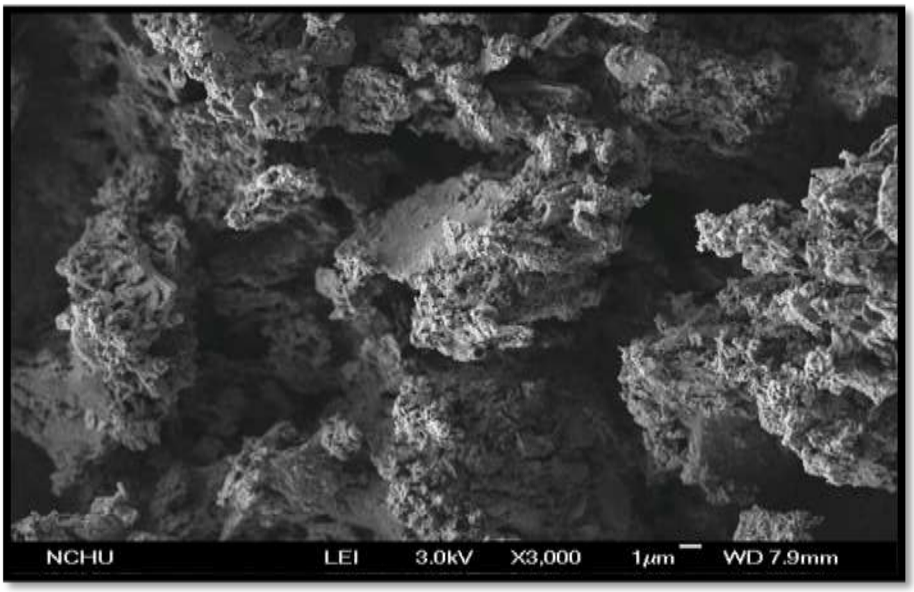
Figure 4-4 The rebuilt WAS pellets with the formula ratio of WAS: laterite: chemical additive is 5:4:1, which the sludge proportion of 50% and their diameters were between 12 to 15 mm.



(a) Su, 2008



(b) Huang, 2010



(c) This study, 2012

Figure 4-5 The SEM image of the reused WAS porous pellets surface.

4.2.3 The B. E. T analysis of the pellets

Table 4-5 shows the comparison of surface area (B.E.T) in this study and other references. This study and Ding *et al.,* (2006) used waste to prepare biofilm carrier. The dried raw WAS powder particle size was 15μm. Ding *et al.,* (2006) used peanut shell to build immobilized media, after carbonation of peanut shell, the diameter of particle is 0.5-1.5μm. Both this work and Ding *et al.,* (2006)'s target pollutants are ammonium. The B.E.T of WAS utilized for preparation of biofilm carrier in this study is 2.7m^2/g which is higher than peanut shell's B.E.T of 2.4 m^2/g. The goal of effluent ammonium in this study is below 1 mg/L, which was lower than the reference from Ding *et al.,* (2006) (13 mg/L). It was proved that for biofilm processes, higher surface area of carriers can provide more sites for microorganisms to adsorb and grow (Wang *et al.,* 2005). Besides, the biofilm carrier prepared by WAS would apply trace element for growth of microbial in this study.

Table 4-5 The comparison of reused immobilized media by surface area (B.E.T) and efficiency in this study and other references.

Reference	**Material**	**Surface area B.E.T (m^2/g)**	**Target**	**Efficiency (mg/L)**
This study	Waste activated sludge (WAS)	2.7	Synthesis wastewater	60-0.8
Huang, 2010	Waste activated sludge (WAS)	2.2	Synthesis Wastewater	61-0.5
Ding *et al.*, 2011	peanut shell	2.4	NH_4^+-N	50-13.7
Jeong and Chung, 2006	Composite of polyethylene	900	Thiocyanate	7,000-1,100
Wang *et al.*, 2005	Polyvinyl chloride	30.7	NH_4^+-N	50-20
Park *et al.*, 2008	Zeolite	320	NH_4^+-N	88-15.1

4.3 Apply the rebuilt WAS pellets in SBBR systems

4.3.1 The daily monitor profiles in system

The two reactors SBBR system with the 20% and 40% ratio pellets were operated for 150 days under three loading stages: Loading Ⅰ (F/M: 0.526 kg COD/ kg MLSS-day or 0.056 kg NH_4^+-N/ kg MLSS-day) for 70 days, Loading Ⅱ(F/M: 0.621 kg COD/ kg MLSS-day or 0.073 kg NH_4^+-N/ kg MLSS-day) for 40 days and followed by Loading Ⅲ(F/M: 0.776 kg COD/ kg MLSS-day or 0.097 kg NH_4^+-N/ kg MLSS-day) for 40 days. Figure 4-6 shows the daily influent and effluent profiles of COD in two reactors. The three loadings operated COD were 520 ± 18.9 mg/L、672 ± 14.5 mg/L and 753± 13.2mg/L for Loading Ⅰ, Ⅱ and Ⅲ phases. The effluents COD were always below 30 mg/L. Figure 4-7 shows the daily influent and effluent profiles of ammonium in two reactors. The three loadings operated ammonia were 70 ± 4.2 mg/L, 80 ± 3.1 mg/L and 92± 2.3 mg/L for Loading Ⅰ, Ⅱand Ⅲ phases, respectively with the COD: N: P ratio of 100: 13.4: .2.1, 100: 12.2: 2.2 and 100:12.2: 2.3 At steady state of each operation phase, the ultimate effluent ammonia were always below 1 mg/L. In Loading Ⅲ, the DO level had to rise from 0.8 to 1.1 mg/L, because the ammonium concentration was too high to treated by the system.

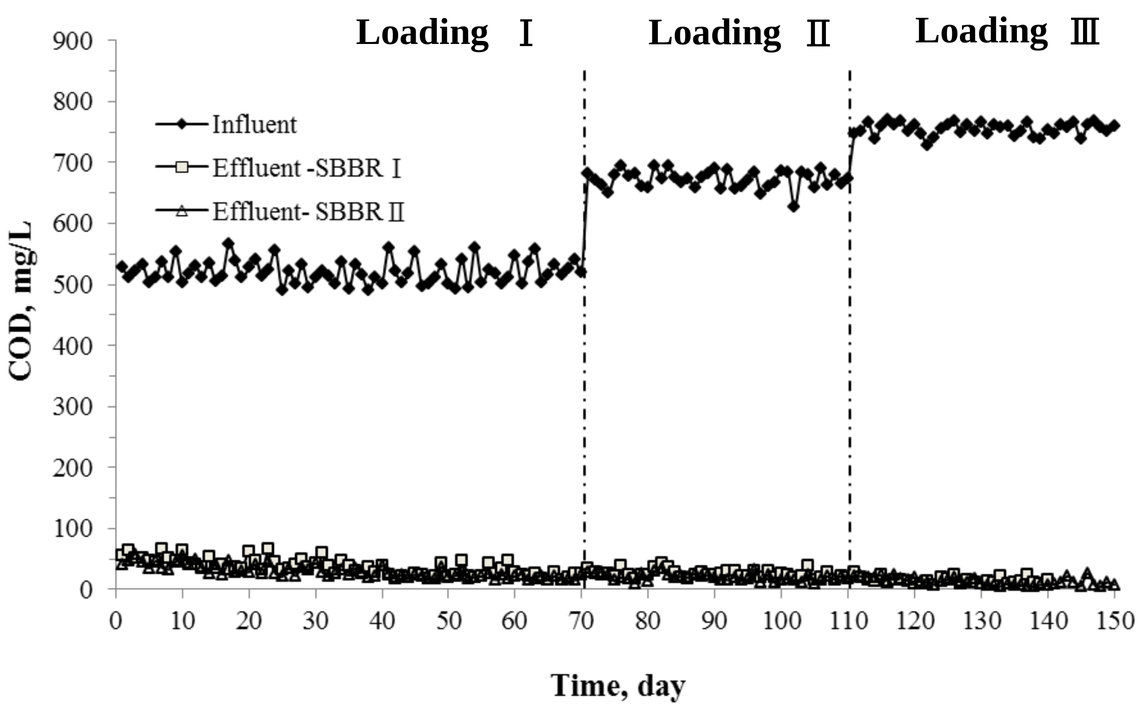


Figure 4-6 The daily profiles of COD in two types of system (SBBR 20% ratio and 40% ratio). The period of Loading Ⅰ (F/M: 0.526 kg COD/ kg MLSS-day) under 70 days, Loading Ⅱ (F/M: 0.621 kg COD/ kg MLSS-day) under 40 days and highest concentration was Loading Ⅲ(F/M: 0.776 kg COD/ kg MLSS-day) under 40 days, respectively.

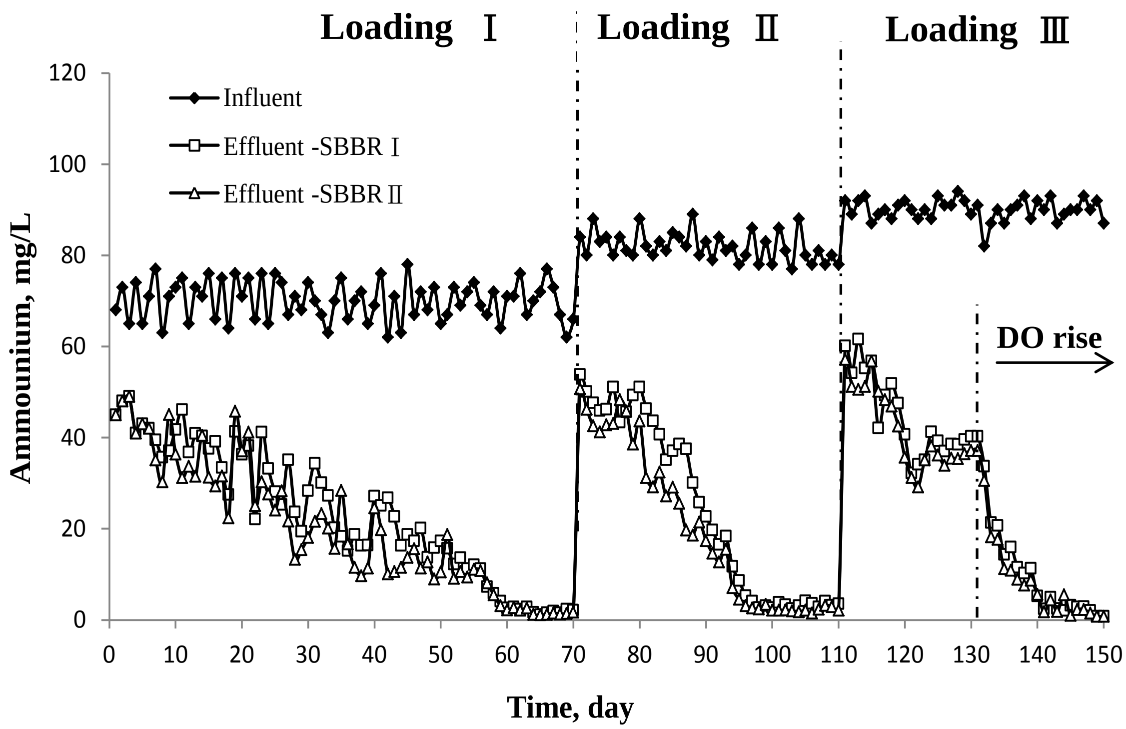


Figure 4-7 The daily profiles of NH_4+-N in two types of system (SBBR 20% ratio and 40% ratio). The operation period of Loading stage I, II and III are 70 days, 40 days and 40 days, respectively. Loading Ⅰ (F/M: 0.056 kg NH_4^+-N / kg MLSS-day), Loading Ⅱ (F/M: 0.073 kg NH_4^+-N / kg MLSS-day) and Loading Ⅲ (F/M: 0.097 kg NH_4^+-N / kg MLSS-day), respectively.

4.3.2 The profiles of a cycle in the two SBBR systems

The preparation of carrier with WAS, and was confirmed that it was applied to the feasibility of biological treatment system in previous study (Su, 2008; Huang, 2010). Designing two reaction systems add the ratio 20% and 40% by volume of pellets to the reactors to conduct biological nutrient removal (BNR) operation. Two systems run parallelly and both under the same operation conditions.

1. SBBR Ⅰ (20% ratio):

Figure 4-8 is the data profiles under Loading Ⅰ (F/M:0.526 kg COD/ kg MLSS-day, 0.056 kg NH_4^+-N/ kg MLSS-day) in SBBR Ⅰ system. Each batch test cycle was 12 hours with 20 minutes per sample taken by online real-time monitoring systems to record ORP, DO and pH. The NH_4^+-N concentration was reduced from 70.0 mg/L to less than 0.8 mg/L. In Loading I, the SBBR Ⅰ system nitrification rate was 0.043 g NH_4^+-N g VSS^{-1} per day (calculated by *Eq. 4-1*, proposed by Carrera *et al.*, 2004).

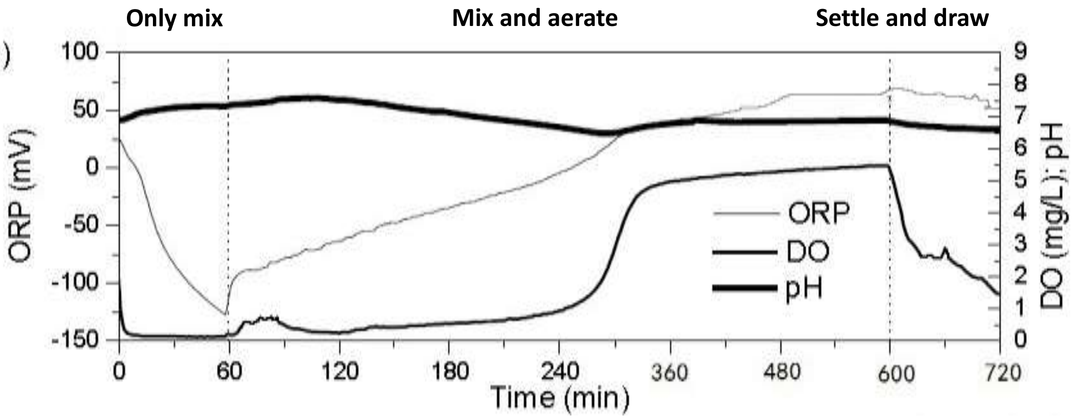
$$r_{nitrification} = \frac{Q_{in}\left(\left[NH_4^+ - N\right]_{in} - \left[NH_4^+ - N\right]_{out}\right)}{V_{reactors}\left[VSS\right]_{reactors}} \qquad Eq.(4-1)$$

(Carrera *et al.*, 2004)

Theoretically SND process, the rate of nitrification is identical to denitrification. In the other hand, there is no excess by product (NO_x) accumulated in the reactor Ding *et al.*, (2011). In reaction process, the rates between generation and consumption of nitrate and nitrite were needed to control both to be equal. In addition, nitrate and nitrite can not be accumulated therefore SND reaction may go on smoothly.

In the batch test, COD and phosphate are not effect on any other substance in reaction, and they can be removed easily. Particularly for phosphate, the "luxury uptake" happens in aerobic condition of system in aeration period. The low DO concentration did not interference this overall bio-reaction (Kim *et al.*, 2008; Jin *et al.*, 2011). The phosphate can remove completely during the aerobic stage at the reaction time of 200 min.

(a)



(b)

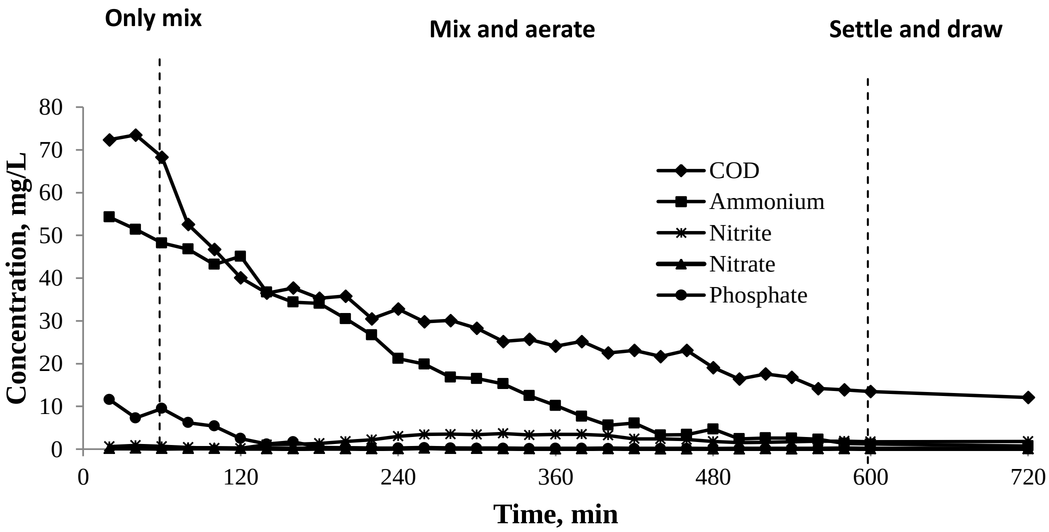
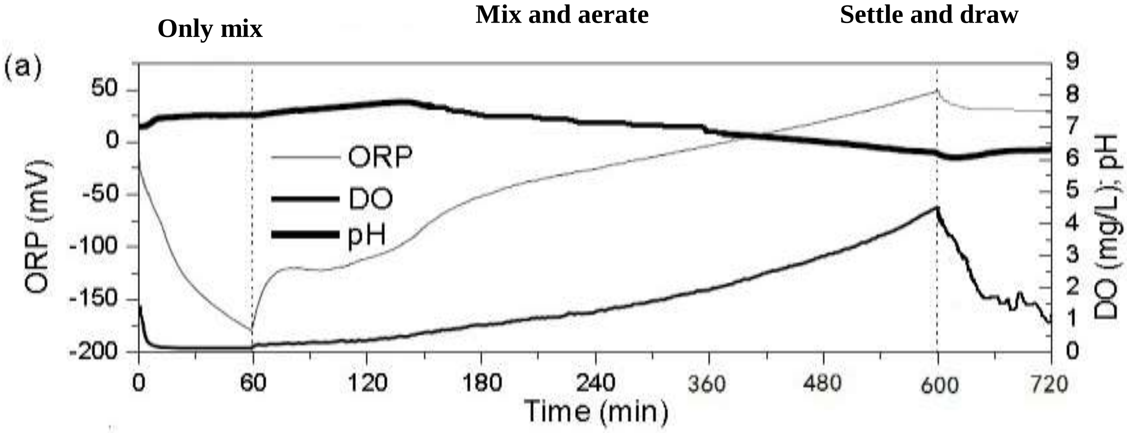


Figure 4-8 The on-line measured parameters (ORP, pH and DO), COD, nitrogen and phosphate concentration in the batch test of the SBBR Ⅰ system (20% ratio) (Loading I); (a): the profiles of ORP, DO and pH; (b): COD, NH_4^+-N, NO_2^--N, NO_3^--N, and PO_4^{3-}-P concentration.

2. SBBR Ⅱ (40% ratio):

Figure 4-9 shows the batch test of SBBR Ⅱ system with 40% ratio pellets in Loading I. Under the same control conditions, the nitrate was almost not detected in the reactor. When ammonium decreased in the system, the nitrite did not increase (below 3.5mg/L) and the nitrate was not detected in system. This means the nitrification transfer ammonium to nitrite and then denitrification happened consecutively. During the reaction, it can be measured by the generation of NH_2OH to prove that reaction in nitrogen removal was following simultaneous nitrification and denitrification (SND) process, rather the traditional two –stage nitrification and denitrification process. The phosphate can remove completely during the aerobic stage at the reaction time of 180 min. The nitrification rate of SBBR Ⅱ system was 0.045 g NH_4^+-N g VSS^{-1} per day. The two SBBR systems, COD and phosphate are not effect on any other substance in reaction, and they can be removed easily. In SBBR Ⅱ, the ammonium can remove below5 mg/L at the reaction time of 360 has minter better then SBBR Ⅰ. According to Park *et al.*, (2008) increase the carrier ratio, nitrification and enhancement is caused by ammonium adsorption and consecutive bioregeneration, resulting in a high concentration of nitrifying bacteria.



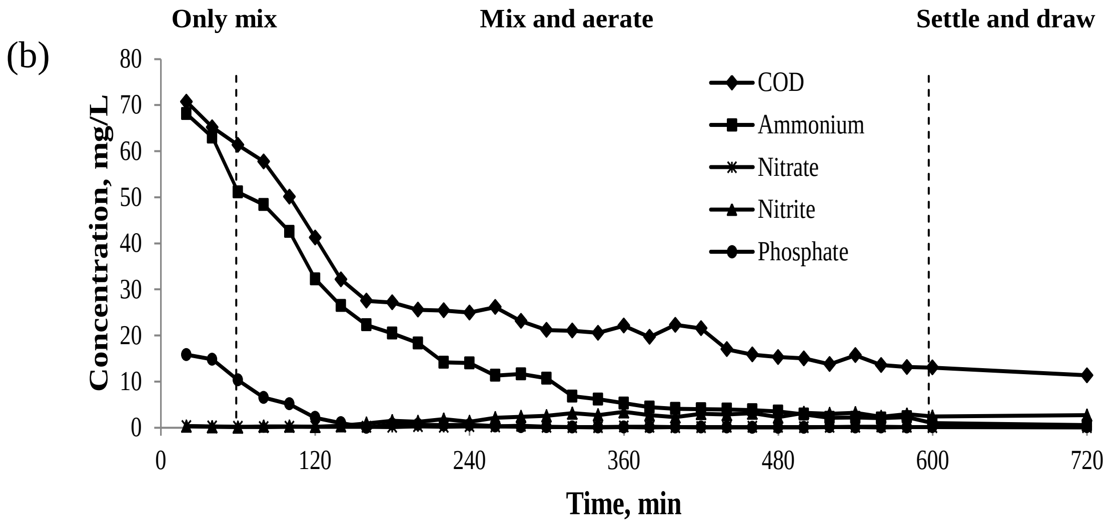


Figure 4-9 The on-line measured parameters (ORP, pH and DO), COD, nitrogen and phosphate concentration in the batch test of the SBBR Ⅱ system (40% ratio) (Loading I); (a): the profiles of ORP, pH and DO; (b): COD, NH_4^+-N, NO_2^--N, NO_3^--N, and PO_4^{3-}-P concentration.

4.3.3 The profiles of batch tests

Figure 4-6 and 4-7 shows the SBBR Ⅰ system in Loading Ⅰ (F/M: 0.526 kg COD/ kg MLSS-day, 0.056 kg NH_4^+-N/ kg MLSS-day, C/N: 7.76) case, the overall operated time is 70 days. Loading Ⅱ (F/M: 0.621 kg COD/ kg MLSS-day, 0.073 kg NH_4^+-N/ kg MLSS-day, C/N: 8.09) operating time of 40 days. The higher concentration was Loading III (F/M: 0.776 kg COD/ kg MLSS-day, 0.097 kg NH_4^+-N/ kg MLSS-day, C/N: 8.18). After the three loadings test reach to a steady state, the reactor was conducted the batch tests. In Figure 4-10 (a), there are not significant differences of COD in three loadings (below 20 mg/L). In Figure 4-7 the ammonium was removed completed after rise the DO level under Loading Ⅲ. Because when microbial absorbs high concentration of ammonium at influent it needs the mounts of oxygen, then, operated to increase DO level for achieving the removal of the target. In such case, the ammonium can be removed below 1 mg/L. The phosphate can remove completely during the aerobic stage at the reaction time of 200 min. Chiu *et al*., (2007) indicated that the SND process was different from the traditional nitrification and denitrification (Figure 2-4). In this batch reaction, the nitrate was not detected in this test (Figures 4-10 (d)), while the hydroxylamine could prove this was following a proposed SND pathway (Figure 4-12).

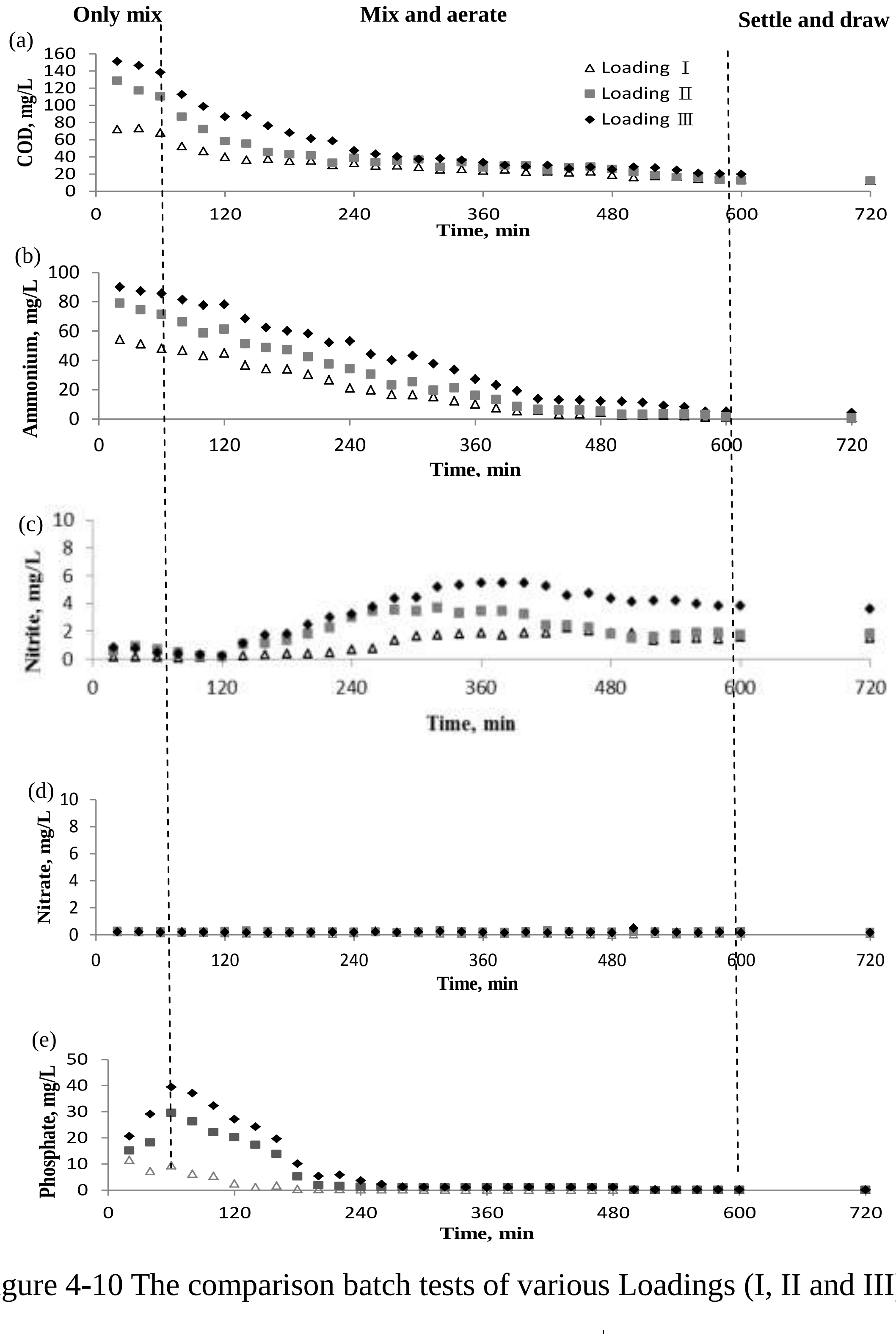


Figure 4-10 The comparison batch tests of various Loadings (I, II and III) in SBBR 20% ratio (a) COD, (b) NH_4^+-N, (c) NO_2^--N, (d) NO_3^--N and (e) PO_4^{3-}-P.

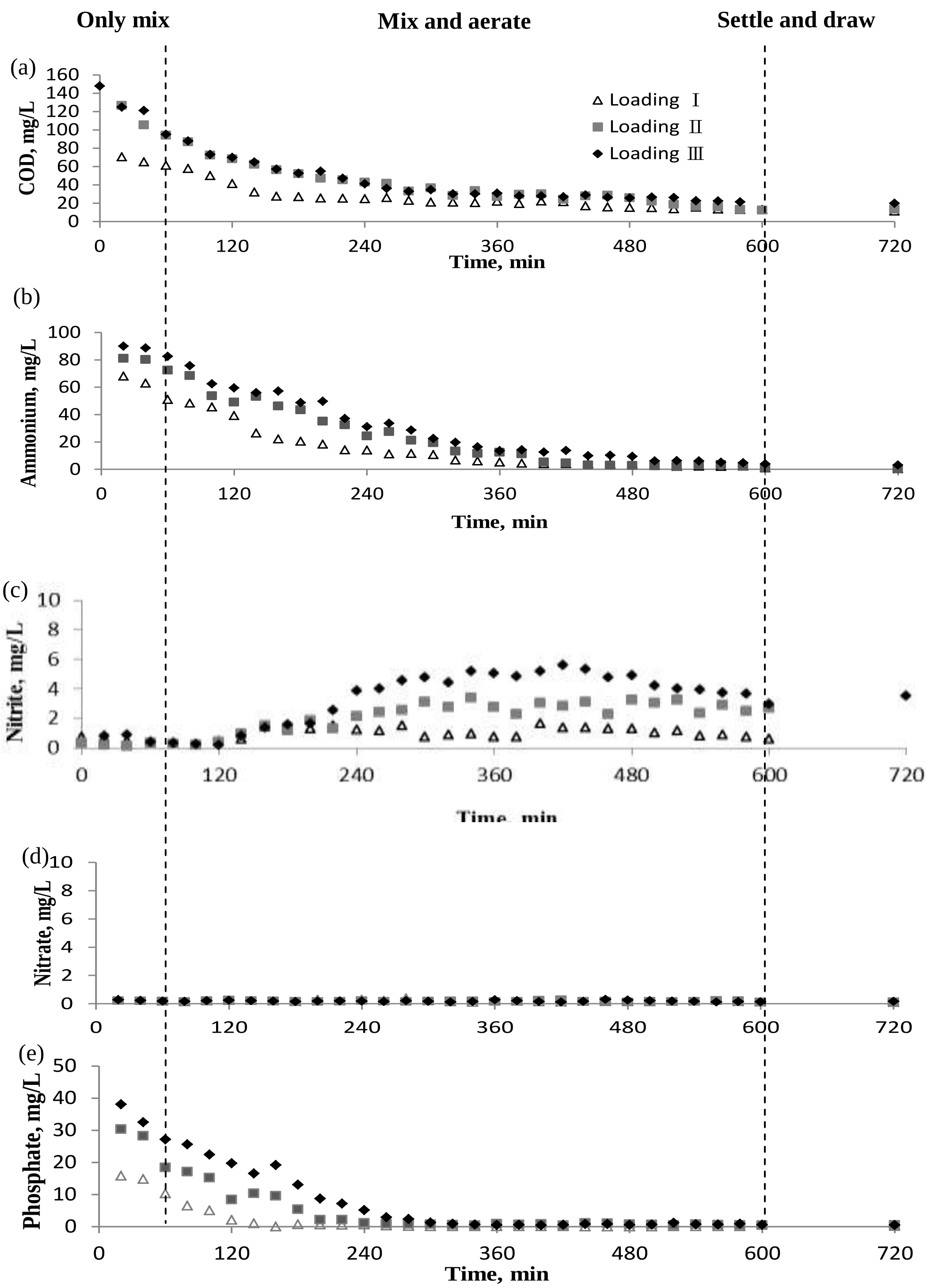


Figure 4-11 The comparison batch tests of various Loadings (I, II and III) in SBBR 40% ratio (a) COD, (b) NH_4^+-N, (c) NO_2^--N, (d)

NO_3^--N and (e) PO_4^{3-}-P.

4.3.4 Identification of the SND process with hydroxylamine

The overall ammonium removal by SND process is show in Figure 2-4, which includes two steps: the nitrification and denitrification reactions. Both steps have their reaction rates: K_N and K_{DN} defined by Tsao, (2001). In the nitrification step, the hydroxylamine generated as mid-product and can be used as an indicator to represent the SND reaction taking place in the system. Theoretically, the higher hydroxylamine released, the more ammonium be converted into nitrite (Figure 4-14), i.e., a high K_N value can be found in the system (Figure 4-13). In the first partly SND process, the nitrification reaction is found have a NH_2OH and nitrite release rate with 7.61×10^{-7} mg/g N H_4^+-N g MLSS removed and 5.61×10^{-7} mg/g N H_4^+-N g MLSS in the system.

Table 4-6 The nitrification removal rate.

Pellet ratio	Stage	NH_2OH/MLSS NH_4^+-N (g)	NO_2^-/MLSS NH_4^+-N(g)
20%	Ⅰ	4.98×10^{-7}	3.31×10^{-5}
	Ⅱ	5.04×10^{-7}	4.49×10^{-5}
	Ⅲ	7.25×10^{-7}	7.52×10^{-5}
40%	Ⅰ	9.03×10^{-7}	4.38×10^{-5}
	Ⅱ	8.05×10^{-7}	5.32×10^{-5}
	Ⅲ	1.13×10^{-6}	8.5910^{-5}
Average		7.61×10^{-7}	5.61×10^{-5}

In the Figure 4-15 it combines three loadings and two types of immobilized media ratios VS. K_{SND} in the reactor and came out one correlation line. It shows that the NH_2OH can satisfactorily indicate the nitrification reaction and affect K_N in the first step of SND reactor. Figure 4-13 shows the total SND removal efficiency (K_{SND}) with also can upgrade due to the high K_N in the system based upon the NH_2OH released from the system.

Simulation the NH_2OH profile in the reactor (Figure 4-12) with the 1st order kinetic model:

$$C = C_0 e^{-kd}$$

Where:

C_o: the initial NH_2OH, mg/L

C: the NH_2OH at time , 440min

K_d: mg/L/min

The correlation between loadings and K_d is shown in Figure 4-18.

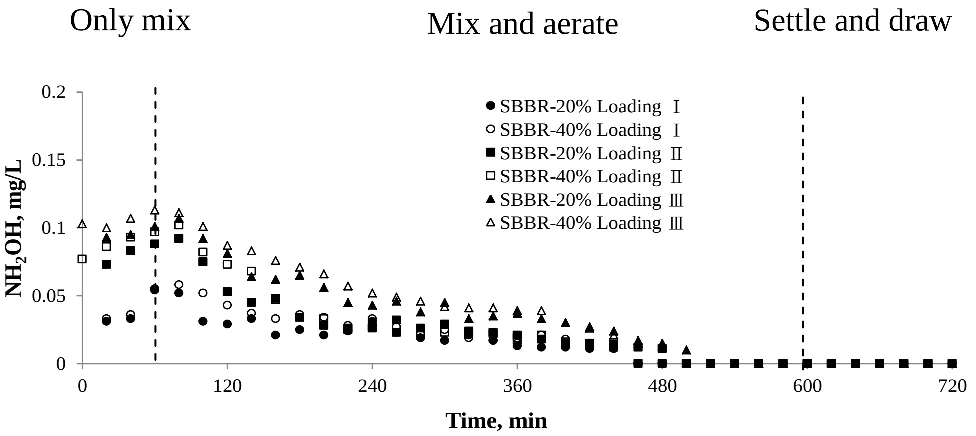


Figure 4-12 The profile of hydroxylamine (NH_2OH) in SBBR 20% and 40% ratio systems with three loading systems.

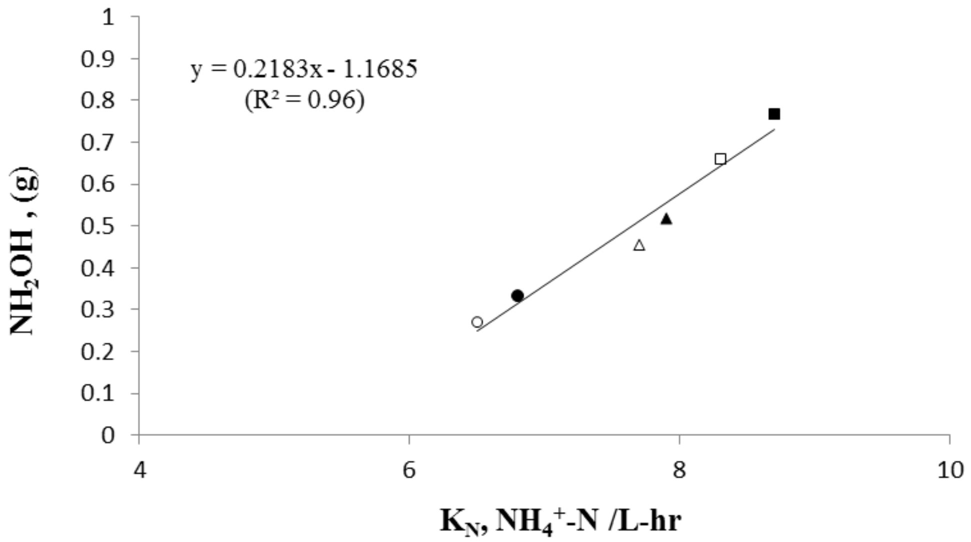


Figure 4-13 The nitrification kinetic constant K_N and NH_2OH (g) generated form the reactor. ○: stage Ⅰ, △: stage Ⅱ, □: stage Ⅲ, SBBR 20%; ●: stage Ⅰ, ▲: stage Ⅱ, ▓: stage Ⅲ, SBBR 40%.

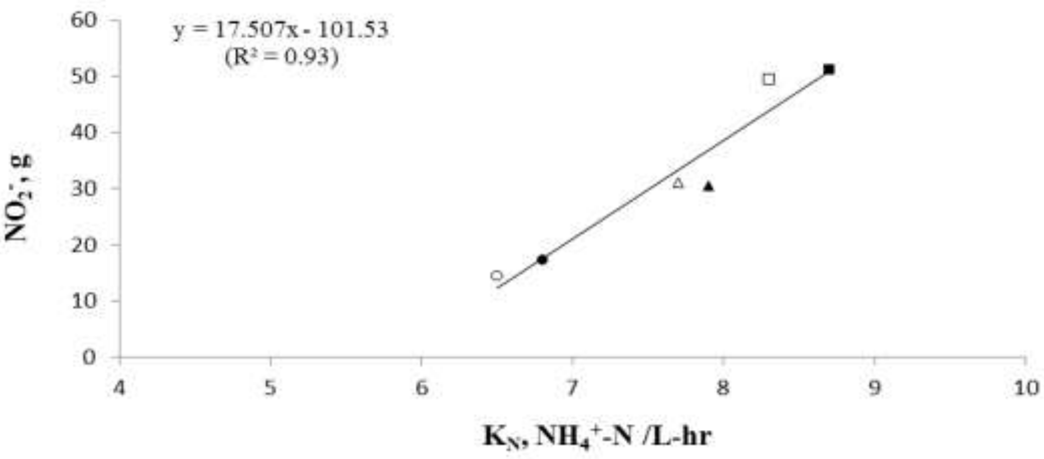


Figure 4-14 The nitrification kinetic constant K_N and NO_2^- (g) generated form the reactor. ○: stage Ⅰ, △: stage Ⅱ, □: stage Ⅲ, SBBR 20%; ●: stage Ⅰ, ▲: stage Ⅱ, ■: stage Ⅲ, SBBR 40%.

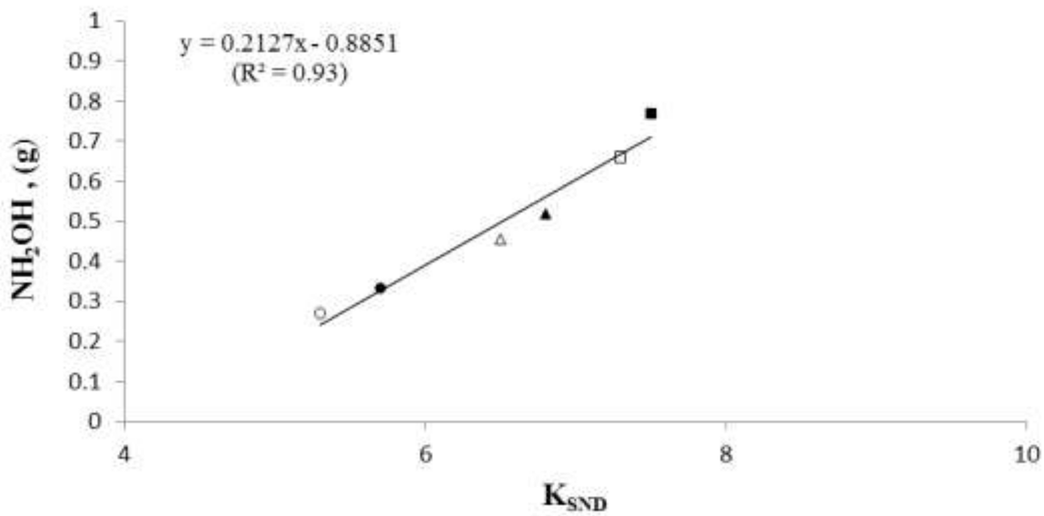


Figure 4-15 The nitrification kinetic constant K_{SND} and NH_2OH (g) generated form the reactor. ○: stage Ⅰ, △: stage Ⅱ, □: stage Ⅲ, SBBR 20%; ●: stage Ⅰ, ▲: stage Ⅱ, ■: stage Ⅲ, SBBR 40%.

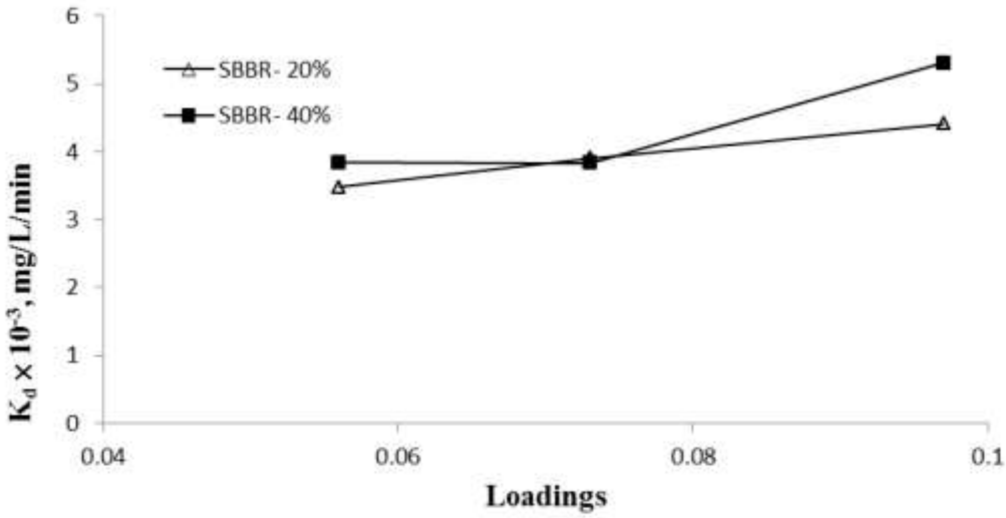


Figure 4-16 The correlation between loadings and K_d for 20% and 40% ratio pellets in SBBR systems.

4.3.5 The biomass of two pellets in systems

During the systems were cultured, we took the pellets out every 10 days. In order to obtain the biomass in pellets, this study drying them under 105°C and weighting until reach to a constant weight. The Figure 4-17 shows the weight variation of the pellets. Biomass was the dry weight of the pellet in the reactor subtract the dry weight of the pellets before put in the reactor. The SBBR 20% reactor biomass total of 4.9g and SBBR 40% reactor biomass total of 11.2g.

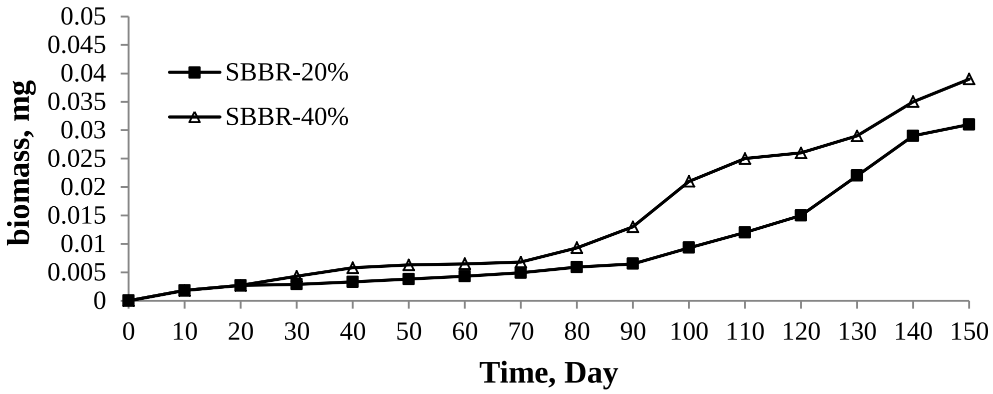


Figure 4-17 The biomass of two pellets (20% and 40% ratio).

4.3.6 The carriers filling ratio to the removal rate

Table 4-7 shows the comparison of carrier filling ratios in this study (20% and 40%) and other references. According to many references (Wang *et al.,* 2005, Park *et al.,* 2008, Jin *et al.*, 2011) in the sequencing batch biofilm reactor (SBBR) operation system, the added different carriers filling ratio have different result of the impact for the removal efficiency. Boejie *et al.*, (2003), applied biofilm processes, the carrier concentration was lower, such as 10 or 20%, the biofilms formed were rough and fluffy with a lower density. However, when the carrier concentration became higher, such as 30%, the biofilms became thinner and only formed in the clefts and fissures on the carrier surface, the oxygen and substrate diffusion limitation was not a problem at all, then the activity of biofilm increased accordingly (Wang *et al.*, 2005). The higher surface area of carriers can provide more sites for microorganisms to adsorb and grow. To certain extent, the higher the carrier concentration or carrier filling ratio, the more biomass can be retained in the reactors. To increase the carrier ratio, nitrification and enhancement is caused by ammonium adsorption and consecutive bioregeneration, resulting in a high concentration of nitrifying bacteria (Park *et al.*, 2008; Ding *et al.*, 2011). This study with the Biofilm carrier has satisfactory COD and ammonium removal in compared to other references (Table 4-7). The reason might be the biofilm carrier was made from WAS, which would contain trace elements foe growth of microbial. This can make a better growth surrounding and improve the activation of bacteria.

Table 4-7 The comparison of carrier filling ratios in this study and other references.

Reference	**Wastewater**	**Carrier filling ratio (%)**	**Removal efficiency (mg/L)**
This study	Synthesis wastewater	20 and 40	COD: 648-30 NH_4^+: 60-0.8
Huang, 2010	Synthesis wastewater	20	COD: 487-20 NH_4^+: 61-0.5
Wang *et al.*, 2005	Synthesis wastewater	50	COD: 200-80 NH_4^+-N: 50-20
Jin *et al.*, 2011	Synthesis wastewater	10	COD:309-31 NH_4^+-N :30-0.3
Park *et al.*, 2008	Synthesis wastewater	40	COD: 245-64 NH_4^+: 88-40.5

4.4 Comparison the K_N, K_{DN} and SND efficiency of different systems

Table 4-8 shows the nitrification rate (K_N), denitrification rate (K_{DN}) and SND efficiency of different systems from this study and other references. Table 4-8 shows the typical SBBR system with 20% pellets and SBBR system with 40% pellets. The efficiency of SND is calculated by Eq. (4-2) (Zeng *et al.*, 2003):

$$Efficiency_{SND} = \frac{Denitrification}{Nitrification} = \frac{NH_4(tot) - NO_x(acc)}{NH_4(tot)} \text{..........................} Eq.(4-2)$$

Where $NH_4\ (tot)$ is the influent concentration of ammonium;

$NO_x(acc)$ is the effluent concentration of NO_x-N.

The both systems perform well (94-98 % removal) compared to other studies. The results show the K_N and K_{DN} are proportional to that of the loadings (from Loading I to II) in SBBR system with rebuilt WAS pellets. The nitrification rate (K_N = 7.6 mg-NH_4^+-N/L-hr) and denitrification rate (K_{DN} =7.7 mg-NH_4^+-N/L-hr) of SBBR 40% ratio system were higher than that of SBBR 20% ratio system (K_N =7.4 mg-NH_4^+-N/L-hr, K_{DN} = 7.8 mg-NH_4^+-N/L-hr) under phase II with the 40% ratio with the 98 % SND removal efficiency.

Table 4-8. The comparison of nitrification rate (K_N), denitrification rate (K_{DN}) and SND efficiency in different systems in this reactor and other references.

Reference	Wastewater		K_N [a]	K_{DN} [b]	K_{SND}
This study, (SBBR-20%)	Synthetic wastewater	Loading I	6.5	6.3	5.3
		Loading II	7.7	7.4	6.5
		Loading III	8.3	7.8	7.3
This study, (SBBR-40%)	Synthetic wastewater	Loading I	6.8	6.5	5.7
		Loading II	7.9	7.6	6.7
		Loading III	8.6	7.9	7.4
Guo, 2009 (SND)	Synthetic wastewater		5.2	4.9	7.2
Huang, 2010(SBBR system, SND)	Synthetic wastewater	Loading I	4.2	4.3	3.7
		Loading II	6.0	6.2	4.3
		Loading III	7.8	7.5	6.1

Su, 2008 (SBBR system with WAS pellets diffusers) (SND)	Synthetic wastewater	Loading I	4.2	4.2	4.5
		Loading II	5.9	5.8	4.9
		Loading III	8.1	7.7	5.9
Chung, 2007 (SBBR system with rebuilt WAS and commercial pellets, SND)	Synthetic wastewater		5.5	5.2	5.3
			5.5	4.9	7.1
Jin, *et al.*,2011 (SBBR)	Municipal wastewater		5.4	4.3.	3.75
Li, 2003 (SBBR)	Municipal wastewater		9.4	9.2	1.1
Gieseke *et al.*, 2002 (SBBR)	Synthetic wastewater		4.1	3.7	2.8

[a] Express as mg-NH_4^+-N/L-hr (nitrification rate)

[b] Express as mg-NO_3^--N/L-hr (denitrification rate)

4.5 Model Development

4.5.1 Overall SND process in SBBR system

From Figure 4-13 (b), the SBBR system with 40% ratio can achieve SND process smoothly. In theoretical SND process, the rate of nitrification is as equal to denitrification. In the other hand, there is no excess by product (NO_x) accumulated in the reactor (Ding *et al.,* 2011). Therefore, the statement of the Nernst equation for the complete SND process can combine *Eq. (4-3)* and *Eq. (4-4).* Due to the excessive carbon substrate existed in the denitrification of SND process, the carbon concentration ($C_xH_yO_z$) can assumed to be constant. Therefore, the *Eq. (4-3)* can be obtained as follows:

$$E = E^0 + \frac{RT}{nF}\ln\left(\frac{[NH_4^+](P_{O_2})^2}{[NO_2^-][H^+]}\right) \text{ .... } \textit{Eq. (4-3)}$$

$$E = i + j\ln([C_xH_yO_z]) + h\ln([NO_2^-]) + k\ln\left(\frac{1}{[OH^-]}\right) \text{ .... } \textit{Eq. (4-4)}$$

$$E = a'' + b''pH + c''\log(NO_2^-) + d''\log(C_xH_yO_z) \text{ .... } \textit{Eq. (4-5)}$$

$$E = a + bpH + c\ln([NH_4^+])([PO_4^{3-}]) \text{ .... } \textit{Eq. (4-6)}$$

(Lee, 2004)

4.5.2 Nernst Equation established in SND Process

1. First stage: phosphate and ammonium removal

According to the reaction model of Nernst equation which covers both anoxic and aerated, therefore, a suitable simulation can be approached. Table 4-9 shows the Nernst equation modeling results of both anoxic and aerobic cases in SBBR systems dealing with nitrogen and phosphate removal. Both the fitted models indicate well correlation coefficient (R^2) value of 0.95 -0.96. This indicates that both *Eq. (4-5)* and *Eq. (4-7)* can describe the overall profiles of ORP in the SBBR systems. Figure 4-18 shows the model simulation and the experimental data, which shows a close correlation. The ORP model can be adapted to the further control of phosphate removal end point of SBBR systems.

$$E = a' + b'pH + c'\log\frac{[NH_4^+]}{[NO_2^-]} \quad \text{...Eq. (4-7)}$$

Table 4-9 Results of the Nernst equation for "only mix" and "mix and aerate" steps in two SBBR systems

	Nernst equation model constants			
This study	a	b	c	R^2
Only mix	-3746.53	335.34	536.43	0.96
Mix and aerate	781.12	-73.93	-28.23	0.95

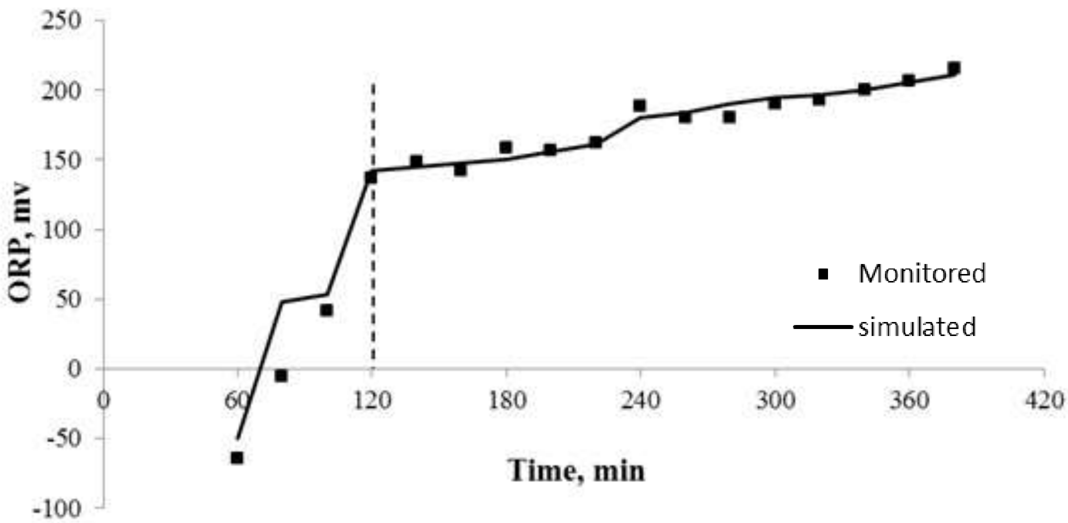


Figure 4-18 The comparison of simulated and experimented ORP profile for "only mix" and "mix and aerate" steps of SBBR system with 40% ratio pellets.

2. Second stage: ammonium removal

Eq. (4-8) is Nernst equation only considered ammonium for excess carbon sources in SND process (Lee, 2004). After phosphate removed completely, this equation can predict the ammonium in reactor.

$$E = a' + b'\,pH + c'\ln\left(\left[NH_4^+\right]\right) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots Eq.(4-8)$$

Table 4-10 shows the second stage Nernst equation modeling results of aerobic cases in SBBR systems with rebuilt WAS pellets. The simulated models indicate well correlation coefficient (R^2) value of 0.95. Figure 4-19 shows the model simulation and the experimental data, which shows a close correlation in second stage reaction.

Table 4-10. Results of the second stage Nernst equation for “mix and aerate” step in SBBR systems with rebuilt WAS pellets.

	Nernst equation model constants			
SBBR with 40% ratio pellets	a	b	c	R^2
Mix and aerate	-318.97	11.77	-35.42	0.95

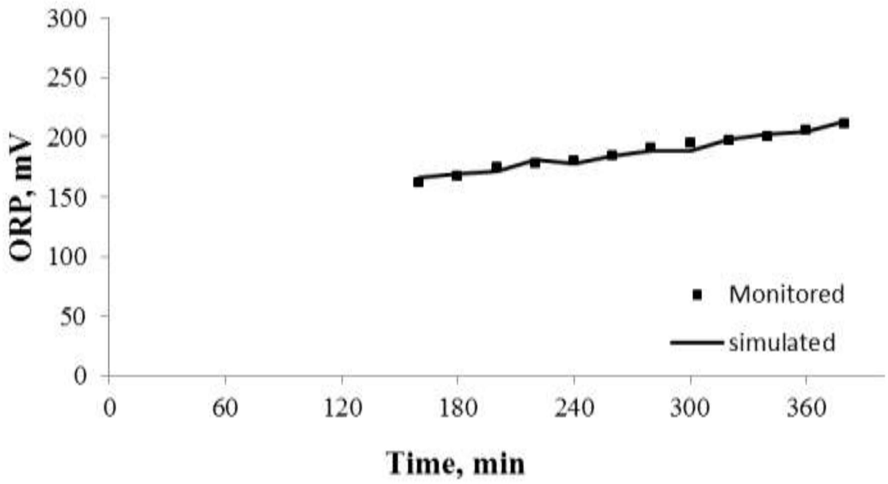


Figure 4-19 The comparison of simulated (second stage model) and experimented ORP profile for “mix and aerate” step of SBBR system with 40% ratio pellets.

4.5.3 Application SBBR SND system

In the SBBR with 40% ratio system, according to the Table 4-10 and *Eq. (4-8),* when the ORP value is above 160 mV, (i.e., the reaction time of 180 min) the phosphate can be removed completely. This means the step 1 is finished, and then the reaction entering step 2. According to the Table 4-10 and *Eq. (4-8),* the ammonium can be removed completely when the ORP value above 200 mV, i.e., the SND reaction will be terminated. The sudden drop of pH value is also a good index to realize the end point of phosphate removal. In this study, the pH value is included in the Nernst model, therefore, it can be considered as one of the key parameters to control the end of the first stage reaction.

CHAPTER 5 CONCLUSIONS AND SUGGESTIONS

5.1 Conclusions

In this study, two SBBR systems build with 20% and 40% ratios of WAS pellets were tests. All the system was cultured the activated sludge under three loading stages and conduct in SND reactions. The following conclusions can be made:

1. The raw pellets can be made of WAS, laterite and chemical additive with an optimal formula of 50 % of WAS according to DOE. The basic characteristics of rebuilt raw pellets with the water absorption of 45.2±5.8 %, bulk density 1.8 ± 0.4 g/cm^3 and the compressive strength 35.5±3.5 kgf/cm^2.

2. The higher NH_2OH released, the more ammonium be converted into nitrite, and the total SND removal efficiency (K_{SND}) also can upgrade due to the high K_N in the system based upon the NH_2OH released from the system. The NH_2OH and NO_2^- release rate during the nitrification reaction are $5.78 \times 10^{-7}$and 9.47×10^{-7}, respectively.

3. According to the batch tests result, the 40% ratio SBBR can make a better growth surrounding and improve the SND reaction.

5.2 Suggestions

1. A 60% of WAS pellets ratio to SBBR system is necessary to deal with high loading waste.

2. The DNA identification is necessary to examine the type and characteristics of biomass.

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