Factors affecting simultaneous nitrification and de-nitrification (SND) and its kinetics model in membrane bioreactor

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ABSTRACT

Experiments have been carried out to investigate the effect of biological factors such as dissolved oxygen (DO), food/microorganism (F/M) ratio, carbon/nitrogen (C/N) ratio and pH on performance of SND in membrane bioreactor (MBR). It was found that a low DO was advantageous to SND on condition that nitrification was not inhibited, while F/M ratio and C/N ratio have reverse effects on SND, and pH should also be controlled in a suitable range. Based on the conventional activated sludge model, a deduction was conducted to illustrate that SND could take place from the theoretical aspect, and it was proved that high organics was effective in improving SND. In addition, a kinetic model for SND was constituted on the basis of batch test result, and the simulation nitrate saturation coefficient K_{NO_3} was much higher than that in a single-sludge wastewater treatment system.

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1. Introduction

The adverse environmental impacts associated with ammonia nitrogen include promotion of eutrophication, toxicity to aquatic organisms and depletion of dissolved oxygen in receiving water bodies due to bacterial oxidation of ammonia to nitrate [1]. Thus, the removal of nitrogen compounds from wastewater is of increasing importance. In the European directive on urban wastewater treatment [2], the maximum allowable total nitrogen concentration of the discharged effluent including ammonia, nitrite and nitrate and organic nitrogen is 20 mg N L^{-1} (daily average). A further reduction to 10 mg L^{-1} is possible [3]. The biological elimination of nitrogen in wastewater treatment plants results from the processes of nitrification and de-nitrification. These two processes have been thought to be two separate reactions by different groups of microorganisms in activated sludge. Aerobic auto-trophic *nitrifiers* oxidize ammonia to nitrite and then nitrate. Under anoxic conditions, nitrite and then nitrate reduced to nitrogen gas by hetero-trophic de-nitrifying bacteria. Since auto-trophic ammonia-oxidizing bacteria have generally been characterized by low growth rates and poor yields, the nitrification is generally a rate-limiting step in a biological nitrogen removal process. Therefore, a major difficulty in biological nitrogen removal is to maintain adequate levels of *nitrifiers* in the aeration vessel.

Because of different environmental conditions of *nitrifiers* and *de-nitrifiers*, total nitrogen removal in wastewater treatment plants is most commonly achieved in a two-stage system or in sequencing batch reactor (SBR) system where nitrification and de-nitrification were achieved by temporal separation. However, recent studies have revealed that these two important steps can occur concurrently in the same reactor [4–8], and this process is termed SND.

In recent years, MBR was proposed as an alternative of conventional activated sludge systems, where the traditional secondary clarifier is replaced by a membrane unit for the separation of the treated water from the mixed liquid without the risk of sludge bulking. Compared with conventional activated sludge systems, MBR technology has many advantages [9]. Efficient retention of biomass makes possible an increase in sludge concentration and disinfection of the treated water. As a result, a highly concentrated sludge can be maintained in the bioreactor. The treatment facility can be built in a very compact way. Excess sludge production can be kept relatively low. Since the treated water is almost free of bacteria, it can be applied for municipal and industrial reuse. Because of these advantages, increasing attentions have been paid to the research of MBR technology.

From previous studies [10–17], it was found that there are a lot of factors which influence SND, such as structure, size, density and concentration of sludge flocs, DO, F/M ratio, C/N ratio and pH,

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Nomenclature

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X_V	activated sludge concentration ($mg\,L^{-1}$)
X_h	hetero-trophic biomass concentration ($mg\,L^{-1}$)
X_a	auto-trophic biomass concentration ($mg\,L^{-1}$)
L_a	influent organics concentration ($mg\,L^{-1}$)
L_e	effluent organics concentration ($mg\,L^{-1}$)
a	sludge yield ($kg\,VSS\,kg\,BOD_5^{-1}$)
a_h	hetero-trophic yield ($kg\,VSS\,kg\,BOD_5^{-1}$)
a_a	auto-trophic yield ($kg\,VSS\,kg\,BOD_5^{-1}$)
θ	sludge retention time (day)
θ_h	hetero-trophic biomass retention time (day)
θ_a	auto-trophic biomass retention time (day)
b	sludge decay coefficient (day^{-1})
b_h	hetero-trophic biomass decay coefficient (day^{-1})
b_a	auto-trophic biomass decay coefficient (day^{-1})
t	hydraulic retention time (day)
N_a	influent TKN concentration ($mg\,L^{-1}$)
N_e	effluent TKN concentration ($mg\,L^{-1}$)
Y_A	auto-trophic bacteria yield ($kg\,VSS\,kg\,NH_3\text{-}N^{-1}$)
Y_H	hetero-trophic yield ($kg\,VSS\,kg\,COD^{-1}$)
μ_A	maximum specific growth rate of auto-trophic bacteria (h^{-1})
μ_H	maximum specific growth rate for hetero-trophic bacteria (h^{-1})
S_{NH}	NH_3-H concentration ($mg\,L^{-1}$)
S_O	dissolved oxygen concentration ($mg\,L^{-1}$)
S_{NO_3}	NO_3-N concentration ($mg\,L^{-1}$)
S_S	organics concentration ($mg\,L^{-1}$)
K_{NH}	NH_3-H saturation coefficient ($mg\,L^{-1}$)
K_{NO_3}	NO_3-N saturation coefficient ($mg\,L^{-1}$)
K_S	organics saturation coefficient ($mg\,L^{-1}$)
K_{OA}	dissolved oxygen saturation coefficient for auto-trophic bacteria ($mg\,L^{-1}$)
K_{OH}	dissolved oxygen saturation coefficient for hetero-trophic bacteria ($mg\,L^{-1}$)
X_{BA}	auto-trophic bacteria concentration ($mg\,L^{-1}$)
X_{BH}	hetero-trophic bacteria concentration ($mg\,L^{-1}$)
η_g	correction factor for biomass anoxic growth ($0 \leq \eta_g \leq 1$)
k, A	constants

etc. however, the detailed mechanism of SND has not yet been discussed. Therefore, the aim of the research is to illustrate the effect of ecological factors such as DO, F/M ratio and C/N ratio on performance of SND in MBR, and try to explain the mechanism of SND according to experimental result and theoretical analysis with the help of conventional activated sludge mathematical model. In addition, a kinetic model is also constituted to simulate the process of SND.

2. Materials and methods

A hollow fiber polyethylene ultra-filtration (UF) membrane unit (purchased from Hydranautics company) with a total surface area of $2.0\,m^2$, mean pore size of $0.05\,\mu m$ and a length of $0.35\,m$ was used as the test membrane. The aerobic reactor was made of poly-methyl methacrylate with an effective volume of 16.3 L, and the temperature of the mixed liquid was maintained at $20 \pm 1\,°C$ with a thermostat. In addition, the air was introduced into the reactor with a micro-bubble air diffuser, and air flow rate was adjusted by an air flow-meter. There were all three systems of MBR, in which the HRT was kept at 6 h, but the values of DO, F/M ratio and C/N ratio were different for the three systems. Three systems were run in parallel,
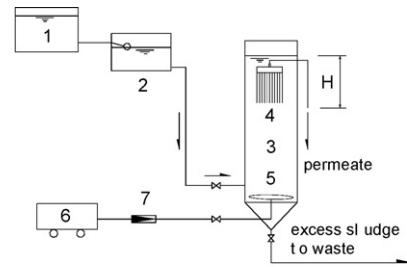
(1) storage tank; (2) constant high level tank; (3) aerobic reactor;
(4) membrane module; (5) air diffuser; (6) air compressor; (7) air flow-meter.

Fig. 1. Schematic of the experimental system: (1) storage tank; (2) constant high level tank; (3) aerobic reactor; (4) membrane module; (5) air diffuser; (6) air compressor; (7) air flow-meter.

and sludge concentrations of $5000\text{–}6000\,mg\,L^{-1}$ be maintained in all MBRs through periodic sludge wastage. A schematic diagram of the process configuration is shown in Fig. 1.

2.1. Raw water for experiment and analytical methods

A synthetic raw wastewater for experiment was made of starch, sugar, NH_4Cl, Na_2HPO_4, NaH_2PO_4, $NaHCO_3$ and Na_2CO_3 with different amounts of organics and nitrogen according to different experimental requirements, and its characteristics are summarized in Table 1.

The three reactors were run for over 1 month under separate conditions to reach steady state. Then the test continued for a total of 3 months, and the effect of ecological factors of DO, F/M ratio and C/N ratio on performance of nitrification and de-nitrification in MBR was analyzed.

All analytical assessments were carried out according to the Standard Methods [18].

2.2. Kinetic approach

In this study, two different kinetic models, including Lawrence–McCarty model [19] and a general model for single-sludge wastewater treatment system [20], were used to draw a deduction and determine the nitrate saturation constant of SND in MBR.

3. Results and discussion

In this test, it was assumed that total removal denoted the removal efficiency between permeate and influent, and biological removal indicated the removal efficiency between filtrate (the mixed liquid samples collected were filtered by qualitative filter papers with pore size of $0.45\,\mu m$) and influent.

3.1. Effect of DO on COD removal

At different test stages, DO of MBR was kept at $0.8\,mg\,L^{-1}$, $1.5\,mg\,L^{-1}$, $3\,mg\,L^{-1}$ and $5\,mg\,L^{-1}$ and the relative results are shown in Fig. 2.

Table 1
The characteristics of the test wastewater.

Parameter	Range	Mean
pH	6.2–8.2	7.6
SS ($mg\,L^{-1}$)	140–250	190
COD ($mg\,L^{-1}$)	210–650	380
NH_3-N ($mg\,L^{-1}$)	10.7–62.1	30.5
TN ($mg\,L^{-1}$)	11.7–67.6	38.4
TP ($mg\,L^{-1}$)	2.1–5.2	3.2

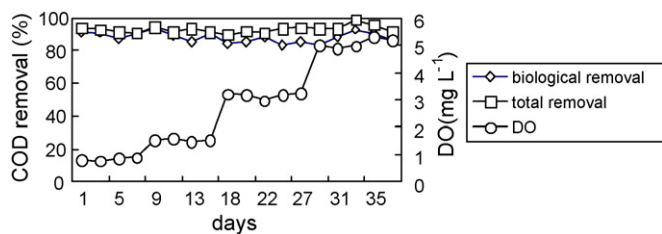**Fig. 2.** COD removal as a function of DO.

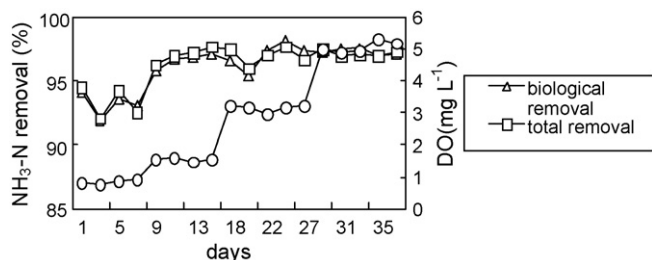**Fig. 3.** NH$_3$-N removal as a function of DO.

Initially, DO was maintained at 0.8 mg L^{-1}, and COD removal was averaged at 92.27%, then DO was increased to 1.5 mg L^{-1} and the mean COD removal was 92.48%. When DO was kept at 3 mg L^{-1} and 5 mg L^{-1}, respectively, COD was removed by average 92.02% and 94.73%. It can be observed that organic substance could be biodegraded significantly in the reactor at DO in the range of 0.8–5 mg L^{-1}. COD of both the filtrate in the reactor and UF permeate was very low. Comparing the COD values of filtrate and permeate during the operational period, it could be found that UF membrane has an excellent stabilization for organic substance removal.

3.2. Effect of DO on NH$_3$-N removal

Fig. 3 shows NH$_3$-N removals at various DO levels.

At initial stage, DO was set at about 0.8 mg L^{-1}, NH$_3$-N was always above 2 mg L^{-1} in both the filtrate and permeate, and the removal was in the range of 92.09–94.52%. At the following stages, it was found that the removal of NH$_3$-N was almost independent of DO when DO was over 1.5 mg L^{-1}. Under those conditions, NH$_3$-N in the filtrate and membrane permeate were both below 1 mg L^{-1}, and NH$_3$-N removals were up to 97%.

3.3. Effect of DO on TN removal

According to Fig. 4, it is evident that DO has a significant effect on TN removal.

At the first test stage of DO 0.8 mg L^{-1}, average removal for TN was 86.58%. Then DO was increased to 1.5 mg L^{-1}, 3 mg L^{-1} and 5 mg L^{-1}, respectively, and corresponding removals for TN decreased to 77.53%, 65.33% and 54.21% in a reverse way. Accord-
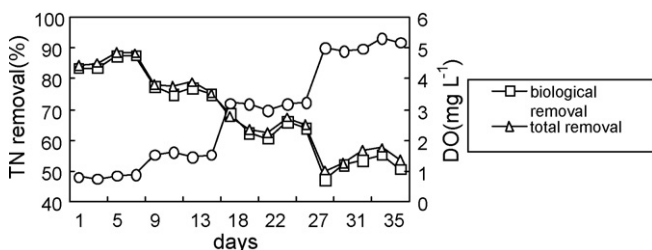
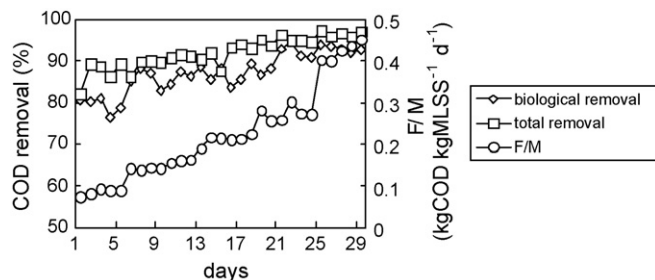

Fig. 4. TN removal as a function of DO.

Fig. 5. COD removal as a function of F/M ratio.

ing to the test results, it can be concluded that DO has a significant effect on TN removal. Because DO can penetrate into sludge flocs at high DO, i.e., the higher DO was, the less anoxic zone in the inner part of flocs was, and hence the lower de-nitrification took place. As a result, at high DO, the most majority of ammonia could be oxidized to nitrite and then nitrate, whereas de-nitrification process was inhibited, thus resulting in high concentration of TN both in the filtrate and membrane permeate. Based on the hypothesis of micro-environment, for a highly concentrated sludge could be maintained in MBR, anoxic zone may be formed in sludge flocs even at a high DO, so partial de-nitrification could take place in MBR [13,21]. Whereas, once DO was too low, nitrification maybe inhibited, which would result in a high level NH$_3$-N in the solution. Therefore, excellent nitrification is prerequisite for a complete SND.

3.4. Effect of F/M ratio on COD removal

The variation of F/M ratio was implemented by varying the influent COD. At this experimental stage, DO was kept at 1.0–1.5 mg L^{-1}, and the effect of F/M ratio on COD removal is shown in Fig. 5.

During this experimental period, average F/M ratio was controlled at 0.086, 0.154, 0.216, 0.272 and 0.423 kg COD kg MLSS^{-1} day^{-1}, respectively. At these five different stages, COD of permeate was always kept at a low level, and excellent removals for COD were obtained. It can be observed from Fig. 5 that COD removal increased with the increase of F/M ratio, whereas it did not mean the higher F/M ratio was, the higher removal for COD would be. Because the permeate COD was kept at a stable level, therefore, a higher removal for COD would be obtained with the increase of influent COD.

3.5. Effect of F/M ratio on NH$_3$-N removal

The effect of F/M ratio on NH$_3$-N removal is presented in Fig. 6.

An excellent nitrification took place in this period, and permeate NH$_3$-N was mostly below 1 mg L^{-1}, and average removals for NH$_3$-N at five stages was 98.69%, 97.02%, 97.81%, 98.06% and 98.48%, respectively. Under the test maximum F/M ratio, nitrification performance of *nitrifiers* was not inhibited by the competition with hetero-trophic bacteria. Due to the exclusion of UF membrane,
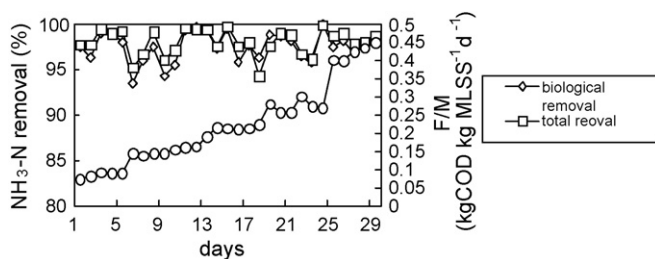

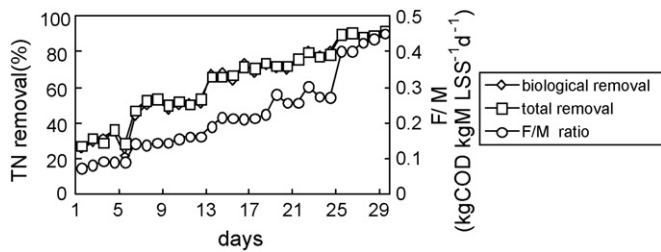**Fig. 6.** NH$_3$-N removal as a function of F/M ratio.

Fig. 7. TN removal as a function of F/M ratio.

nitrifiers could be retained in the reactor completely and make nitrification proceed smoothly.

3.6. Effect of F/M ratio on TN removal

It could be seen from Fig. 7 that the TN removal increased with the rise of F/M ratio.

Under the condition of nitrification took place thoroughly in MBR, influent with high organics could supply relatively sufficient organic substance for de-nitrification. At first stage, F/M ratio was 0.086 kg COD kg MLSS^{-1} day^{-1}, average removal for TN was 30.33%, when F/M ratio was increased to 0.423 kg COD kg MLSS^{-1} day^{-1}, mean removal for TN reached 89.90%. Therefore, it is considered that high F/M ratio is advantageous to TN removal on condition that nitrification was not inhibited.

3.7. Effect of C/N ratio on performance of SND in MBR

At this test stage, the emphasis was put on the effect of C/N on performance of SND in MBR. DO was maintained at about 1 mg L^{-1}, and F/M ratio was kept at 0.30 kg COD kg MLSS^{-1} day^{-1}, then the results are presented in Table 2.

Based on results shown in Table 2, it is evident that NH$_3$-N in UF permeate increased with the decrease of C/N ratio, while TN in permeate being also increased with the decrease of C/N ratio. In this study, the variation of C/N ratio was carried out by increasing influent NH$_3$-N. As increase of NH$_3$-N load brought a shock to the biological system, and nitrification took place not thoroughly, therefore there was a rise of NH$_3$-N in permeate. Therefore, TN increase in permeate was caused by the following two reasons: firstly, the increase of NH$_3$-N in permeate. Secondly, influent COD was insufficient for biological de-nitrification and there was a high level of NO$_x$$^-$-N remained in permeate.

3.8. Effect of pH on performance of SND in MBR

In order to find out the effect of pH on performance of SND in MBR, DO was maintained at about 1 mg L^{-1}, F/M ratio at 0.45 kg COD kg MLSS^{-1} day^{-1}, and C/N ratio about 30, then the experimental results are presented in Table 3.

According to results given in Table 3, the COD removals were significant at influent pH approach neutral, when pH increased or decreased far from 7, the permeate COD had a certain rise, but

still lower than 60 mg L^{-1}, which meant that hetero-bacteria had a strong buffering ability for the variation of pH. But pH has a significant influence on the removal of NH$_3$-N and TN. Initially, the average pH value of influent was 4.8, the removals of NH$_3$-N and TN were 56% and 45%, respectively. Then pH was adjusted to around 7.2, the removals of NH$_3$-N and TN increased to about 99% and 91%, respectively. When pH was set at about 9.7, the removals of NH$_3$-N and TN sharply decreased to about 75% and 60%, respectively. The nitrification process was inhibited badly when pH was lower than 5. In the continuous flow reactor of the test, because of the dilution of mixed liquid, pH values of 5 and 9.6 of influent were adjusted to 6.3 and 8.9, but both of them are not in the range of optimum pH for nitrification and de-nitrification. Based on the experimental results, it can be concluded that pH is an important factor affecting SND.

3.9. Mechanism research on SND in MBR

There exist a large quantity and species of microorganisms in sludge flocs, the relationships between different groups are complex. Each group of bacteria has its optimum living environment. For all species in the activated sludge, some ecological factors favor the growth of certain groups but may be harmful to the growth of some other ones. Therefore, a suitable ecological environment should be created for *nitrifiers* and *de-nitrifiers* in biological nitrogen removal systems, and the pattern of DO and substrate concentration is illustrated in Fig. 8 [22].

As shown in Fig. 8, an anoxic zone and an aerobic zone is required in sludge flocs to form the essential environment for SND. To obtain a steady state, all ecological factors such as pH, temperature, DO, F/M and C/N influencing SND are required to keep stable. The optimum pH values for nitrification and de-nitrification are in the range of 8.0–8.4 and 6.5–7.5, respectively, and the optimum pH for SND is about 7.5, and the experimental results have substantiated the deduction. The optimum temperature for nitrification and de-nitrification are in the range of 20–30 °C and 20–40 °C, respectively. When the temperature was below 15 °C, the multiplication rate and metabolism rate of *de-nitrifiers* became slower, and de-nitrification rate reduced too. It has been confirmed from this test that DO should not be below 1.5 mg L^{-1} for nitrification, otherwise the process will be inhibited. For de-nitrification process, DO should be kept below 0.8 mg L^{-1}. High DO is unsuitable for SND, for DO will penetrate into the bio-flocs and anoxic zone is difficult to be formed [23].

The size and density of sludge flocs also affected the diffusion of DO. A large floc caused a long diffusion distance within it, therefore needed much more DO and was more likely to form an anoxic zone in the sludge flocs. The denser the flocs, the more quantity of microbes contained in its unit volume, and hence the more oxygen was consumed. As a result, the oxygen was more difficult to diffuse into the sludge flocs and led to the formation an anoxic zone within it [24].

The supply of organic substance as a carbon source is another important factor for SND [25]. There exists a substrate overlap between hetero-trophic aerobic bacteria in aerobic zone and *de-nitrifiers* in anoxic zone, they will compete for the same food
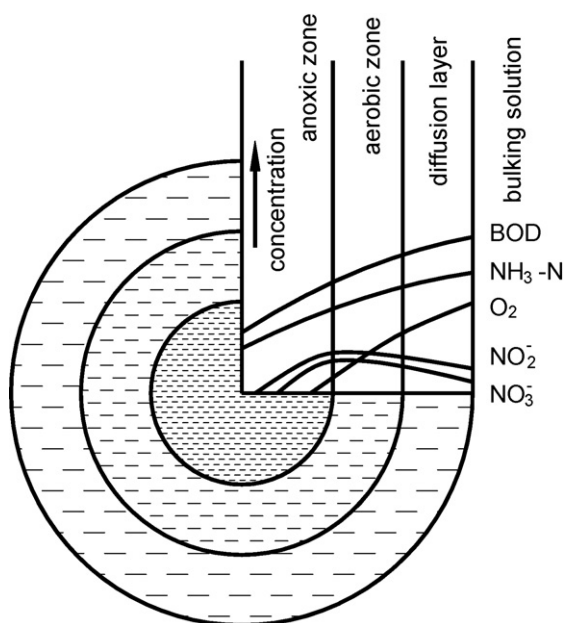
Table 2
Effect of C/N ratio on SND in MBR.

COD/N	COD			NH$_3$-N			TN		
	Influent (mg L^{-1})	Effluent (mg L^{-1})	Removal (%)	Influent (mg L^{-1})	Effluent (mg L^{-1})	Removal (%)	Influent (mg L^{-1})	Effluent (mg L^{-1})	Removal (%)
39.37	421.4	19.3	95.42	10.7	0.1	99.07	11.7	0.9	92.31
21.29	398.6	17.4	95.63	18.7	0.1	99.47	20.4	2.1	89.71
15.37	412.3	22.2	94.62	26.8	0.6	97.76	29.2	8.2	71.92
10.68	422.2	20.4	95.17	39.5	1.0	97.47	43.1	19.5	54.76
6.12	379.8	19.5	94.87	62.1	1.6	97.42	67.6	55.4	18.05

Table 3
Effect of pH on SND in MBR.

pH	COD			NH$_3$-N			TN		
	Influent (mg L^{-1})	Effluent (mg L^{-1})	Removal (%)	Influent (mg L^{-1})	Effluent (mg L^{-1})	Removal (%)	Influent (mg L^{-1})	Effluent (mg L^{-1})	Removal (%)
4.8	639.9	58.6	90.84	19.3	8.4	56.48	21.5	11.8	45.12
4.7	628.6	23.5	96.26	20.7	8.8	57.49	21.1	12.4	41.23
7.1	624.4	12.5	97.99	22.6	0	100	23.2	2.4	89.66
7.3	631.2	15.6	97.53	20.6	0.1	99.51	21.8	2.0	90.83
9.6	621.6	46.8	92.87	20.4	5.0	75.49	21.2	8.5	59.91
9.7	630.2	50.6	91.97	22.4	5.5	75.45	23.1	8.8	61.90

source. The outer space of sludge floc is occupied by hetero-trophic aerobic bacteria, therefore it is more easy for them to get food from bulking solution than *de-nitrifiers* in the inner anoxic zone. During the process of organic substance diffusion from bulking solution into aerobic zone and further into anoxic zone, a large amount of organics will be utilized by hetero-trophic aerobic bacteria and the remaining organics cannot meet the requirement for de-nitrification. In order to solve this problem, the following measures should be adopted: Firstly, the quantity of supplied organics should be adequate to maintain a higher F/M value, otherwise, the low F/M value would lead to much consumption of organic substance and insufficient supply of carbon substrate for de-nitrification. However, when the organic substance was supplied too much and the DO was limited, the bacterial activity of the floc in the aerobic zone was not too high, which made much more organics not be degraded and then diffused into anoxic zone of the floc. Secondly, DO should not be too high, a high DO will strengthen the penetration of oxygen, and become difficult to form an anoxic zone in the floc, also it will strengthen the activity of hetero-trophic aerobic bacteria in aerobic zone, and increase the rate of oxidation. Even though there is anoxic zone in the sludge floc, the de-nitrification will be reduced because of no or lack of organic substrate. Thirdly, NO_2^- may directly intrude into anoxic zone and be de-nitrified instead of being oxidized by *nitrobacteria* into nitrate, thus reduced the demands of organics and oxygen. When 1 g NO_2^- or NO_3^- is reduced into N_2, the demand of methanol is 1.53 g or 2.47 g, respectively. Fourthly, the dead microorganisms in sludge flocs will release organics that will serve as carbon source for de-nitrification.

In MBR, when each ecological factor is in a relatively stable condition, even if a certain factor has a slight fluctuation, highly concentrated sludge flocs have ability to balance its disadvantageous effect on SND. For example, the activity of hetero-trophic aerobic bacteria will strengthen with a slight increase of DO, which will make them consume more DO and organic substance as well as lessen the volume of anoxic zone. In this case, the de-nitrification will be affected, whereas system still has certain capacity for SND. In addition, the variation of F/M will induce the activity variation of hetero-trophic aerobic bacteria, *Nitrosomonas*, *nitrobacteria* and *de-nitrifiers*, then they will cooperate to implement SND. The MBR is also effective in maintaining optimum pH level without the addition of external acid or base source. During nitrification, oxidizing 1 g NH_3-N will consume 7.14 g (in CaCO$_3$) alkalinity, whereas reducing 1 g NO_3^- will produce 3.5 g alkalinity as a compensation for alkalinity loss in de-nitrification [8].

There also exists "food chains" in MBR. For instance, ammonia produced through ammonification by hetero-trophic aerobic bacteria will serve as the substrate for *Nitrosomonas* and *nitrobacteria*, nitrite produced by *Nitrosomonas* will be consumed by *nitrobacteria*. In addition, nitrite and nitrate produced by either *Nitrosomonas* or *nitrobacteria* will be utilized by *de-nitrifiers*. It is necessary to co-exist a large species of microorganisms for SND in MBR.

3.10. A deduction based on conventional activated sludge mathematical model

According to Lawrence–McCarty model [19], the following equation can be deduced in activated sludge system:

$$X_V = a\frac{\theta(L_a - L_e)}{t(1 + b\theta)} \tag{1}$$

Based on Eq. (1), when MBR was run in steady state, the amount of hetero-trophic bacteria can be expressed as follows:

$$X_h = a_h\frac{\theta_h(L_a - L_e)}{t(1 + b_h\theta_h)} \tag{2}$$

In the same way, the amount of auto-trophic biomass can be expressed in Eq. (3):

$$X_a = a_a\frac{\theta_a(N_a - N_e)}{t(1 + b_a\theta_a)} \tag{3}$$

Dividing Eq. (3) by Eq. (2), then Eq. (4) was obtained:

$$\frac{X_a}{X_h} = \frac{N_a - N_e}{L_a - L_e} \cdot \frac{a_a}{a_h} \cdot \frac{\theta_a}{\theta_h} \cdot \frac{1 + b_h\theta_h}{1 + b_a\theta_a} \tag{4}$$

For hetero-trophic bacteria, a_h and b_h were 0.6 and 0.06, respectively. As to auto-trophic bacteria, a_a and b_a were 0.3 and 0.05, respectively [26]. Under steady state, θ_a and θ_h both can be regarded as constants. Meantime, there was a low organics and TKN in effluent, and Eq. (4) can be simplified into following equation:

$$\frac{X_a}{X_h} = k\frac{N_a}{L_a} \tag{5}$$

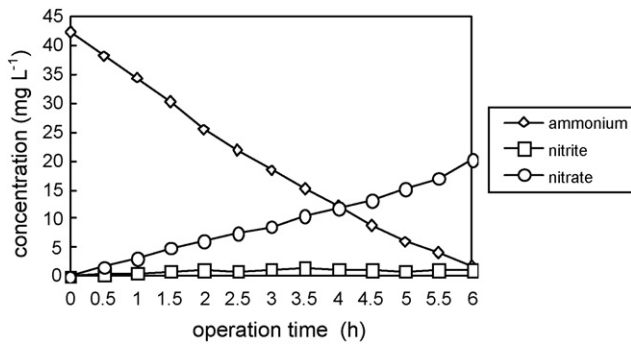**Fig. 8.** Pattern of DO and substrate concentration in sludge.

Fig. 9. Variation of filtrate ammonium, nitrite and nitrate with operation time.

It can be seen from Eq. (5) that the ratio of auto-trophic biomass concentration to hetero-trophic biomass concentration has a linear relationship with the ratio of influent TKN to organics, which is to say, mineralization and nitrification can proceed simultaneously, and *de-nitrifiers* reduce nitrite or nitrate to N_2O and N_2 by competition with hetero-trophic bacteria for substrate under low DO condition. Therefore, TN can be reduced by SND, and the existence of organics enhanced the performance of SND.

3.11. A kinetic model for SND

5 L activated sludge was drawn from MBR and was put into a reactor with volume of 10 L. Ammonium chloride was used as nitrogen source, and sodium acetate solution with $400\,mg\,L^{-1}$ was fed into reactor intermittently as carbon source. The experimental conditions as follows: MLSS, $5500\,mg\,L^{-1}$; DO, $0.8–1.0\,mg\,L^{-1}$; pH, 6.8–8.1; temperature, 20–22 °C, then variations of ammonium, nitrite and nitrate are shown in Fig. 9.

Main assumptions are as follows when constituting kinetic model is:

1. The amount of auto-trophic bacteria and hetero-trophic bacteria was independent of operation time, which means that nitrogen removal by bio-synthesis was ignored.
2. Nitrification and de-nitrification proceed simultaneously, and both reactions adapt to Monod model.

Therefore, the variation of ammonium can be attributed to nitrification by the following expression [20]:

$$\frac{dS_{NH}}{dt} = -\frac{1}{Y_A}\mu_A\left(\frac{S_{NH}}{S_{NH}+K_{NH}}\right)\left(\frac{S_O}{K_{OA}+S_O}\right)X_{BA} \tag{6}$$

In Eq. (6), Y_A, μ_A, S_O, K_{OA} and X_{BA} are all constants. According to IAWQ NO.1 model, K_{NH} was in the range of $0.6–3.6\,mg\,NH_3$-$N\,L^{-1}$. During the test period, at the majority of time, NH_3-N concentration was far bigger than K_{NH}, therefore, Eq. (6) can be written as:

$$\frac{dS_{NH}}{dt} = -k \tag{7}$$

It can be seen from Eq. (7) that ammonium decreased in a linear way during nitrification period, which was in line with experimental result. According to test data, k value is estimated to be 6.74.

The mass balance equation for $NO_3{}^-$-N is:

$$\frac{dS_{NO_3}}{dt} = \left(\frac{dS_{NO_3}}{dt}\right)_{nitrification} + \left(\frac{dS_{NO_3}}{dt}\right)_{de\text{-}nitrification} \tag{8}$$

$NO_2{}^-$-N was always in a low level during experimental period, and it was assumed that ammonium was converted to nitrate com-
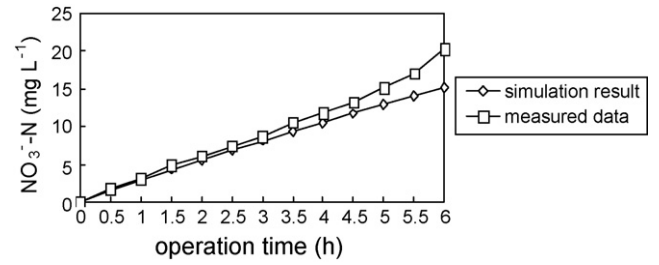

Fig. 10. Comparison of nitrate between measured data and calculated result.

pletely in nitrification process. Therefore, Eq. (9) can be obtained:

$$\frac{dS_{NO_3}}{dt} = -\frac{dS_{NH_3}}{dt} + \left(\frac{dS_{NO_3}}{dt}\right)_{de\text{-}nitrification} \tag{9}$$

For de-nitrification process:

$$\left(\frac{dS_{NO_3}}{dt}\right)_{de\text{-}nitrification} = -\frac{1-Y_H}{2.86Y_H}\mu_H X_{BH}\left(\frac{S_S}{K_S+S_S}\right)\eta_g$$
$$\times \left(\frac{K_{OH}}{K_{OH}+S_O}\right)\left(\frac{S_{NO_3}}{K_{NO_3}+S_{NO_3}}\right) \tag{10}$$

In Eq. (10), Y_H, μ_H, S_O, K_S, K_{OH}, η_g and X_{BH} are all constants, during the experiment, a certain organics was fed into reactor to supply carbon source for de-nitrification, and the organics was kept in a limited range. For K_S was usually about $20\,mg\,L^{-1}$, and is far lower than S_S, therefore, the item of $S_S/(K_S+S_S)$ can be regarded as constant. On this base, Eq. (11) can be obtained:

$$\frac{dS_{NO_3}}{dt} = k - A\left(\frac{S_{NO_3}}{K_{NO_3}+S_{NO_3}}\right) \tag{11}$$

Solving Eq. (11), and the following Eq. (12) can be deduced:

$$t = \frac{S_{NO_3}}{k-A} + \frac{K_{NO_3}}{k-A}\ln\left[\frac{AK_{NO_3}}{AK_{NO_3}+(k-A)S_{NO_3}}\right] \tag{12}$$

Experimental date was used to simulate Eq. (12), and constant A and K_{NO_3} were simulated to be 4.82 and 4.3, respectively.

In this kinetic model, nitrate saturation coefficient K_{NO_3} was $4.3\,mg\,L^{-1}$, far bigger than that in conventional single-sludge wastewater treatment system. For the implementation of SND was dependent on the formation of micro-aerobic and anoxic environment, there was a lower nitrate concentration in anoxic zone than in bulking solution due to the limitation of mass transfer. Therefore, under same bulking nitrate concentration, compared with single-sludge system, de-nitrification takes place slower for SND.

Compared simulation result with measured data is shown in Fig. 10. It is found that the kinetic model can simulate SND with considerable accuracy.

4. Conclusions

The effect of DO, F/M ratio, C/N ratio and pH on simultaneous nitrification and de-nitrification in MBR was studied. Under the experimental raw water and DO of $0.8\,mg\,L^{-1}$, $1.5\,mg\,L^{-1}$, $3\,mg\,L^{-1}$ and $5\,mg\,L^{-1}$, respectively, the average removal for COD was 92.27%, 92.48%, 92.02% and 94.73%, respectively. As to NH_3-N, the removal increased with DO when DO was lower than $1.5\,mg\,L^{-1}$, and the removal was almost independent of DO when DO was over $1.5\,mg\,L^{-1}$. In addition, it was found that a low DO concentration was advantageous to SND on condition that nitrification was not inhibited, and mean removal for TN was 86.58%, 77.53%, 65.33% and 54.21%, respectively when DO was $0.8\,mg\,L^{-1}$, $1.5\,mg\,L^{-1}$, $3\,mg\,L^{-1}$ and $5\,mg\,L^{-1}$, respectively. Experimental results showed that F/M

ratio and C/N ratio had positive effects on SND. To obtain an excellent SND, pH should also be controlled at a suitable range.

Based on the conventional activated sludge mathematical model, a deduction was conducted to explain that mineralization and nitrification could proceed simultaneously, and illustrated that SND could take place in one reactor from the theoretical aspect. Therefore, it was proved that high concentration of organics in influent was effective in improving performance of SND.

In addition, a kinetic model for SND was also constituted. It was found that the simulation nitrate saturation coefficient K_{NO_3} was much higher than that in a single-sludge wastewater treatment system due to the limitation of mass transfer. Under the same bulking nitrate concentration, compared to single-sludge system, de-nitrification takes place slower for SND.

Acknowledgments

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