

## Chapter 1 Introduction

All forms of inorganic nitrogen in water can cause eutrophication.

Ammonia in water ( $\text{NH}_{3(\text{aq})}$ ) is toxic to many aquatic lives, such as fishes and microorganisms, while excess ammonium ion ( $\text{NH}_4^+$ ) and ammonia will both exhaust dissolved oxygen (DO) in receiving water. Moreover, the presence of nitrite and nitrate ions ( $\text{NO}_2^-$  and  $\text{NO}_3^-$ ) in drinking water is a potential problem of public health. The removal of nitrogenous substances from water is a typical issue to deal with both in environmental and healthy aspects. Conventional biological nitrogen removal (BNR) process includes three parts: 1. pre-anoxic condition: which is for transformation of organic nitrogen to ammonium ion; 2. anoxic condition: the nitrifiers oxidize ammonium ion into nitrite and further into nitrate ion; and 3. anoxic condition: nitrate or nitrite ion will be reduced to nitrogen gas by denitrifiers, and release to atmosphere.

Recently, simultaneous nitrification and denitrification (SND) has been discovered in various forms of reactor. SND means that nitrification and denitrification occur at the same time in the same reactor without anoxic mixing stage for nitrate or nitrite reduction.

The major advantages of SND system include: 1. no separate spaces

needed for oxic and anoxic period; 2. no operational problem in changing period of nitrification and denitrification. However, SND process might cause energy waste due to the continuous aeration and mixing during oxic period.

Using submerged membrane in the bioreactor to replace conventional gravitational settling has been a common way for solid-liquid separation. This study combined sequencing batch reactor (SBR) and membrane bioreactor (MBR) to develop the sequencing batch membrane bioreactor (SBMBR). The major characteristics of SBMBR system are land-saving for conventional sedimentation tank, and filtering out the pathogenic organisms. In this research, the feasibility of introducing SND process to SBMBR system was studied along with the online monitoring parameters to investigate the nutrient removal efficiency, real-time control point, model fitness and adaptability of effluent reuse as recycle water.

## **Chapter 2 Literature review**

### **2-1 Simultaneous nitrification and denitrification (SND) process**

In recent years, SND (Simultaneous nitrification and denitrification) has been shown to occur simultaneously in the same reactor without using separate reactors for the oxic and anoxic processes (Demoulin et al., 1997; Zeng et al., 2003). Nitrification, denitrification and “nitrite shunt” pathway are shown in Figure 2-1. Oxidic denitrification, attention was first drawn to the SND phenomenon almost two decades ago, by unaccounted for nitrogen losses; as for example, up to 80% inorganic nitrogen was reported missing in the full-scale sequencing batch reactor (SBR) plant in Iowa (Irvine et al., 1987). At the same time, others reported SND process in a variety of full-scale continuous processes (Kugleman and Spector, 1988; Moriyama et al., 1990) in biological contactor units (Masuda et al., 1991) and in upflow fixed-bed reactors (Halling and Hjuler, 1992). More recently, nitrification and denitrification has been confirmed to occur concurrently in the same reactor and in a variety of processes (Watanabe et al., 1992; Gupta et al., 1994; Munch et al., 1996; Sen and Dentel, 1998; Menoud et al., 1999; Furehacker et al., 2000; Watanabe et al., 2002; Hibiya et al., 2003).

Despite its prevalence, there is still a lack of agreement over whether the prevailing mechanism behind the SND phenomena is pure-culture or mixed culture.

The SND process are performed by either pure-culture or mixed culture. In the pure-culture SND, a single microorganism is capable of achieving nitrification and denitrification (Dalsgaard et al., 1995; Gupta, 1997; Shrestha et al., 2002). While in a mixed-culture SND, a consortium of different nitrifying and denitrifying microbial organisms co-exists in the same reactor and achieves SND in various scales of treatment system (Demoulin et al., 1997; Yoo et al., 1999; Zeng et al., 2003). Many authors suggested mixed-culture SND will occur simultaneously inside (anoxic) or outside (oxic) the biomass flocs if the DO is kept at adequate low levels. Normally, the suggested acceptable DO in an SND process is between 0.5 to 2.0 mg/L (Demoulin et al., 1997; Pochana and Keller, 1999; Yoo et al., 1999). Because nitrification and denitrification proceed simultaneously in an SND system, the alkalinity is continuously generated by nitrification and consumed by followed denitrification to balance the solution pH. Thus, the SND system requires less quantity of external alkalinity addition for

pH adjustment. Besides, either nitrite or nitrate will not accumulate in the reactor and result the SND system in a higher denitrification rate and lower biomass yield than the conventional two-step biological nitrogen removal (BNR) process (Gupta, 1997, Keller et al., 1997 and Zeng et al., 2003).

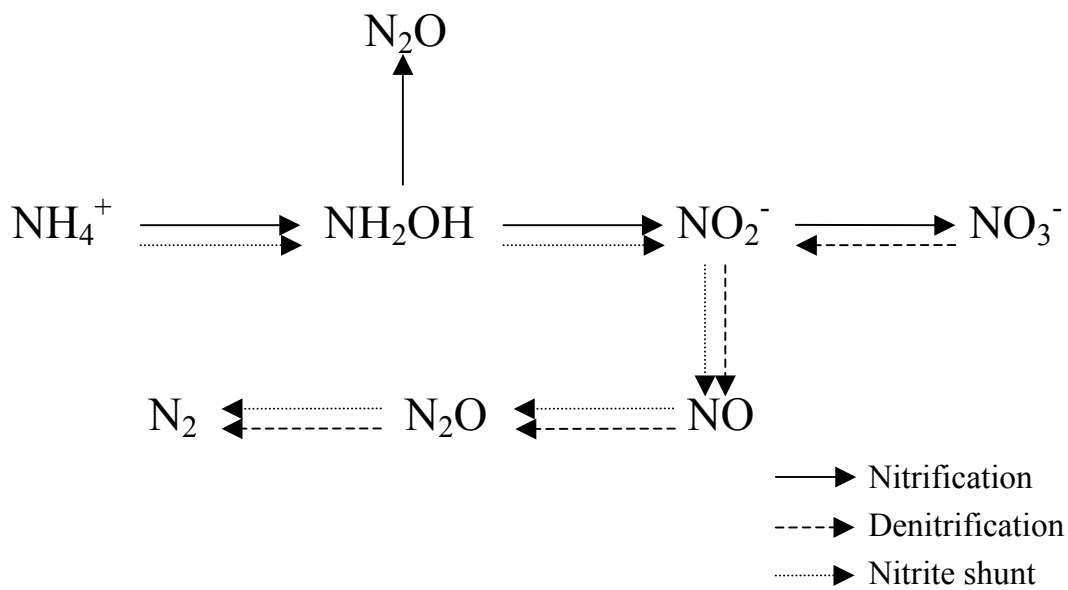


Figure 2-1. Nitrogen transformations of nitrification, denitrification and “nitrite shunt” pathway. (Wrage et al., 2001)

Pochana and Keller (1999) reported that the efficiency of denitrification decreased when DO was above 0.2 mg/L; while Bliss and Barnes (1986) noted that nitrification would be ceased when DO was under 0.2 mg/L. Carbon supply was also an important factor in SND

process. Low-DO aeration provides anoxic zones to enhance anoxic denitrification, and some residual carbon reserves to stimulate anoxic denitrification (Pochana and Keller, 1999; Stevens et al., 1999; Zhao et al., 1999). Anoxic zones could be occurred inside/outside the flocs and/or the area which DO can not reach in the reactor. Therefore, nitrification and denitrification can occur at the same time in the same reactor.

SND is also effective in maintaining neutral pH level in the reactor, without the addition of external acid/base source. This is important since a narrow optimal range between pH 7.5 and 8.6 is known to exist for the nitrifying bacteria. During nitrification alkalinity is consumed, but alkalinity is produced during denitrification. The optimal pH lies between 7 and 8 for denitrification with different optimums for different bacterial populations (Yoo et al., 1999). Thus, SND phenomena have been discovered in various systems; Table 2-1 lists some literatures related to different conditions in SND process.

Table 2-1. SND efficiencies under various C/N ratios and systems.

Wastewater	Reactor form	C/N ratio*	SND efficiency	Authors
Domestic	CAST**	10.9 (COD: TN)	96%	Demoulin et al., 1997
Abattoir	SBR	18.3	97%	Keller et al., 1997
Abattoir	SBR	14.5	80%	Pochana and Keller, 1999
Synthetic (domestic)	IDEA***	9.7	95%	Yoo et al, 1999
Domestic	3-stage Bardenpho process	17.2	50%	Zhao et al., 1999
Synthetic (domestic)	SBR	10.0	98%	Zeng et al., 2003
Synthetic (domestic)	MBR	11.8	85%	Zhang et al., 2005
Synthetic (domestic)	SBR	20.0	88%	Holman and Wareham, 2005

\* C/N ratio: TCOD/NH<sub>4</sub>-N; \*\* CAST: Cyclic Activated Sludge Technology; \*\*\* IDEA: Intermittently Decant Extended Aeration.

## **2-2 Sequencing batch membrane bioreactor (SBMBR) system**

### **2-2-1 SBMBR**

Sequencing batch membrane bioreactor (SBMBR) was defined as add membrane module for filtration in the sequencing batch reactor (SBR). The development of SBR system is mature so that treatment efficiency and stability can reach a desired standard. SBR provides the advantages of easy-operating, reliability and flexibility which the conventional activated sludge system can not reach, and also reduce the land area demand, designing and operating costs (蔡氏與邱氏, 2000). Solid-liquid separation in the activated sludge system is done by sedimentation of sludge. In SBR procedure, wastewater is stored in the equalization basin, and then conducted into the reactor till reaches the influent time or the highest watermark. Wastewater is treated with batch process; therefore, time-separation is instead of space-separation that is in conventional continuous-flow system. Operationally, there are many phenomena causing the negative effects of sludge sedimentation, include bulking, foaming, floating and so on, result in the bad effluent quality, instability, even can not approach the legal standard



(Visvanathan et al., 1997). Thus, the applications of membrane for filtration were considered potentially useful for the sludge sedimentation in the activated sludge system.

Yamamoto et al. (1989) first addressed the concept of membrane bioreactor (MBR) operation for improvement of conventional activated sludge system. Placing the membrane module to filtrate and draw effluent from the sludge tank. This not only saves the sludge recirculation device and lowers the initial charges for system in conventional secondary treatment plant, but also provides stable and superior treatment quality. MBR system which saves the land and equipment area necessary for the final sedimentation tank is available for countries of the high population density, such as Japan, South Korea and France. MBR system is applied quite extensively in treatment processes of domestic wastewater, municipal sewage, industrial wastewater, dye wastewater and landfill leachate (Kishino et al., 1996; Dijk and Roncken, 1997; Rozzi et al., 1999; Defrance et al., 2000).

Compared with other conventional secondary bioreactors, a reactor with membrane module possesses several advantages:

(1) Complete solid-liquid separation by using membrane filtration can

maintain high biomass in the system (Wen et al., 1999). This will reduce necessary land area for plant and lower the systematic F/M ratio. The number of sludge self-decomposition relatively increase, even needs no sludge withdrawn, can reduce the amount of wasted sludge and save sludge treatment cost (Yamamoto et al., 1989).

(2) High biomass in membrane filtration system can treat high loading wastewaters and receive severe kinds of influent loadings (Ueda and Hata, 1999).

(3) Sludge sedimentation and bulking problem can be neglected due to stability in membrane filtration system; effluent quality from membrane filtration is stable and fine (Visvanathan et al., 1997).

However, membrane filtration will waste plenty of energy in wastewater withdrawing, caused by membrane fouling. Fouling may be the worst problem in membrane filtration process (Bouhabila et al., 2001). It is caused by solutes and biomass attached on membrane surface; when membrane operated for while, it needs to be cleaned or wasted (Chang et al., 2001). Fouling problem increases the operating cost of membrane filtration, but this does not limit the development of MBR, there are more than 500 commercial MBRs in operation worldwide

(Stephenson et al., 2000).

## 2-2-2 Hollow fiber membrane (HFM)

### 2-2-2-1 Porous sizes and materials of HFM

Figure 2-2 represents the standard structure of HFM. The porous sizes of HFM applied in MBR system are ranged from 0.1  $\mu\text{m}$  to 0.4  $\mu\text{m}$  (Stephenson et al., 2000). According to IUPAC (International Union of Pure and Applied Chemistry), membrane can be classified with structure into macropores ( $>50\text{nm}$ ), mesopores (2-50nm), micropores ( $<2\text{nm}$ ) and nonpores. On the other hand, membrane classified according to porous size can be MF (microfiltration, 0.1-2  $\mu\text{m}$ ), UF (ultrafiltration, 0.01-0.1  $\mu\text{m}$ ), NF (nanofiltration, 0.001-0.01  $\mu\text{m}$ ) and RO (reverse osmosis, 0.0001-0.001  $\mu\text{m}$ ). The MF style (large porous size) in HFM is used commonly in wastewater treatment. MF is also suitable for pre-treatment unit of RO and other filtration forms.

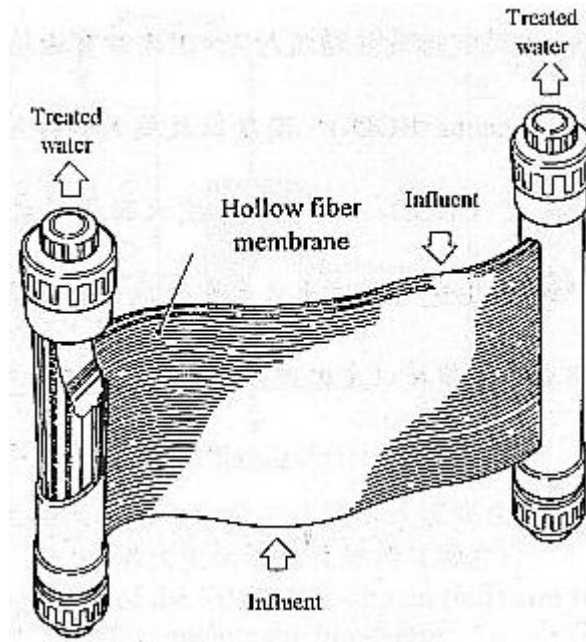


Figure 2-2. Diagram of hollow fiber membrane.  
(Mitsubishi Rayon Co., LTD)

Materials of HFM are classified into 2 major parts: hydrophilic materials, such as PE (polyethylene), PS (polysulphone), PVF (polyvinilydene fluoride) and PA (polyamide); and hydrophobic materials, likes PP (polypropylene). Hydrophilic materials are limited to organic substances and proteins (adsorption of microbes in activated-sludge tank); therefore, this can retard the clogging problem inside the membrane pores. In contrast, hydrophobic materials are not suitable in biological reactors. Hydrophobic materials easily adsorb the organic substances and proteins result in pores clogging (Gander et al., 2000a).

### 2-2-2-2 Clogging problem in membrane filtration

In membrane separation process, the main operational problem is membrane fouling (Ueda et al., 1997). Discussion on membrane fouling usually regards as TMP (Trans-Membrane pressure) and/or flux. HFM must be sited above the aeration equipment for ensuring effluent quality and preventing membrane from fouling to lengthen filter run. The main principle is using upflow air bubbles to crash HFM and remove the granules left near the chink in the membrane fiber during operation. Theoretically, upflow rate on membrane surface must be greater than 40 cm/sec (Figure 2-3). Therefore, aeration can provide dissolved oxygen for activated-sludge in the aerobic biological reactors, and remove sludge pieces which attached on the membrane surface. Thus, system can stabilize the operation, and effectively maintain the trans-membrane pressure and flux to lengthen filter run.

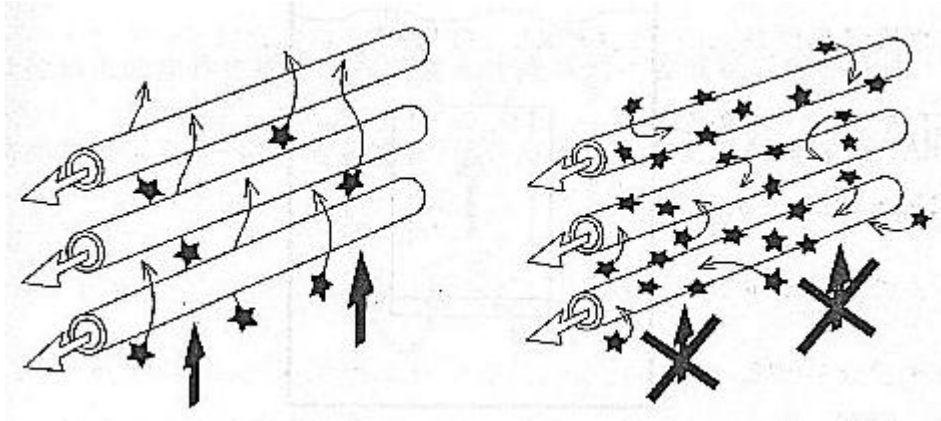


Figure 2-3. Effect of upflow air on hollow fiber membrane washing.  
(Nagaoka et al., 1999)

## **2-3 Online monitoring parameters and Nernst equation modeling**

### 2-3-1 Online monitoring parameters

ORP (Oxidation Reduction Potential) has been proved to be an important environmental factor in secondary wastewater treatment process. ORP provides information of the whole reaction; this can be applied as process control. ORP monitoring technology is stable and commercial, thus, it has been valued gradually.

Burbank (1981) indicated that online ORP monitoring system can provide special information, for example, sudden change of influent quality, toxic substances in wastewater and abnormal conditions in bioreactors. Study from Peddie et al. (1990) represented that ORP in oxic system is correlated linearly with logarithm of DO concentration. ORP is a very sensitive monitoring indicator in low DO conditions. The major reason for Peddie et al. also consider ORP as a control parameter in wastewater treatment is ORP can reflect certain phenomena in systems, including electronic activity, chemical composition, microbial activity, pH, temperature and so on.

ORP, pH and DO monitoring patterns can successfully identify end points of reactions in a wastewater treatment (Kishida et al., 2003).

“Nitrogen break point” in ORP profiles, “ammonia valley” in pH profiles and “DO elbow” can indicate the end point of nitrification; while “nitrate knee” in ORP profiles and “nitrate apex” in pH profiles which point out the end of denitrification. The flexible hydraulic retention time (HRT) from each period could be obtained with these control points; stable removal rate of nitrogen and energy saving were achieved using a real-time control strategy. Using ORP as a controlling parameter have several advantages: (1) to obtain the certain end-point of reaction; (2) to be a controlling parameter of a complicated reaction; (3) to attain the optimal operating point to save cost and energy; (4) to improve treatment efficiency and effluent water quality (Chang and Hao, 1996; Zipper et al., 1998; Khanal and Huang, 2003).

### 2-3-2 Nernst equation modeling

Chang et al. (2004) addressed that the Nernst Equation can be successfully applied to the nitrification and denitrification; there is a relation exists between ORP and nitrogen compound. A normal oxidation-reduction reaction can be expressed as Eq. (1).





where A and B are reactants; C and D are products; a-d are the stoichiometric coefficients for A-D, respectively. The Nernst Equation can be described as:

$$E = E_0 + \frac{RT}{nF} \times \ln\left(\frac{(A^a)(B^b)}{(C^c)(D^d)}\right) \quad \text{Eq. (2)}$$

E = ORP (mV);  $E_0$  = standard redox potential (mV); R = gas constant (8.314 Jmol<sup>-1</sup>K<sup>-1</sup>); T = absolute temperature (K); n = number of electron transferred during oxidation-reduction reaction; F = Faraday constant (96,500 Cmol<sup>-1</sup>). They have reported that the Nernst Equation can be used to describe the relationship of ORP and nitrogen compounds in the nitrification and denitrification. The conversion of NH<sub>4</sub><sup>+</sup> to NO<sub>3</sub><sup>-</sup> is represented by the following chemical equation:

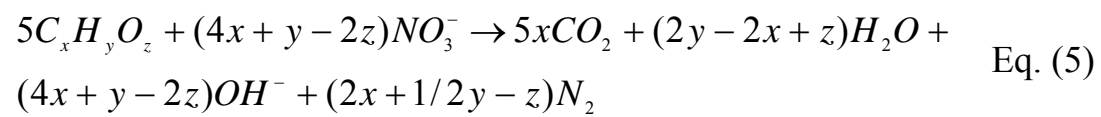


The Nernst equation of nitrification was expressed as follows (Chang et

al., 2004):

$$E = a' + b' pH + c' \log\left(\frac{[NH_4^+]}{[NO_3^-]}\right) \quad \text{Eq. (4)}$$

Biological denitrification for conversion of nitrate to nitrogen gas under anoxic conditions is heterotrophic and is expressed by the following stoichiometric equation:



The Nernst equation of denitrification was expressed as:

$$E = a'' + b'' pH + c'' \log([NO_3^-]) \quad \text{Eq. (6)}$$

## 2-4 Objectives

According to the literatures mentioned, SND phenomenon may be occurred in SBMBR system if the operating conditions are feasible.

However, the feasibility of the SBMBR effluent as recycle water should be focused on. The objectives in this study can be described as follows:

1. To investigate SND phenomenon in SBMBR system under different C/N ratios and DO levels with SND efficiency and  $R_{SND}$ .
2. To discover the feasibility of real-time control strategies and apply Nernst equation to fit the dynamic profiles of SND process.
3. To discuss the feasibility of SBMBR effluent as recycle water. The membrane operating data is also be studied for analyze the fouling problems in different SBMBR systems.

## Chapter 3 Experimental methods and equipment

### 3-1 Experimental equipment and monitoring systems in SBMBR

#### 3-1-1 Experimental equipment

(1) The reactor is square-shaped and made of acrylic fiber.

Working height of the reactor is 60.0 cm; internal diameters are 24.0 cm × 24.0 cm and with a working volume of 35.0 L.

(2) Hollow fiber membranes are made by Mitsubishi Rayon Co., LTD. The membrane properties are listed in Table 3-1.

Table 3-1. The properties of hollow fiber membranes

Type	UMF0234LI
Material	polyethylene (PE)
Filtration area	0.2 m <sup>2</sup>
Porous size	0.4 μm
Suitable flow rate	40 L/day
Initial operating pressure	<10 kPa

(3) Stirrer: Oriental Motor, Japan, operated at 150 rpm.

(4) Aeration pump: Serial No. 1030114, Medo Co., Japan. Air flow rate is 14.0 L/min.

(5) Peristaltic pump: Masterflex, Peristaltic pump, System Model No. 7533-80, Cole-Parmer, USA.

(6) Teflon duct: Reorder#06409-15, Cole-Parmer, USA

### 3-1-2 Monitoring systems

- (1) pH: pH controller (Suntex PC-310, Taiwan, ROC) equipped with glass membrane electrode (Mettler-Toledo, Switzerland) and is calibrated with pH 4.0 and pH 7.0 standard solution.
- (2) ORP: ORP controller (Suntex PC-310, Taiwan, ROC) equipped with ORP electrode (composed of platinum indication electrode and reference electrode, Mettler-Toledo, Switzerland) is corrected with zero-point (0 mV) and 220 mV standard solution.
- (3) DO: microprocessor DO controller (Suntex DC-5100) equipped with WTW TriOxmatic 690 DO electrode (Germany) is calibrated with internal aero-correction process.
- (4) Computerized monitoring and controlling system: P II 266 computer (Microsoft OS Windows 2000); LabVIEW (Laboratory Virtual Instrument Engineering Workbench) monitor software and AD/DA card (AT-MIO-16E-10).

## 3-2 SBMBR system and operation

### 3-2-1 Synthetic stock feed

In this study, synthetic wastewater was introduced into the SBMBR to simulate the domestic wastewater. The composition of the stock solution is shown in Table 3-1. Each chemical was weighted and mixed in a 5-L beaker. There was no pH adjustment for the synthetic stock feed due to the final pH was 7.1-7.3. Then this stock solution was preserved in a 4°C refrigerator; each month mixed once. The influent was made by adding 70 mL stock solution into 17.5 L underground water, and the influent quality was shown in Table 3-2.

Table 3-2. Composition of the synthetic stock feed in Run 1 (C/N = 8.0) and Run 2 (C/N = 11.0).

Drug	Dose (in 3 L distilled water)
KH <sub>2</sub> PO <sub>4</sub>	40 g
Glucose	18 g
Peptone	9 g
Urea	60 g
NH <sub>4</sub> Cl	Run 1: 150 g Run 2: 100 g
Full-fat milk powder*	150 g
Low-fat milk powder*	122 g
FeCl <sub>3</sub> (10%)	2 mL
CH <sub>3</sub> COOOH (99.8%)	58 mL
NaHCO <sub>3</sub>	256 g

\* Nutrients of full and low fat milk powder contain: Protein = 26.5%; Lactose = 36.8%; Minerals = 5.7%; Fat = 28%; Water content = 3%

Table 3-3. Characteristics of the synthetic influent in Run 1 (C/N = 8.0) and Run 2 (C/N = 11.0).

Items	Average (mg/L)	SD	n**
Total COD	410.7	8.7	10
Soluble COD*	301.5	7.6	10
Alkalinity	433.4	10.3	7
TKN	Run 1: 64.8	Run 1: 3.3	3
	Run 2: 49.6	Run 2: 2.1	
NH <sub>4</sub> -N	Run 1: 51.1	Run 1: 2.6	8
	Run 2: 37.4	Run 2: 1.5	
NO <sub>x</sub> -N	ND	-	10
PO <sub>4</sub> -P	37.5	3.2	10
pH	7.2	0.1	12

ND: not detectable; \* filtered with 0.45 µm filter; \*\* number of analysis

### 3-2-2 System operation procedure

Two pilot-scale sequencing batch membrane bioreactors (SBMBR) which contained 35.0 L effective working volume were operated as shown in Figure 3-1. The two SBMBRs were differentiated with various airflow rates during oxic stage: SBMBR1 was with high airflow rate (high DO case, 14.0 L/min, i.e. DO = 3-4 mg/L), while SBMBR2 was with low airflow rate (low DO case, 1.4 L/min, i.e. DO = 0-1 mg/L). Biomass was enriched in an anoxic-oxic (AO) sequence. The two pilot-scale SBMBR was operated with a cycle time of 12 h in an air-conditioned room (temperature kept at room temperature, i.e. about

25°C). Each cycle consisted of a 1-h anoxic stage and an 8-h oxic stage (high and low airflow rate), followed by a 3-h drawing (suction and aeration) stage (Table 3-3). Each stage has different function for C, N, and P removal. Their characteristics are summarized in Table 3-4. The ORP, pH, and DO were continuously monitored and recorded by LabView program. The hydraulic retention time (HRT) was set at 1 day (two cycles per day) and the water temperature was maintained at room temperature. Characteristics of the synthetic influent are shown in Table 3-2, while the operating conditions (Run 1 and Run 2) are shown in Table 3-3. Mixed liquor suspended solid (MLSS) kept at 5,041±364 mg/L by withdrawing sludge regularly. SND efficiency was calculated with Eq. (7), expresses as follows (Zeng et al., 2003):

$$\text{Efficiency}_{\text{SND}} = \frac{\text{Denitrification}}{\text{Nitrification}} = \frac{\text{NH}_4(\text{tot})^* - \text{NO}_x(\text{acc})^*}{\text{NH}_4(\text{tot})^*} \dots\dots\dots\text{Eq. (7)}$$

where  $\text{NH}_4(\text{tot})^*$  is the influent concentration of  $\text{NH}_4\text{-N}$ ;  $\text{NO}_x(\text{acc})^*$  is the effluent concentration of  $\text{NO}_x\text{-N}$ . The rate of SND was calculated as the amount of  $\text{NO}_x$  simultaneously denitrified by the end of the  $\text{NH}_4$  oxidation period, divided by the length of time required to remove all



ammonium (hours). This was addressed by Third et al. (2003), and expressed as follows: (the unit of  $R_{SND}$  is  $\text{mg N/L}\cdot\text{hr}$  in this study)

$$R_{SND}(\text{mmol} \cdot \text{L}^{-1} \cdot \text{h}^{-1}) = \frac{NH_4^+ \text{ oxidised} - NO_x^- \text{ produced (mM)}}{\text{time(h)}} \dots\dots\dots\text{Eq. (8)}$$

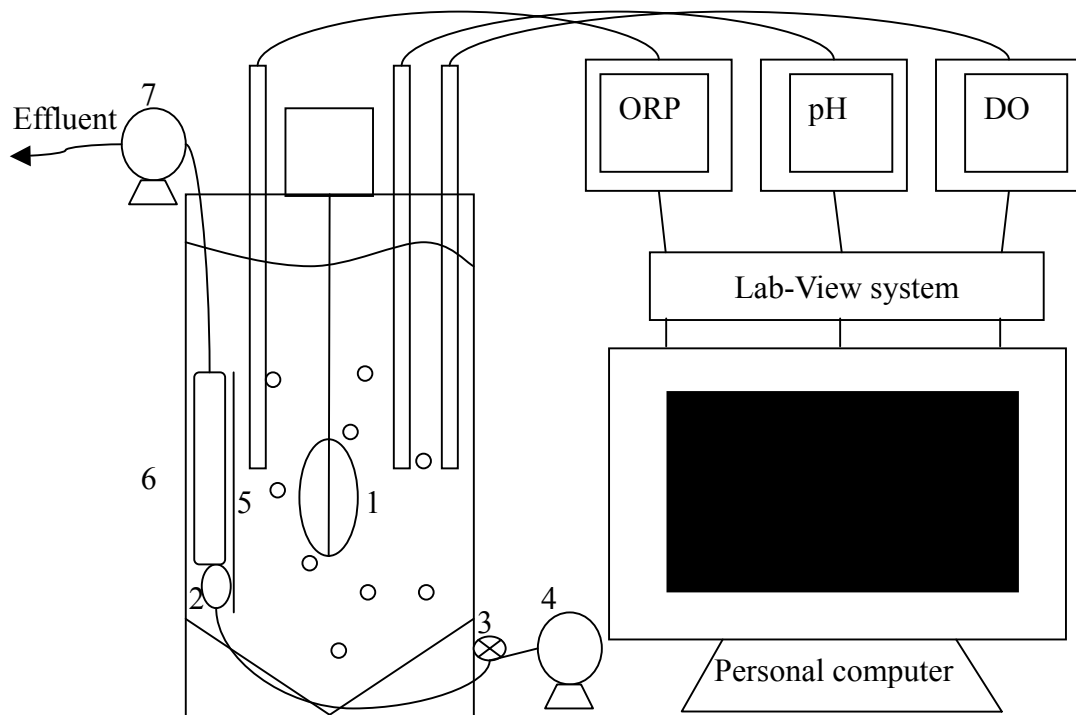


Figure 3-1. Schematic diagram of SBMBR is set with fixed time operation. 1. stirrer; 2. aeration stone; 3. valve; 4. aeration pump; 5. porous plat; 6. hollow fiber membrane; 7. peristaltic pump.

Table 3-4. Operating conditions of SBMBR1 (high airflow rate, 14.0 L/min) and SBMBR2 (low airflow rate, 1.4 L/min).

Parameters	Run 1	Run 2
Anoxic stage		1 hr
Oxic stage		8 hr
Drawing stage		3 hr
Working volume		35.0 L
HRT		1 day
SRT		60 days (SBMBR1) 180 days (SBMBR2)
MLSS		5,041±364 mg/L
Biomass yield		97 mg/L·day (SBMBR1)
(as MLSS)		38 mg/L·day (SBMBR2)
Temperature		Room temperature
TCOD/NH <sub>4</sub> <sup>+</sup> -N ratio	8.0	11.0

Table 3-5. Characteristics of each operation stages.

Stage	Function
Anoxic	<ol style="list-style-type: none"> <li>1. Organic nitrogen decomposes to ammonia.</li> <li>2. PAOs uptake short-chain volatile fatty acids (VFAs) and release <i>o</i>-phosphate.</li> <li>3. Control sludge bulking problem.</li> </ol>
Oxic (high DO case)	<ol style="list-style-type: none"> <li>1. Activated sludge uses oxygen as an electron acceptor to proceed with oxidation and reach the C removal.</li> <li>2. <b>Nitrifiers use oxygen as an electron acceptor to proceed with nitrification; ammonia transforms to nitrite and nitrate. Denitrifiers may not activate in this absolute oxic stage</b></li> <li>3. PAOs uptake <i>o</i>-phosphate; P removal was completed with sludge withdraw.</li> </ol>
Oxic (low DO case)	<ol style="list-style-type: none"> <li>1. Activated sludge uses oxygen as an electron acceptor to proceed with oxidation and reach the C removal.</li> <li>2. <b>Low airflow rate makes the reactor to form a deficient DO condition that favors both nitrification and denitrification.</b></li> <li>3. PAOs uptake <i>o</i>-phosphate; P removal was completed with sludge withdraw.</li> </ol>
Drawing	Permeate was drawn with continuous suction; sustained aeration is for lower membrane clogging.

### 3-3 Analytical methods

Parameters routinely assayed with various items (Table 3-5).

Table 3-5 lists the analysis methods that were performed in accordance with standard methods 20<sup>th</sup> edition (APHA et al., 1998). Mixed-liquor samples were collected each 30 min and centrifuged at 3,500 rpm, then filtered by 0.45 $\mu$ m glass fiber membrane filter. Treated samples were preserved at 4°C and analyzed within 7 days.

Table 3-6. Analysis methods and instruments

Item	Analysis methods and instruments
ORP	ORP meter, Method 2580 B* (Suntex PC-310)
pH	pH meter, Method 4500-H <sup>+</sup> B* (Suntex PC-310)
DO	DO meter, Method 4500-O G* (Suntex DC-5100)
COD	Method 5220 B*
NH <sub>4</sub> -N	Method 4500-NH <sub>3</sub> F*
TKN	Method 4500-N <sub>org</sub> C*
NO <sub>3</sub> -N	Pump: L-7110, column oven: L-7300 and conductivity
NO <sub>2</sub> -N	detector: L-7470, Hitachi Co., Tokyo, Japan, Method 4110*
PO <sub>4</sub> -P	Method 4500-P D*
Alkalinity	Method 2320*
MLSS	Method 2540 D*
MLVSS	Method 2540 E*
Turbidity	Method 2130 B*
Total coliform	Method 9222 B*

\* Standard Methods for the Examination of Water and Wastewater 20<sup>th</sup> Edition (APHA et al., 1998)

## Chapter 4 Results and discussion

### 4-1 SND phenomenon in SBMBR system

In this study, different C/N ratios (8.0 and 11.0) and different airflow rates (14.0 and 1.4 L/min) were discussed. Biomass in each SBMBR was maintained at  $5,041 \pm 364$  mg/L as MLSS. ORP, pH and DO are well-known online monitoring parameters to indicate the endpoints of conventional biological nitrogen removal process (Kishida et al., 2003). In this study, these monitoring parameters were adapted to explain the phenomenon of SND.

#### 4-1-1 SND phenomenon

##### 4-1-1-1 System with limited carbon case: Run 1 (C/N = 8.0)

Figure 4-1 shows the profiles under the condition of high airflow rate (14.0 L/min, i.e. DO = 3-4 mg/L, SBMBR1) and low C/N ratio (8.0, Run 1), in which effluent nitrate was found to be 21 mg/L. High airflow rate is good for ammonia removal; however, denitrification will be inhibited, i.e. SND reaction is incomplete. C/N ratio for denitrification ( $\text{TCOD}/\text{NO}_x\text{-N}$ ) is calculated with influent ammonia concentration subtracts effluent nitrate concentration. Thus,

TCOD/NO<sub>x</sub>-N ratio was 13.6 in this condition. Nitrate accumulated at the end of the batch test and implied SND reaction did not accomplish. Lack of carbon source and too high a DO concentration were thought to be the possible factors which inhibited SND reaction and caused nitrate accumulation (Keller et al., 1997). Online monitoring parameters are shown in Figure 4-1(a). In the ORP profile, it increased gradually in the oxic stage and then the curve kept at steady after 360 min (Figure 4-1(a)). This indicated that ammonia was almost kept unchanged with 5 mg/L till the end (Figure 4-1(b)). While pH increased during pre-anoxic stage and slightly dropped hereafter. When nitrification ceased (240 min), pH decreased sharply, and then kept in a constant level of 4.5. DO kept at zero from 60- to 240-min, when ammonia was depleted at 240 min, DO raised to a peak level of 3.5 mg/L. While ORP, pH and DO showed a strong correlation with ammonia decomposition, the characteristics of key control points of SCOD and nitrate profile from ORP, pH and DO did not appear in Figure 4-1(b). SCOD decreased slightly after rapid drop at the beginning; then it kept below 20 mg/L till the end. Nitrite and nitrate accumulated at the beginning of the oxic stage, and finally nitrate accumulated to about 21

mg/L in the effluent. Mass nitrate accumulation might be due to lack of carbon source (i.e. low C/N ratio) and excess DO concentration (Keller et al., 1997).

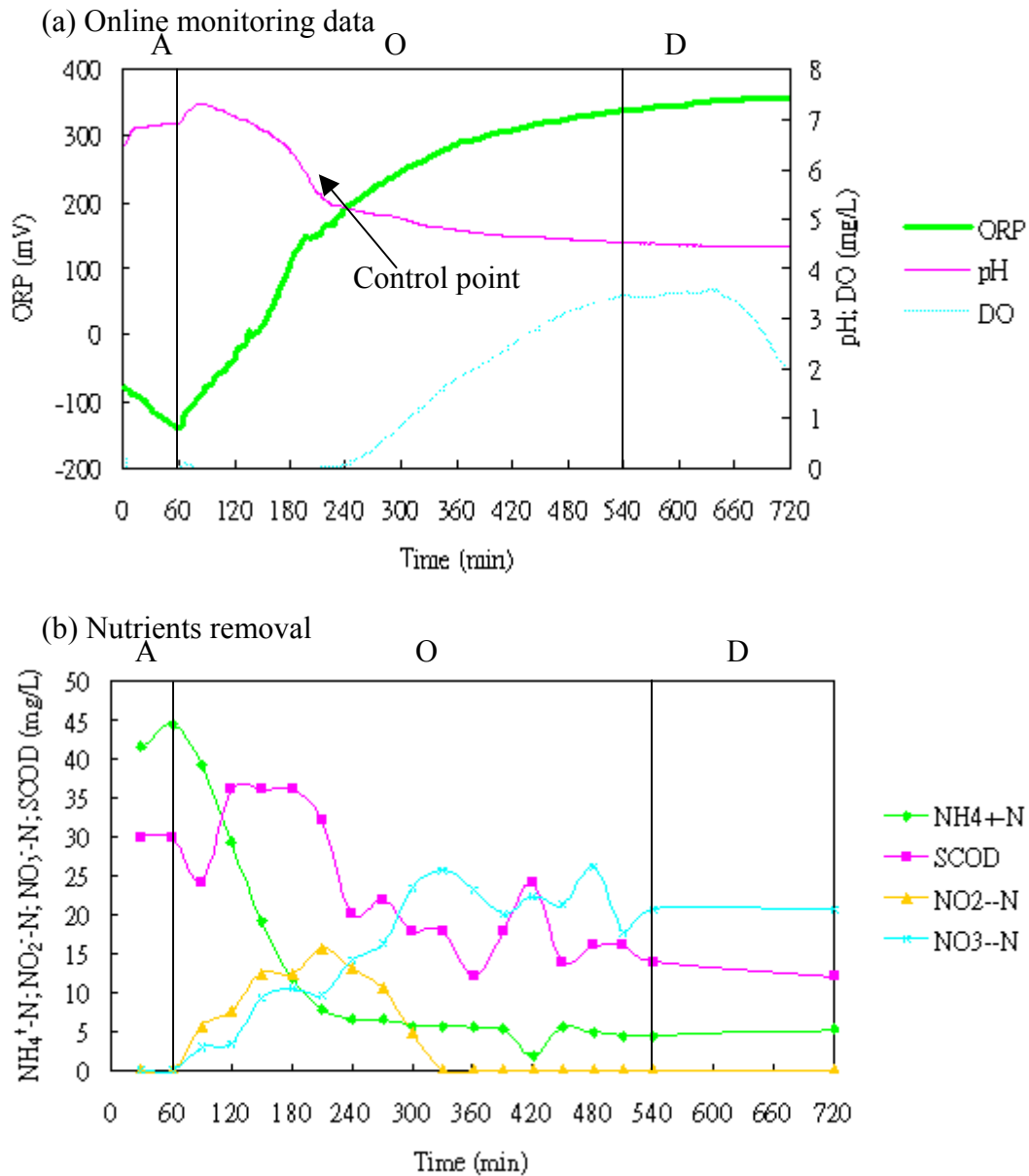


Figure 4-1. (a) Online monitoring parameters: ORP, pH and DO; (b)  $\text{NH}_4^+\text{-N}$ ,  $\text{NO}_x\text{-N}$  and SCOD profiles of SBMBR1 (airflow rate = 14.0 L/min) in Run 1 (C/N = 8.0). A: anoxic stage; O: oxic stage; D: drawing stage.

Figure 4-2 shows the substrate and monitored factors profiles under the condition of low airflow rate (1.4 L/min, i.e. DO = 0-1 mg/L, SBMBR2) and low C/N ratio (8.0, Run 1), in which effluent nitrate was found to be 13 mg/L. TCOD/NO<sub>x</sub>-N ratio was 10.9 in this condition. With lower C/N ratio (8.0), denitrification was inhibited as a result of nitrate accumulation, although the DO levels were low. In the ORP profile, ORP increased gradually to 0 mV until reached 420-min and then it jumped rapidly to 150 mV in 60 min in Figure 4-2(a). The breakpoint of ORP profile at 450-min indicated ammonia was almost exhausted entirely (Figure 4-2(b) of NH<sub>4</sub><sup>+</sup>-N). The pH increased at the anoxic and initial oxic stage (480 min), and then dropped at the later oxic stage to the level of 4.8 mg/L. DO remained the low level close to zero till ammonia was depleted at 420 min. SCOD of entire batch test was relatively low at the range of 10-30 mg/L as shown in Figure 4-2(b). Stevens et al. (1999) cited that some residual carbon stored in the bacteria may remain available for denitrification or other biological activities. The bulk SCOD concentration is low, i.e. the denitrification activity due to lack of carbon source, can not achieve completely. Nitrate accumulated since 300-min and lasted to the end of about 13



mg/L in the effluent. Nitrate accumulation was thought to be the lack of carbon source and brought incomplete denitrification thereafter.

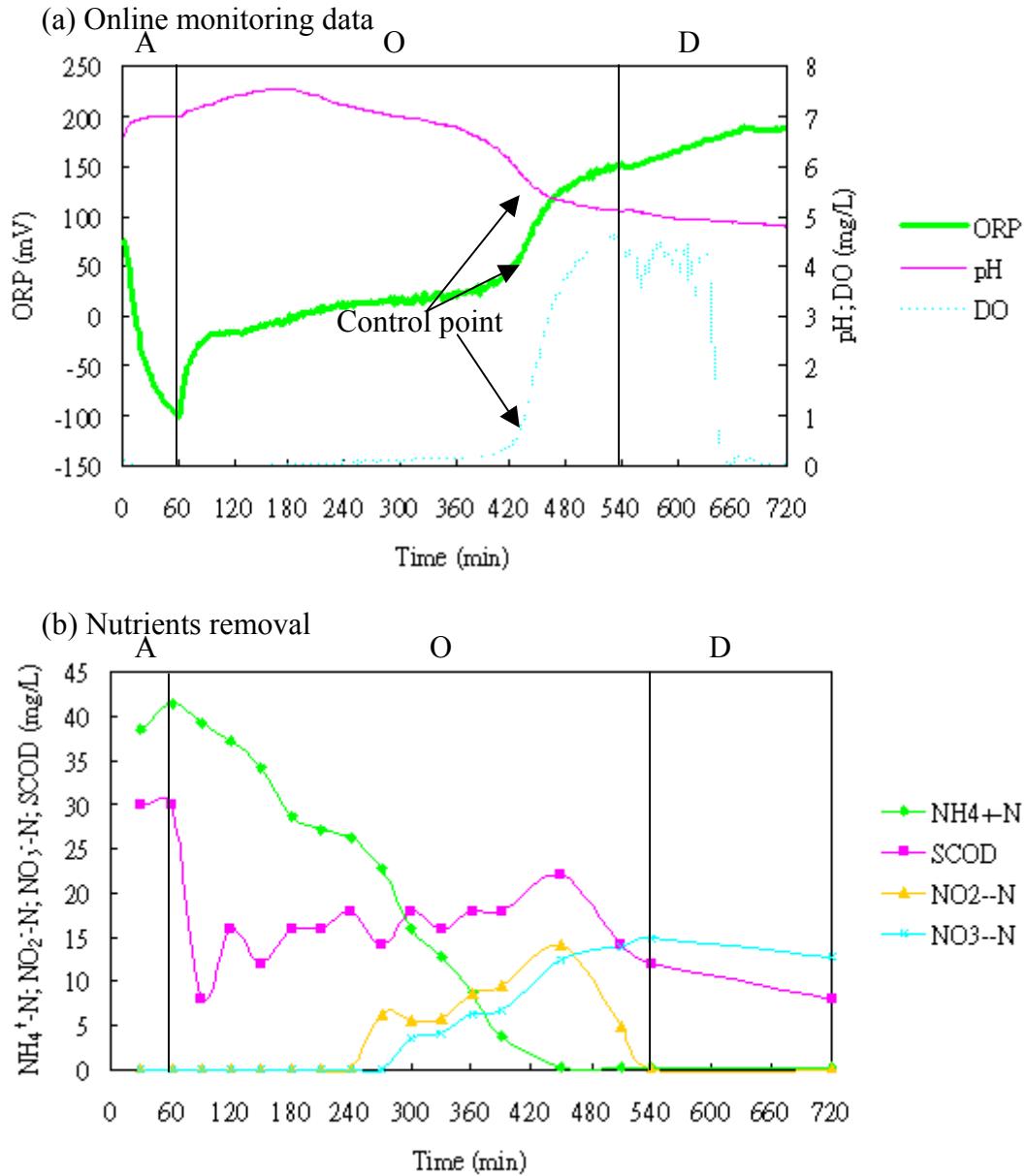


Figure 4-2. (a) Online monitoring parameters: ORP, pH and DO; (b)  $\text{NH}_4^+$ -N,  $\text{NO}_x$ -N and SCOD profiles of SBMBR2 (airflow rate = 1.4 L/min) in Run 1 (C/N = 8.0). A: anoxic stage; O: oxic stage; D: drawing stage.

#### 4-1-1-2 System with excess carbon case: Run 2 (C/N = 11.0)

Figure 4-3 shows the profiles under the condition of high airflow rate (14.0 L/min, i.e. DO = 3-4 mg/L, SBMBR1) and high C/N ratio (11.0, Run 2), in which both ammonia and nitrate were accumulated slightly but less than those in Run 1 (C/N = 8.0). The effluent concentrations of ammonia and nitrate were approximately 0 and 13 mg/L, respectively. TCOD/NO<sub>x</sub>-N ratio was 16.1 in this condition. Because influent ammonia concentration in Run 2 was lower than that in Run 1 (Run 1 : Run 2 = 51.1 : 37.4), the nitrification rate in Run 2 is much faster. ORP increased from -80 mV to 150 mV then kept at stable to the end in Figure 4-3(a). Compared to Figure 4-1(a) (C/N = 8.0 and high airflow rate), the breakpoint of ORP at 240-min indicated that ammonia was almost depleted. The pH increased slightly from 7.0 to 7.5 during anoxic period, then dropped slowly to 6.5 to the end. DO value raised from the beginning of aeration to a large extent of 7.1 mg/L.

Nitrate build-up occurred during the period of 150- to 720-min; this indicated the activity of denitrification was inhibited by the excess level of DO condition (Figure 4-3(b)). Nitrification ended at 240-min due to

the depletion of ammonia. Effluent SCOD was diminished to below 10 mg/L; this showed that there was some non-biodegradable COD left in this system. Nitrate started to accumulate since 150-min and to an extent of 10 mg/L till the end. In Figure 4-3(b), the amount of nitrate accumulation (10 mg/L) reduced to one-half of that in Figure 4-1(b) (21 mg/L), this indicated that lack of carbon source ( $C/N = 8.0$ ) could be a critical problem for the inhibition of denitrification in SND reaction.

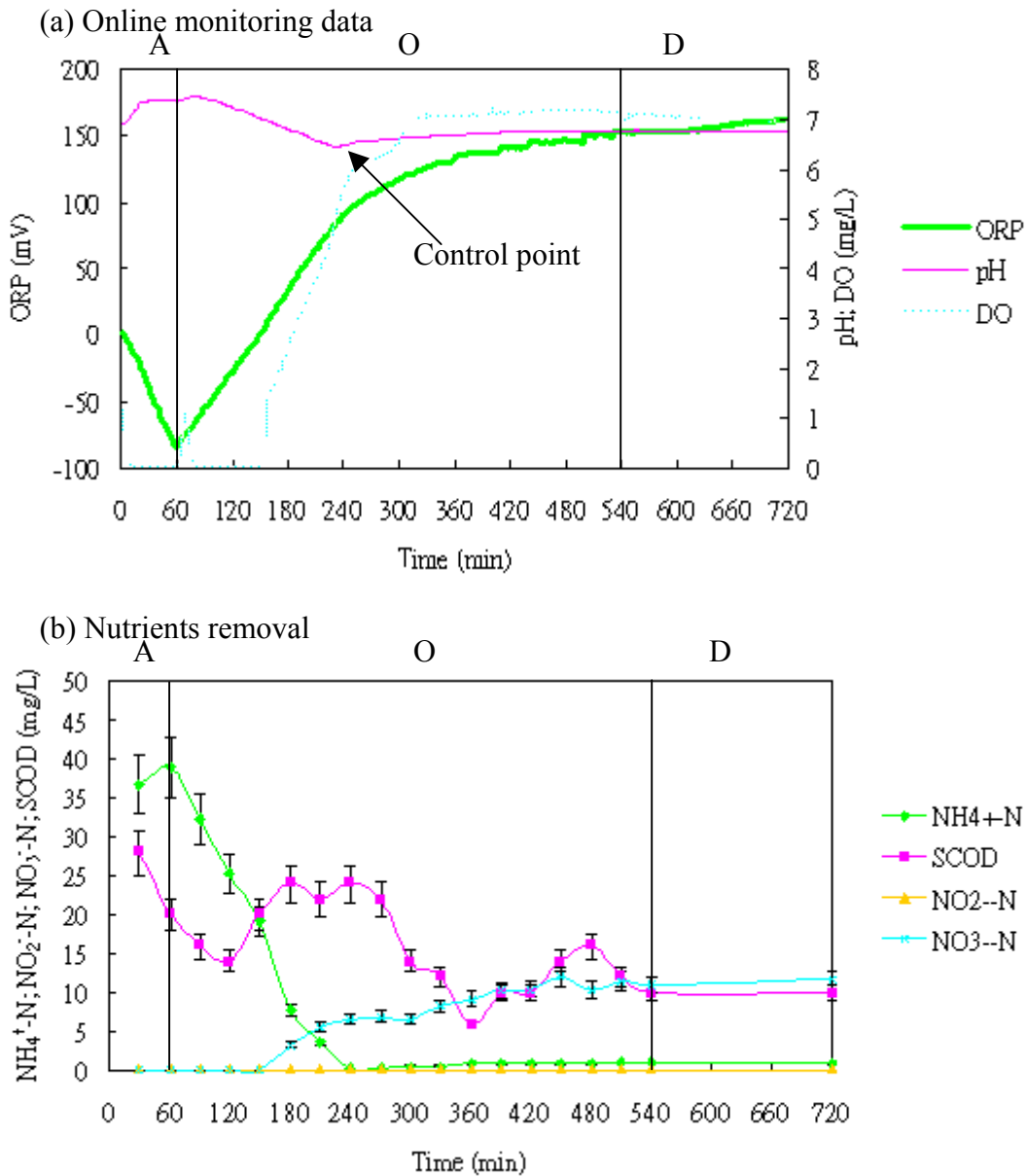


Figure 4-3. Triplicate tests of (a) Online monitoring parameters: ORP, pH and DO; (b)  $\text{NH}_4^+\text{-N}$ ,  $\text{NO}_x\text{-N}$  and SCOD profiles of SBMBR1 (airflow rate = 14.0 L/min) in Run 2 (C/N = 11.0). A: anoxic stage; O: oxic stage; D: drawing stage. A: anoxic stage; O: oxic stage; D: drawing stage.

Figure 4-4 shows the profiles under the condition of low airflow rate (1.4 L/min, i.e. DO = 0-1 mg/L, SBMBR2) and high C/N ratio (11.0, Run 2). The results implied both ammonia and nitrate were negligible

in this system. The effluent concentrations of ammonia and nitrate were approximately 1.8 and 2.0 mg/L, respectively. TCOD/NO<sub>x</sub>-N ratio was 11.6 in this condition. Since there was nitrate accumulating to a limit extent, the effect of SND phenomenon was found significantly. ORP increased slowly from -120 mV to 0 mV then a breakpoint was found at 480-min as shown in Figure 4-4(a). As for pH, the curve increased slightly from 7.0 to 7.8, and then dropped slowly to 7.0. At 480-min, there was a bending point of pH profile, it is similar to the “ammonia valley” proposed by Al-Ghusain et al. (1994). It is interesting when aeration was proceeding and the pH was still going up. It rose from 7.0 to 7.3 within the time between 480- and 540-min. Neither nitrification nor denitrification activity was found accomplished after the pH bending point occurred at 480-min. DO was kept below 1 mg/L from 60- to 480-min. When ammonia was depleted, DO was raised to an extreme level of 7 mg/L immediately.

Denitrification activity would replenish alkalinity, which was consumed by nitrification activity during oxic stage. Thus, the depletion of alkalinity in SND process is milder than that in conventional nitrification and denitrification process (Gupta, 1997).

Very limit amount of nitrate build-up occurred after 300-min; it indicated the activity of denitrification was slightly inhibited by the lack of carbon source. From literature, the effectiveness of the denitrification process decreases when DO concentrations above 0.2 mg/L (Pochana and Keller, 1999). Nitrification ended at 480-min, when there was still a small amount of ammonia left in the system in Figure 4-4(b) (<1 mg/L). This may be due to organic nitrogen decomposed to ammonia under deficient DO condition (Al-Ghusain et al., 2002). Low-DO aeration provides insufficient oxygen concentrations that favor simultaneous nitrification and denitrification (SND). The system with excess carbon (i.e. C/N = 11.0), which provides enough electron to conduct SND reaction and has a residual SCOD below 20 mg/L left in solution. In Figure 4-4(b), the amount of nitrate accumulation (2 mg/L) reduced to one-fifth of that in Figure 4-2(b) (10 mg/L); this strongly indicated that lack of carbon source could be a critical problem for the SND phenomenon.

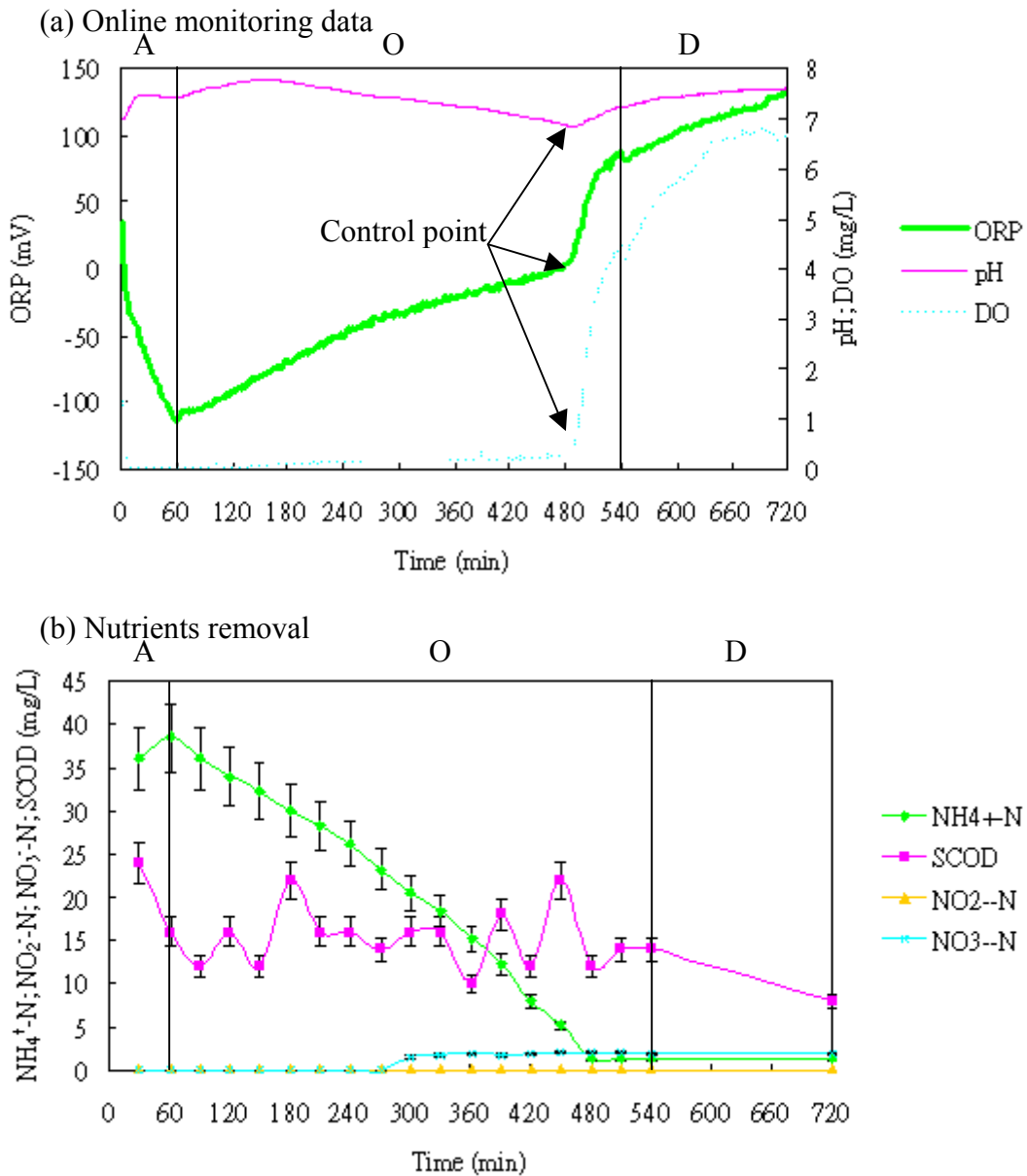


Figure 4-4. Triplicate tests of (a) Online monitoring parameters: ORP, pH and DO; (b)  $\text{NH}_4^+\text{-N}$ ,  $\text{NO}_x\text{-N}$  and SCOD profiles of SBMBR2 (airflow rate = 1.4 L/min) in Run 2 (C/N = 11.0). A: anoxic stage; O: oxic stage; D: drawing stage.

#### 4-1-2 The alkalinity profiles in SND process

Carbonaceous alkalinity, can be used as inorganic carbon source for nitrification and buffer in the bulk solution, is an important substance in

the nitrification process. This section compares the cases of low and high DO levels on the SND reaction in Run 2, i.e. excess carbon source (C/N = 11.0). A reactor that performs SND phenomenon should require less alkalinity as buffer quantity than conventional two-steps nitrification and denitrification reaction. In SND process, alkalinity generated during denitrification can partially be recovered for that depleted in nitrification (Gupta, 1997). Figure 4-5 represents the typical alkalinity profile for both low and high DO levels in Run 2 (C/N = 11.0). Higher DO levels in SBMBR1 resulted in an inhibition of denitrification, thus great loss of alkalinity (600 mg/L, without recovery) occurred. In contrast, the low DO levels provided the sufficient anoxic zones to enhance comprehensive denitrification, therefore, the alkalinity dropped for 500 mg/L only due to partial recovery in the SND system.



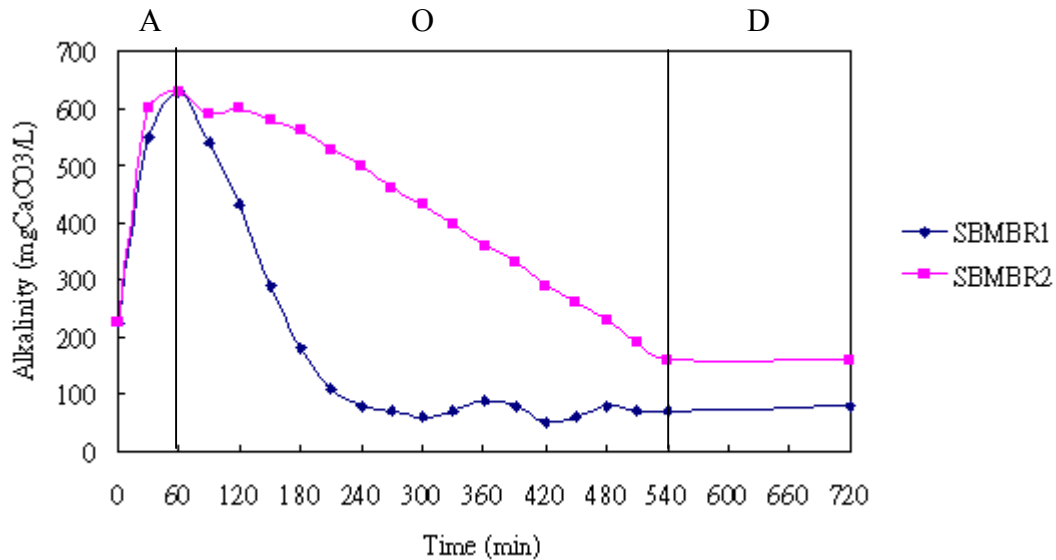


Figure 4-5. Typical changes of alkalinity of SBMBR1 (high airflow rate) and SBMBR2 (low airflow rate) systems in Run 2 (C/N = 11.0). A: anoxic stage; O: oxic stage; D: drawing stage.

#### 4-1-3 System performance

In low C/N ratio in Run 1 (8.0) may not provide sufficient carbon source and inhibit denitrification. Although the low DO aeration in oxic stage provided a favorable condition for denitrification, yet insufficient carbon source caused nitrate and/or nitrite accumulate under low DO and/or low C/N ratio cases (Figure 4-1(b), 4-3(b)). In contrast, Run 2 had a higher C/N ratio (11.0) with excess carbon source, thus, very little nitrate was observed to accumulate under low airflow rate and high C/N ratio case (Figure 4-4(b)).

Table 4-1 shows the effluent quality under C/N ratios (8.0 and 11.0)

and airflow rates (14.0 and 1.4 L/min). Low DO case (SBMBR2) is always more stable than high DO case (SBMBR1), in addition, better effluent quality was observed in low DO case (SBMBR2). Higher residual alkalinity left in effluent helped to explain the SND phenomenon of low DO case (SBMBR2) in Run 2 (C/N = 11.0). However, the final removal rate can achieve at high levels (above 90%). In limited carbon case (Run 1, C/N = 8.0), the removal ratios of COD and ammonia in high DO case (SBMBR1) are 95.6% and 90.6%, respectively; while those in low DO case (SBMBR2) are 96.9% and 99.5%. On the other hand, in excess carbon case (Run 2, C/N = 11.0), the average (triplicate tests) removal rates of COD and ammonia in high DO case (SBMBR1) are 96.3% and 98.0%, respectively; while those in low DO case (SBMBR2) system are 97.0% and 96.6%

Table 4-1. Effluent qualities and removal ratios under various operating conditions.

	Run 1 (C/N = 8.0)		Run 2 (C/N = 11.0)	
	High DO (SBMBR1)	Low DO (SBMBR2)	High DO (SBMBR1)	Low DO (SBMBR2)
SCOD*	14	10	10-12	8-12
Alkalinity*	40	60	60-80	140-180
NH <sub>4</sub> -N*	6	2	1-2	2-3
NO <sub>3</sub> -N*	21	13	6-12	1-3
Removal ratio (SCOD)	95.6%	96.9%	96.3% (averaged)	97.0% (averaged)
Removal ratio (NH <sub>4</sub> -N)	90.6%	99.5%	98.0% (averaged)	96.6% (averaged)

\* expressed as mg/L; high DO = 3-4 mg/L; low DO = 0-1 mg/L.

The difference between various operating conditions can be easily found in Table 4-2. Increasing C/N ratio can enhance SND efficiency and rate, no matter how high the DO level is, however, the improvement of SND efficiency in low DO case (SBMBR2) was much better than that in high DO case (SBMBR1). SND efficiency and rate of low DO case (SBMBR2) in Run 2 (C/N = 11.0) are the highest due to no nitrate and/or nitrite accumulation; these are similar to the data proposed by Zeng et al. (2003). Data from Yoo et al. (1999) showed a higher reaction rate of 6.6 mg N/L·hr within relatively short hydraulic retention time (HRT). Interestingly, SND efficiency of high DO case (SBMBR1) in Run 2 (C/N = 11.0) can be improved to a level as similar as that of

low DO case (SBMBR2) in Run 1 (C/N =8.0) by increasing C/N ratio.

Table 4-2. SND efficiencies and rates under various operating conditions. Compared to other studies for influent ammonia concentration of about 40 mg/L (C/N = 10.0).

	Run 1 (C/N = 8.0)		Run 2 (C/N = 11.0)		Zeng et al., 2003	Yoo et al., 1999
	SBMBR1	SBMBR2	SBMBR1	SBMBR2		
SND efficiency	59.0%	75.2%	68.2%	94.9%	98%	95%
$R_{SND}$	2.3	3.6	3.1	4.2	4.15	6.6

$R_{SND}$  expressed as mg N/L·hr; SBMBR1 and SBMBR2 are high and low airflow rate, respectively.

## **4-2 Real-time control strategies and modeling**

ORP, pH and DO profiles in each operating conditions are shown in from Figure 4-1(a) to Figure 4-4(a). This study focus on online monitoring parameters in each stage (anoxic, oxic and drawing) of SBMBR system to find out real-time control strategies and feasible model.

### 4-2-1 Real-time control strategies

#### 4-2-1-1 ORP profile

ORP change is associated with species, chemical concentrations and reaction temperature, which are participate in the redox reaction. Among these factors, species and concentration are the major concerns. DO have the highest reduction potential among all the electron accepters, therefore, DO affect ORP the most. Aeration stop or DO levels decrement will cause the drop of ORP, and the system is toward to a reductive state. At the beginning of anoxic stage, ORP drop quickly, and then tend to change gently; at the end of anaerobic stage, ORP drop below -100 mV. When the system reaction tranferes into aerobic stage, ORP curve rises sharply at the beginning, and then tend to change gently.

ORP are all beyond 100 mV in the condition of high airflow rate (14.0 L/min, i.e. DO = 3-4 mg/L, SBMBR1), while below 100 mV in the condition of low airflow rate (1.4 L/min, i.e. DO = 0-1 mg/L, SBMBR2). Real-time control strategies based on ORP breakpoint at each stage in Run 2 (C/N = 11.0) are listed in Table 4-3.

Table 4-3. Real-time control strategies of ORP (breakpoints) at each batch operation stage of high DO (SBMBR1) and low DO case (SBMBR2) in Run 2 (C/N = 11.0).

Stage	Breakpoint	Note
Anoxic	No	Oxidant (DO and NO <sub>x</sub> ) were low; reductant (NH <sub>4</sub> ) kept on accumulate.
Oxic (high DO case)	No	ORP rose quickly; reductant oxidized quickly and oxidant accumulated.
Oxic (low DO case)	Yes	ORP rose in a relative slow rate; <b>no NO<sub>x</sub> accumulation was observed.</b>
Drawing	No	No obvious reaction in this stage.

#### 4-2-1-2 pH profile

pH change due to the concentration variation between aquatic H<sup>+</sup>, OH<sup>-</sup> and other ions. In high DO case (SBMBR1), the relative reaction that caused H<sup>+</sup> and OH<sup>-</sup> concentration change is nitrification (denitrification was unapparent), while SND in low DO case (SBMBR2).

Thus, pH change in high DO case (SBMBR1) was larger than that in low DO case (SBMBR2). The final pH was 6.7 in high DO case (SBMBR1) while 7.5 in low DO case (SBMBR2). Real-time control strategies based on pH (bending points) at each stage in Run 2 (C/N = 11.0) are listed in Table 4-4.

Table 4-4. Real-time control strategies of pH (bending points) at each batch operation stage of high DO (SBMBR1) and low DO case (SBMBR2) in Run 2 (C/N = 11.0).

Stage	Bending point	Note
Anoxic	No	The range of pH did not change largely.
Oxic (high DO case)	Yes	Nitrification, H <sup>+</sup> was released, so that alkalinity was depleted; pH decreased. Denitrification was unapparent.
Oxic (low DO case)	Yes	<b>SND, alkalinity was depleted in a lower rate</b> ; pH changed in a range of 7.0-8.0.
Drawing	No	No obvious reaction in this stage.

#### 4-2-1-3 DO profile

DO change in reactor is highly correlated with aeration. In the no or low aeration period, DO levels are zero. DO levels are increasing only in the aeration period. The aeration period in this system included

aerobic and drawing stage. At the initiation of the aeration period, large amounts of reductants were left in high DO case (SBMBR1), so that microbes need much more oxygen as electron acceptor to proceed with oxidation. Free oxygen accumulates when the reductant levels decrease, thus, DO levels rise. Thereafter, microbial aspiration is the only reaction in this system, so that DO levels increase slowly. In low DO case (SBMBR2), low airflow rate provided just-sufficient oxygen for denitrification, so that low DO levels were observed. However, low airflow rate caused ammonia to deplete at a slow rate. Real-time control strategies of DO (breakpoints) in each stage of Run 2 (C/N = 11.0) are listed in Table 4-4.

Table 4-5. Real-time control strategies of DO (breakpoints) at each batch operation stage of high DO (SBMBR1) and low DO case (SBMBR2) in Run 2 (C/N = 11.0).

Stage	Breakpoint	Note
Anoxic	No	DO dropped to zero in first few minute, and then maintained undetectable.
Oxic (high DO case)	No	DO rose largely; the reactor was full of oxidants
Oxic (low DO case)	Yes	DO was low until breakpoint occurred; <b>no NO<sub>x</sub> accumulation observed.</b>
Drawing	No	No obvious reaction in this stage.



#### 4-2-1-4 Real-time control of SND phenomenon

The ORP, pH and DO profiles of SND process are similar to those of nitrification. The possible differences between them are (1) a slow rising in ORP profile; and (2) a small dropping in pH profile in SND process. The typical control breakpoints can be found in the profiles of SND process: “nitrogen breakpoint” in ORP profiles; “ammonia valley” in pH profiles, and the “DO elbow” (Al-Ghusain et al., 1994; Wareham et al., 1994). The final results of SND reaction compared to the conventional BNR process are summarized in Table 4-6.

Table 4-6. Typical SND control breakpoint or bending point of ORP, pH and DO profiles in high DO (SBMBR1) and low DO (SBMBR2) cases (Run 2).

	Breakpoint or bending point		
	ORP	pH	DO
High DO case (most nitrification)	No	Yes	No
Low DO case (SND phenomenon)	Yes	Yes	Yes

#### 4-2-2 SND modeling

The SND process is basically dominated by a series of redox reactions. This study adopts on-line ORP measuring technology to simulate SND reaction with Nernst equation. SND is a combined process of nitrification and denitrification, thus we can derived Eq. (9) from Eq. (4) plus Eq.(6):

$$E = (a'+a'') + (b'+b'')pH + c'\log\left(\frac{[NH_4^+]}{[NO_3^-]}\right) + c''\log([NO_3^-]) \quad \text{Eq. (9)}$$

The constants  $a'$ ,  $b'$ ,  $c'$ ,  $a''$ ,  $b''$  and  $c''$  are defined as follows: (Chang et al., 2004)

$$a' = E^0 + \frac{2RT}{nF} \ln P_{O_2} + \frac{RT}{nF} \ln\left(\frac{1}{[H_2O]}\right)$$

$$b' = \frac{2.3026 \times 2RT}{nF}$$

$$c' = \frac{2.3026 \times RT}{nF}$$

$$a'' = E^0 + \frac{(5x)RT}{nF} \ln\left(\frac{1}{P_{CO_2}}\right) + \frac{(2x+1/2y-2z)RT}{nF} \ln\left(\frac{1}{P_{N_2}}\right) + \frac{(2y-2x+z)RT}{nF} \ln\left(\frac{1}{H_2O}\right) + 2.3026 \times 14 \times \frac{(4x+y-2z)RT}{nF}$$

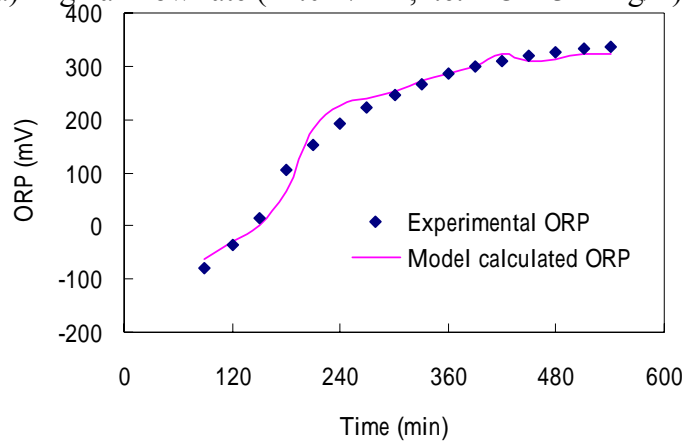
$$b'' = -2.3026 \times \frac{(4x+y-2z)RT}{nF}$$

$$c'' = 2.3026 \times \frac{(4x + y - 2z)RT}{nF}$$

#### 4-2-2-1 System with limited carbon case: Run 1 (C/N = 8.0)

Figure 4-7 shows the original experimental ORP data of SBMBR systems in Run 1 and the ORP curve calculated using Eq. (9). The oxic stage is mainly discussed (60-540 min) with Nernst equation in this study. The variation trend of the measured ORP curve is well-fitted in most parts by the calculated ORP curve. However, a slight deviation is toward the central part of the calculated ORP curve in Figure 4-7(a). The slight deviation may be caused by the errors introduced during the process of digitizing the ORP data from the experimental data. The experimental ORP data in Figure 4-7(b) were few, because there were no nitrite and/or nitrate accumulated (undetectable) before 360-min in the low DO case (SBMBR2).

(a) High airflow rate (14.0 L/min, i.e. DO = 3-4 mg/L)



(b) Low airflow rate (1.4 L/min, i.e. DO = 0-1 mg/L)

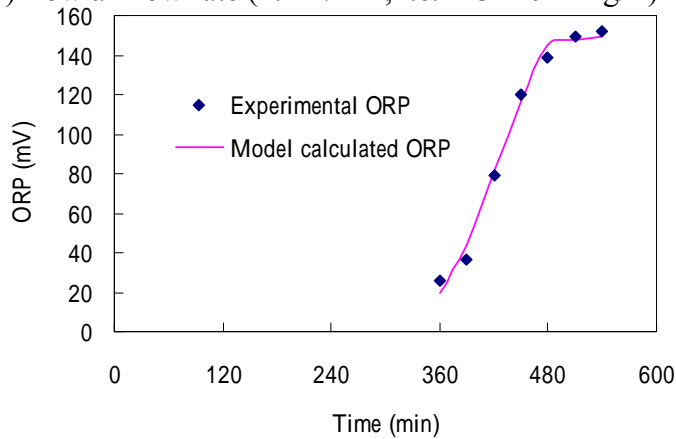


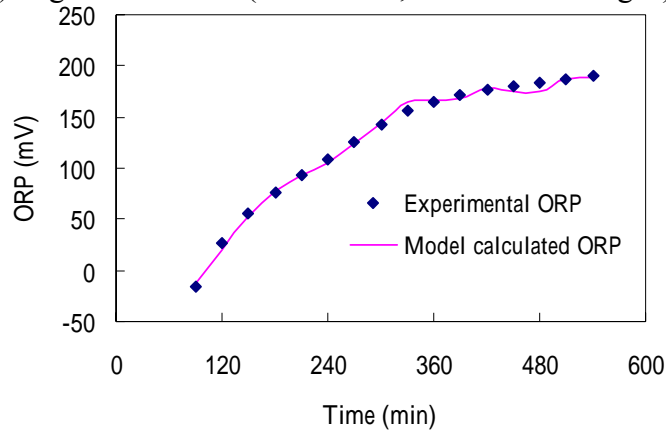
Figure 4-6. Model fit using Nernst equation of (a) high DO case (SBMBR1) and (b) low DO case (SBMBR2) in limited carbon case (Run 1, C/N = 8.0).

#### 4-2-2-2 System with excess carbon case: Run 2 (C/N = 11.0)

Figure 4-8 shows the original experimental ORP data of SBMBR systems in Run 2 (C/N = 11.0) and the ORP curve calculated using Eq. (9). The trend of the measured ORP is also well-predicted in most parts by the calculated ORP. A slight difference is observed in the latter region of the calculated ORP curve in Figure 4-8(a). The error

levels were all below 10 mV, indicated that the ORP curve which calculated with Eq. (9) is well matched with the experimental ORP data. Calculated ORP curve in Figure 4-8(b) shows a higher accuracy than that in Figure 4-8(a); the maximum error not exceeded 4 mV. Therefore, using Eq. (9) to simulate the relationship between ORP and nitrogen compounds is very feasible.

(a) High airflow rate (14.0 L/min, i.e. DO = 3-4 mg/L)



(b) Low airflow rate (1.4 L/min, i.e. DO = 0-1 mg/L)

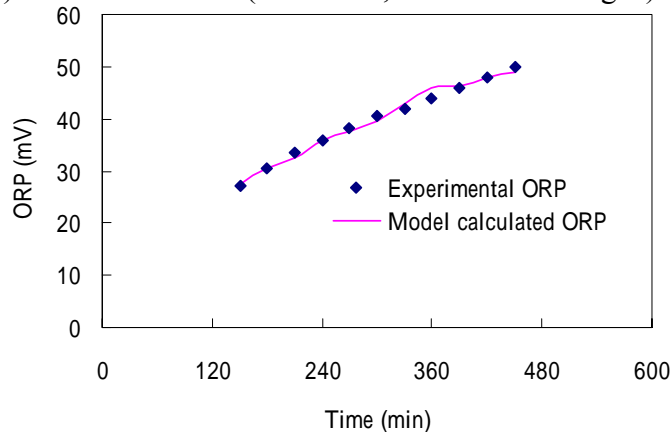


Figure 4-7. Model fit using Nernst equation of (a) high DO case (SBMBR1) and (b) low DO case (SBMBR2) in excess carbon case (Run 2, C/N = 11.0).

The Nernst equation developed in Eq. (9) is used to simulate the observed ORP for the following SND process. It is obvious from these results that simulated ORP can fit the experimental data for the SND process. The results of various regression analyses are listed in Table 4-7. High R-square values in all cases indicate that feasibility for applying Eq. (9). This also helps to illustrate that SND phenomenon can occur in the unfavorable situations, however, SNDs phenomenon in these situations are accounted for fewer parts of the biological nitrogen removal (BNR) process.

Table 4-7. Nernst equation constants and R-square values of different operating conditions.

		Nernst equation constants				R-square
		$a'+a''$	$b'+b''$	$c'$	$c''$	
Run 1 (C/N = 8.0)	High DO case (SBMBR1)	+983	-129	-44	-79	0.981
	Low DO case (SBMBR2)	+715	-72	-29	-83	0.990
Run 2 (C/N = 11.0)	High DO case (SBMBR1)	+460	-61	-6	+66	0.996
	Low DO case (SBMBR2)	+154	-15	-6	-5	0.985

### 4-3 Membrane operational characteristics

#### 4-3-1 Clogging problem of membrane filtration

Figure 4-9 indicates the flux changes during continuous operational period for high DO case (SBMBR1) and low DO case (SBMBR2) systems in high C/N ratio (11.0, Run 2). Clogging on membrane module is shown in Figure 4-10(a), while membrane module after cleaning is shown in Figure 4-10(b). Biomass was maintained at  $5,041 \pm 364$  mg/L as MLSS with regular sludge withdrawn; flux was calculated with filtrate volume and membrane filtration area ( $0.2 \text{ m}^2$ ) after 3 hours suction. The flux of high DO case (SBMBR1) was always somewhat higher than that of low DO case (SBMBR2). This may be due to the high airflow rate generate much more turbulence than low airflow rate, thus, sludge attached on the membrane surface can be easily scratched off. The flux of high DO case (SBMBR1) decreased from  $37.5$  to  $28.2 \text{ L/m}^2 \cdot \text{hr}$  within 8 cycles due to membrane fouling; the flux of low DO case (SBMBR2) decreased from  $37.5$  to  $27.2 \text{ L/m}^2 \cdot \text{hr}$  within 8 cycles. A 3-hr set drawing stage can not reach the required discharge capacity of  $17.5 \text{ L}$  ( $29.2 \text{ L/m}^2 \cdot \text{hr}$ ); hence the water cleaning procedure was applied in cycle-9. The fluxes of hollow fiber

membranes after cleaning with water were 36.7 and 35.0 L/m<sup>2</sup>·hr.

Jet water can be used to clean the membrane surface roughly, however, the effect of water cleaning decreased. In cycle-16, fluxes after cleaning were down to 25.3 and 23.8 L/m<sup>2</sup>·hr. Because there were some fine solutes and sludge particles adsorbed inside the pores.

Chemical cleaning procedure using sodium hypochlorite (NaOCl) was applied to solve this problem. After chemical cleaning, the fluxes of hollow fiber membranes increased to 38.3 and 35.0 L/m<sup>2</sup>·hr. Apply water cleaning to the membrane filtration not only lower the cost, but also reduce the cleaning time. The result shows the filter run can be lengthened to approximately 8 cycles with water cleaning. Although the effect of water cleaning is lower than that of chemical cleaning, the advantages of water cleaning procedure are fast, easy and low cost. This makes it suitable for the full-scale operation.



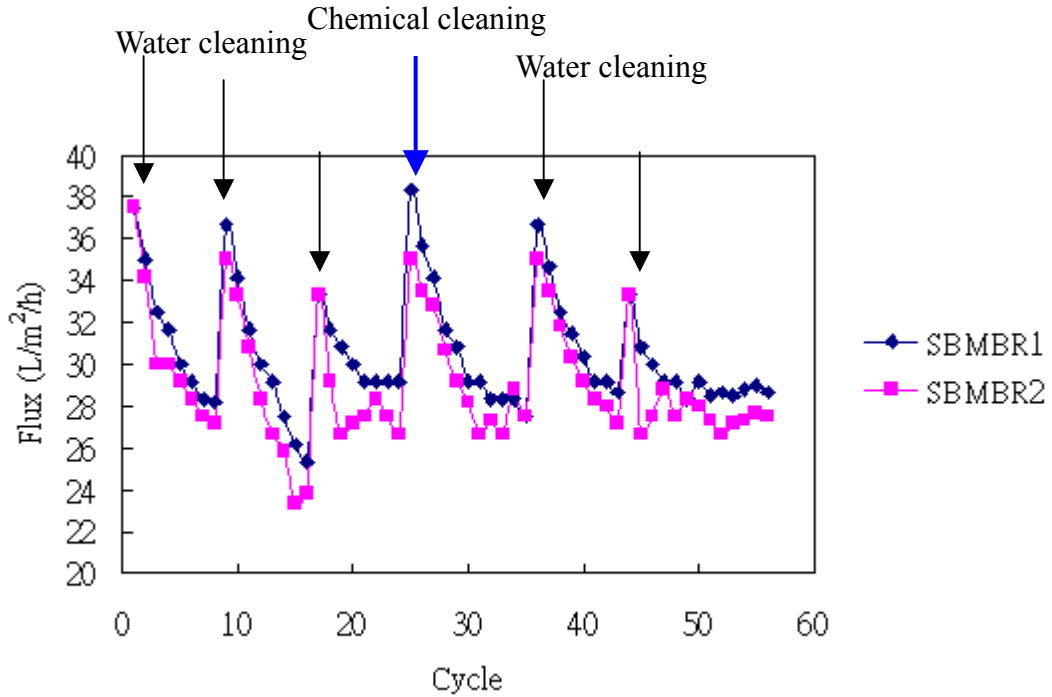


Figure 4-8. Variation of flux with operating cycles for high DO case (SBMBR1) and low DO case (SBMBR2) in Run 2 (C/N = 11.0). Each cycle takes 12 hrs to achieve, thus, two cycles per day. Water and chemical cleaning are done by jet water and NaOCl, respectively.

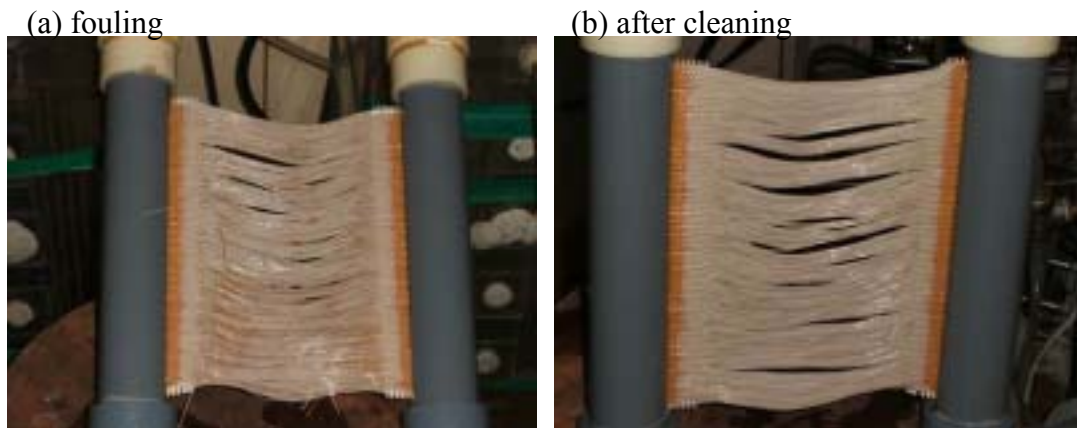


Figure 4-9. Membrane module (a) fouling and (b) after water or chemical cleaning procedure in all runs.

#### 4-3-2 Feasibility of SBMBR effluent reusing

The shortage of water resource in Taiwan is a serious domestic problem. Therefore, the concept of water reuse has been a consequential trend nowadays. In Taiwan, recycle water standard has not yet been set, thus, the government adapted the standard from Japan. Commonly, treating equipments of recycle water were set after secondary treatment process, such as biofilter and activated carbon procedure. In this study, we have tried to compare the effluent from SBMBR with recycle water standard.

From Table 4-8, SBMBR effluent with additional disinfection process of chlorination and ozonation can be used as sprinkling and landscape water. However, it should be used directly, but not be stored. Irrigation with recycle water needed to be de-chlorinated for prevention of the plant-coking, which is caused by residual chlorine. Disinfection with ozone must be considered economically. In addition, color in raw water, ozonation equipment and capability must be also considered. Landscape water is associated with beauty, thus, color removal is necessary to deal with. According to the experience from Japan, color standard is set by 10 will be needed to extend ozonation treatment

and/or activated-carbon adsorption equipment. Additionally, applying the disinfection process needs to consider the type of landscape, purpose (fish culture and so on) and scale.

In this study, synthetic wastewater was treated with SND process in SBMBR system. The effluent from such system may be used as toilet flushing water with disinfection of chlorination to an extent for retaining residual chlorine. Meanwhile, ensure the sanitation and safety during the period of storage.



Table 4-8. Comparison between recycle water and effluent from low DO case (SBMBR2) in Run 2 (C/N = 11.0).

Purpose Item	Sprinkling (Irrigation, cooling...)	Landscape (Car washing)	Toilet flushing	This study (Low DO case)
E. coli (colony/mL)	ND	ND	<10	ND
BOD (mg/L)	-	<10	-	<10
pH	5.8-8.6	5.8-8.6	5.8-8.6	6.5-7.5
Turbidity (NTU)	<10	<5	-	2
Odor	comfortable	comfortable	comfortable	comfortable
Appearance	comfortable	comfortable	comfortable	comfortable
Color (Pt-Co)	<40	<10	<40	4 (ADMI)
Residual chlorine (mg/L)	>0.4	Ozonation	retain residual chlorine	-
Note	not contact with human body	not contact with human body	-	-

資料來源：日本再生水水質標準

## Chapter 5 Conclusions and suggestions

### 5-1 Conclusions

In this study, SBMBR system has several advantages from combination of SBR and MBR system. Conclusion can be made as follows:

1. Sludge retained in the reactor due to membrane filtration, however, MLSS was kept at 5,000 mg/L with sludge withdrawn. Low DO case (SBMBR2, low airflow rate) has the higher sludge retention time (180 days) than high DO case (60 days, SBMBR1, high airflow rate). Drawing stage includes filtration and aeration; this is similar to extended aeration, therefore, inhibited the yield of excess sludge.
2. From batch tests,  $R_{SND}$  was 4.2 mg N/L·hr in SBMBR2 (low DO case), while 3.1 mg N/L·hr in SBMBR1 (high DO case) in Run2 (C/N = 11.0). This indicated that moderate DO levels (0-1 mg/L) are favorable for SND reaction. On the other hand, in SBMBR2 (low DO case),  $R_{SND}$  was 3.6 mg N/L·hr in Run 1 (C/N = 8.0). However, with higher C/N ratio (Run 2, C/N = 11.0),  $R_{SND}$  was enhanced to 4.2 mg N/L·hr in SBMBR2 (low DO case). This

reveals a sufficient carbon source ( $C/N > 10$ ) could enhance the SND phenomenon.

3. Filtrate with hollow fiber membranes can remove the particles greater than  $0.4 \mu\text{m}$  from effluent. The average turbidity in effluent was 2 NTU, thus, solid-liquid separation was completed successfully.
4. After chemical cleaning procedure, membrane fouling problem can be effectively solved. Water cleaning procedure can lengthen the filter run, nevertheless, the effect of water cleaning can not sustain long.
5. Online monitoring parameters are applied to proceed with real-time control in SND reaction. The results showed the system that performed SND phenomenon should have breakpoints and bending points in online monitoring profiles; they indicated the end of SND reaction. Modeling with Nernst equation in different airflow rates and  $C/N$  ratios were feasible, although slight deviations were observed.

## 5-2 Suggestions

1. Phosphorus accumulating organisms (PAOs) might play an important role in SND reaction, thus, phosphorus removal could be concentrated to understand the relationship between SND and phosphorus removal.
2. In this study, influent with fixed components was studied; however, real wastewater is unstable. Influent variation treatment and membrane capability, even continuous inflow, could be discussed in the consequent study.
3. Introduce intermittent aeration (IA) and continuous flow in oxic stage to compare membrane filtration and SND phenomenon with low DO aeration. IA may not deteriorate the treatment efficiency and lower the consumption of energy.

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## **Appendix**

### **Membrane washing**

The ways that hollow fiber membrane washing can be separated into two parts: in-line chemical cleaning and out-of-system chemical cleaning procedure. In this study, out-of-system chemical cleaning procedure was introduced due to the advantages of easy, convenience and higher washing efficiency.

#### **1. In-line chemical cleaning procedure**

Chemical agent was backwashed from the inside to the membrane surface.

Chemical agent:

Sodium hypochlorite (NaOCl, residual chlorine: 3,000 mg/L)

Operational procedure:

- (1) Shut down the peristaltic pump;
- (2) Idle membrane module for more than 2 min, then shut down the

- aeration pump;
- (3) Chemical agent pours into the line with hydraulic head loss (suitable head loss: 1 m);
  - (4) Open the cleaning agent valve and idle for more than 2 hrs;
  - (5) Shut down the valve and open the aeration tube;
  - (6) Start the peristaltic pump;
  - (7) Confirm that the flux or trans-membrane pressure (TMP) has been lowered.

It should be warned that effluent from in-line chemical cleaning procedure contains large number of residual chlorine. Therefore, the reductant (sodium thiosulfate) must be poured into the tube of chemical cleaning agent to proceed neutralization.

## 2. Out-of-system chemical cleaning procedure

If chemical cleaning tube is long or some tiny particles and/or solutes clogged with the membrane pore, hollow fiber membrane must be taken out from the system to rinse, immerse and clean with chemical



agent.

Chemical agent:

Mix of sodium hypochlorite (NaOCl, residual chlorine: 3,000 mg/L) and sodium hydroxide (NaOH, 4%)

Operational procedure:

- (1) Remove all the tubes and take the membrane module out of the reactor;
- (2) Rinse out the sludge cake which is attached on membrane surface with jet water;
- (3) Immerse the membrane module in the tank that is filled with chemical agent (more than 15 hrs);
- (4) Take the membrane module out and rinse the residual chemical agent from membrane;
- (5) Place the membrane module back to the reactor and link all the tubes;
- (6) Start the peristaltic pump;
- (7) Confirm that the flux or trans-membrane pressure (TMP) has been

lowered.

**“Warning”** Before dispose the chemical cleaning waste, sodium thiosulfate should be used to reduce sodium hypochlorite, and then neutralize sodium hydroxide with hydrochloric acid. If the procedure was upside-down, then the toxic gas would be generated.