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EFFECT OF A DENITRIFYING BIOFILM ON NITRIFICATION IN A DOUBLE-MEMBRANE SYSTEM FOR SIMULTANEOUS NITRIFICATION AND DENITRIFICATION

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ABSTRACT

The effect of a denitrifying biofilm on nitrification in a double-membrane simultaneous nitrification/denitrification system is studied in this paper. The nitrification rates in this system were found to be higher than those in the nitrification-only reactor. Under alkalinity-limiting conditions, system produced a higher nitrification rate when the denitrifying biofilm was fed with a denser methanol. In contrast, the system produced a lower nitrification rate when the denitrifying biofilm was fed with a rarer methanol in a sufficient amount of alkalinity. Since nitrification and denitrification simultaneously occur in an inorganic, anoxic bulk environment, and alkalinity is recovered from the denitrifying side of the tank. Results show the methanol concentration in the denitrifying biofilm had an obvious effect on both the denitrifying rates and alkalinity yield rates. The observations provide an approach to operate this system more flexible.

INTRODUCTION

Nitrogen removal by biological processes from wastewater usually occurs in two stages: aerobic nitrification and anoxic denitrification. In nitrification, the ammonium is transferred to nitrite/nitrate, which is then reduced to nitrogen gas during denitrification [1]. This conventional two-stage nitrogen removal system has many disadvantages [2]. First, separating the nitrification and denitrification units requires too much space and is a complex operation [3]. Second, the residual organic carbon in the nitrification reactor must be kept under a low level [4], making an additional carbon source necessary for the further denitrification [5]. Third, the addition of alkalinity is waste because it is consumed in the nitrification reactor and produced in the denitrification reactor. Most of these disadvantages result from differences of process performance between nitrifying and denitrifying bacteria.

It appears that combining nitrification and denitrification in a single reactor can decrease the overall reaction time and recover the partial alkalinity from denitrification, which is necessary to nitrification. However, it is difficult to combine these two groups of microorganism involved in a single reactor because of their contrary habitats.

Being autotrophs, nitrifiers need an inorganic water environment to grow up. Heterotrophs, on the other hand, have a higher growth rate than autotrophs and can outgrow autotrophs in nutrient-rich environments[6,7]. In other words, organic carbon enhances autotrophic denitrification but inhibits nitrification. From another standpoint, oxygen is necessary for nitrification but decreases denitrification efficiency due

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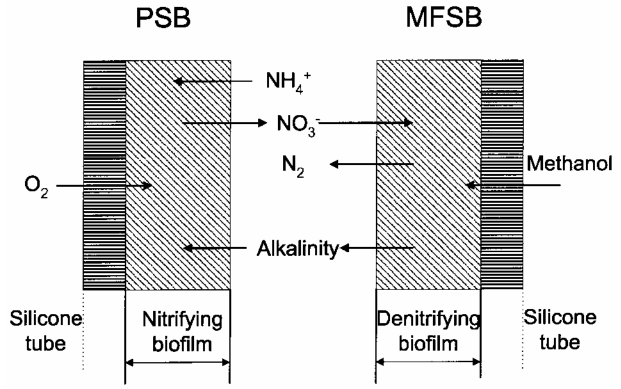

Fig. 1. Interactions between the PSB (nitrifying biofilm) and MFSB modules (denitrifying biofilm) in the novel simultaneous nitrification/denitrification system.

to competition for electron acceptors with nitrate and nitrite-nitrogen [8-11]. It can be concluded that simultaneous nitrification and denitrification can be available only if the problems of oxygen and organic carbon can be overcome.

In our earlier work, a simultaneous nitrification/denitrification system was developed [12]. This system contains two types of membrane bioreactors (MBRs) in a single tank. The nitrifying MBR, named permeable-supported biofilm (PSB) reactor, was developed by Timberlake *et al*[13]. The other MBR in the same tank, termed membrane-feeding substrate bioreactor (MFSB), was designed for denitrification in another work [14]. Both of these two MBRs diffuse substrate across the silicon tubular membrane to the biofilms formed on the outside surface of the tubes, thereby minimizing the interference between the nitrifying and denitrifying biofilms. In the system described in this study, nitrification and denitrification simultaneously occur in an inorganic, anoxic bulk environment, and alkalinity is recovered from the denitrifying side of the tank. Figure 1 shows the interaction between both the PSB and MFSB in this system. In this study, the effects of the MFSB on the PSB were studied and discussed. Under different operational conditions, the factors and mechanisms of which affect the system nitrification rate were investigated.

MATERIALS AND METHODS

Synthetic Wastewater

The mineral solution per liter of water contained KH_2PO_4 (8.5 mg), K_2HPO_4 (21.75 mg), $Na_2HPO_4.7H_2O$ (33.4 mg), $CaCl_2.2H_2O$ (27.5 mg), $MgSO_4.7H_2O$ (22.5 mg), and $FeCl_3.6H_2O$ (0.25 mg). Different amounts of $NaHCO_3$, ammonium sulfate and sodium nitrate were applied in different runs (Table 1).

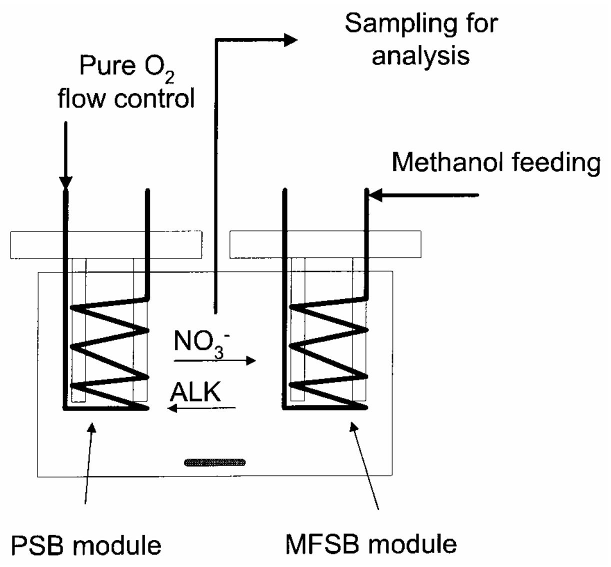

Fig. 2. Apparatus for double-membrane simultaneous nitrification/denitrification system under a batch-scale.

Membrane-feeding Substrate Bioreactor (MFSB)

The MFSB was obtained from an earlier work (Chang and Tseng, 1998). The contents of the reactor were mixed with a magnetic stirrer by a speed of 100-150 rpm. A silicone rubber tube (1.5 mm [i.d] and 2.5 mm [o.d] by 6 m long, surface area is 7.4×10^{-6} m^2) obtained from Fuji Systems Co. (Japan) was immersed and wound around the pillars in the reactor.

Permeable-support Bioreactor (PSB)

All the components of the PSB used in this study were similar to those of the MFSB illustrated in an earlier work [14], but the fed substrate was changed from methanol solution to pure oxygen. In the PSB, pure oxygen flowed into the silicon tube as the sole oxygen source for nitrification.

Experimental Procedures

The PSB and MFSB must first be incubated individually. The PSB was inoculated with activated sludge used for treatment of livestock waste. A mineral solution containing ammonium sulfate and alkalinity was used to enrich the nitrifiers. When the bulk DO was lower than 0.2 mg per liter, the biofilm on the membrane was considered thick enough to resist oxygen diffusion from the tube side. Before combining the PSB with the MFSB in the same reactor, a batch test for nitrification in the PSB was performed. After, the PSB was placed with the MFSB in the same reactor for simultaneous nitrification/denitrification tests

Table 1. Summary of experimental conditions.

Run no.	Nitrogen in substrate (mg/L)	Alkalinity added	Carrier gas for PSB	Methanol conc. in MFSB (COD)
1	NO_3^--N = 10	0.5 g/L $NaHCO_3$	pure oxygen	30 g/L
2				14 g/L
3				7 g/L
4	NH_4^+-N = 50	No	pure oxygen	30 g/L
5				14 g/L
6			air	30 g/L

(Fig. 2). The gas and methanol solution were fed to the silicon tube at 15 ~ 20 mL per min and 30 mL per min for the PSB and MFSB, respectively. All batch tests were controlle at 24 ± 2°C. Several experimental runs were performed under varying conditions (Table 1).

Analysis

The electrode method was used for pH, DO (WTW, Germany), and ORP (Broadley James Co., U.S.A.) measurements. Nitrate and nitrite were measured in an ion chromatograph analyzer (Alltech, U.S.A.). The procedures in Standard Method [15] for measuring COD, ammonium nitrogen, and alkalinity were followed.

RESULTS AND DISCUSSION

Denitrification in the MFSB-only Reactor

In our previous work, the results obtained in batch denitrifying reactors using a new carbon adding method have been discussed. The MFSB supplied the organic carbon (methanol) to a denitrifying biofilm by diffusing across the silicone membrane which biofilm formed on the other side. The batch tests showed that the residual COD could be controlled under 50 mg/L during denitrifying period. The denitrification rate of the MFSB were 2.0-3.5 g and 4.9-6.0 g NO_3^--N/m^2-d while the 14 g and 30 g methanol per liter flowed into the silicone tube, respectively [14]. Denitrification rates in MFSB are proportional to the methanol concentration in the silicone tubes rather than initial nitrate concentration in the bulk phase.

Nitrification in the PSB-only Reactor

Initially, an external alkalinity source was not added in the PSB batch test. The natural alkalinity of the tap water was the only alkalinity source (ca. 40-70 $CaCO_3$ mg per liter). Because of the limited alkalinity, the bulk pH dropped rapidly and nitrification did not occurred.

After adding 0.5g of $NaHCO_3$ as the additional alkalinity source into the PSB reactor (Table 1, runs 1-3), nitrification occurred. Figure 3 shows the pH, DO, nitrite, and nitrate variations along with the time course of the PSB-only reactor. The initial DO value was high because the synthetic wastewater was stirred in the open tank. The bulk DO then dropped when nitrification began. This indicated that either the oxygen in the bulk phase or diffused from the aerated tube was utilized by the nitrifiers (biofilm). After nitrification was completed, the amount of diffused oxygen was greater than that needed by the biofilm, causing an "oxygen breakthrough," which was similar to the "COD breakthrough" phenomenon in the MFSB observed in an earlier study [14]. In other words, the PSB can maintain low bulk DO during the nitrification period. Nitrite was not accumulated under this low DO condition.

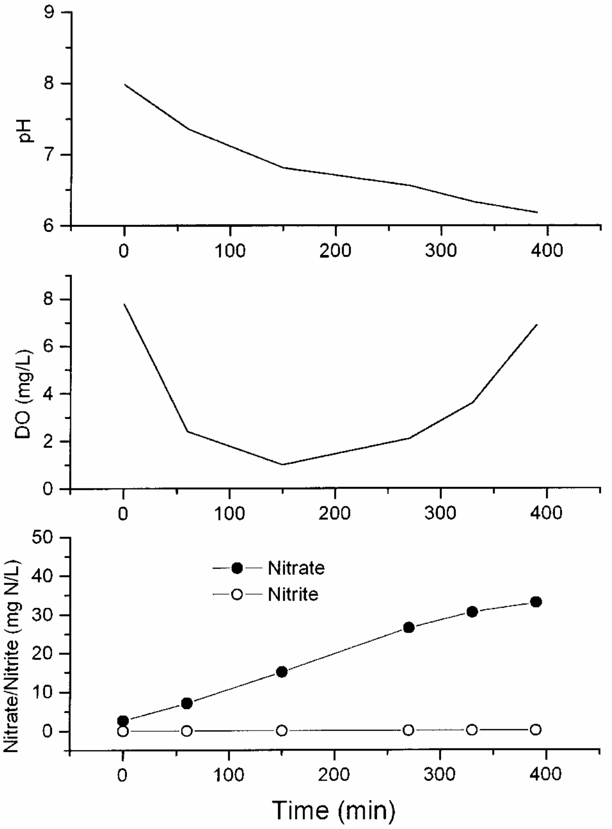

Fig. 3. pH, DO, nitrate, and nitrite profiles in the nitrification-only bioreactor (feeding pure oxygen into the PSB).

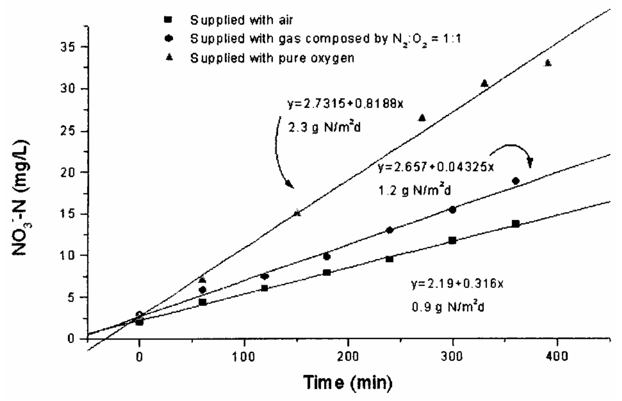

Fig. 4. Nitrification rates obtained from feeding different gases in the PSB-only nitrification reactors.

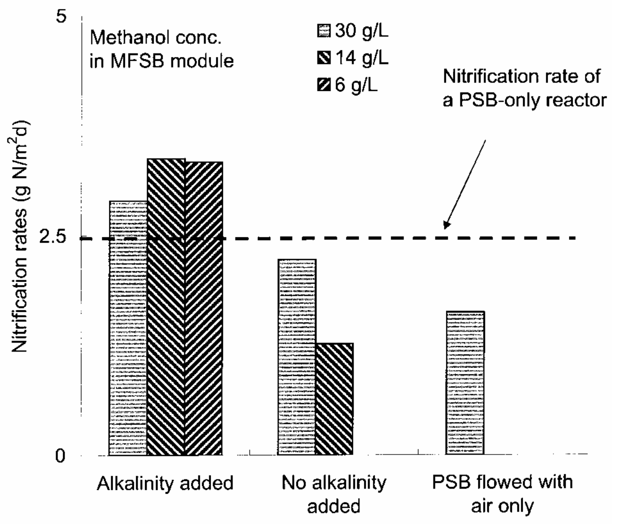

Fig. 5. Nitrification rates of different controlled conditions.

In the PSB nitrifying system, the nitrification rate is proportional to the partial pressure of oxygen of the carrier gas in the silicon tubes. Figure 4 shows that higher nitrification rates were obtained with a higher partial pressure of oxygen in the silicon tube. Thus, the oxygen diffusion was a limiting factor of nitrification in this system.

Total Nitrogen Removal in the Double-membrane Nitrification/Denitrification Bioreactor

In the double-membrane system, the PSB and MFSB modules are combined for simultaneous nitrification/denitrification. The nitrification rates in this system were evaluated with comparison to the PSB-only reactor. Pure oxygen or air was supplied into the silicone tube of the PSB to obtain the maximum efficiency of total nitrogen removal under different experimental conditions.

Figure 5 shows the nitrification rates for different conditions in this system. Nitrification was enhanced by the MFSB module, which produced the extra alkalinity. In the case of alkalinity addition, the nitrification rates ranged between 2.9 ~ 3.4 g N per m^2 of membrane surface area per day (Fig. 5, alkalinity-added series), which is greater than that in the PSB-only reactor (2.5 g N per m^2 of membrane surface area per day, horizontal dashed line in Fig. 5). Compared to the fact that nitrification cannot occur without the addition of alkalinity in a PSB-only reactor, this system has an acceptable nitrification rate without external alkalinity addition.

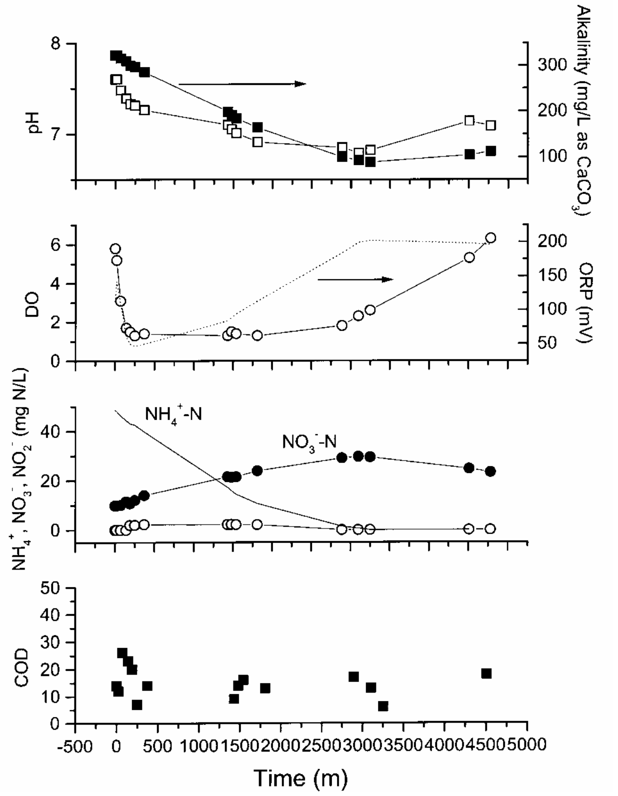

Fig. 6. pH/Alkalinity, DO/ORP, nitrate/nitrite and residual COD profiles in the double-membrane bioreactor (methanol concentration in the denitrifying biofilm is 30 g/L as COD).

Obviously the alkalinity produced by the denitrifying biofilm enhances the nitrification rate. Since alkalinity is a significant factor in nitrification [16], alkalinity consumption in the double-membrane system was significantly lower than the theoretical value given for the nitrification-only system [12]. A comparison of the nitrification rates (Fig. 5) shows that the nitrification rates were enhanced by the addition of an external alkalinity source. It is suggested that alkalinity can be recovered from the denitrification region to the nitrification region in this system. When an external alkalinity source was not added, relatively higher nitrification rates were found in the system that had a higher methanol concentration in the MFSB module (Fig. 5). Since a higher methanol concentration in the tube of the MFSB produces a higher denitrification

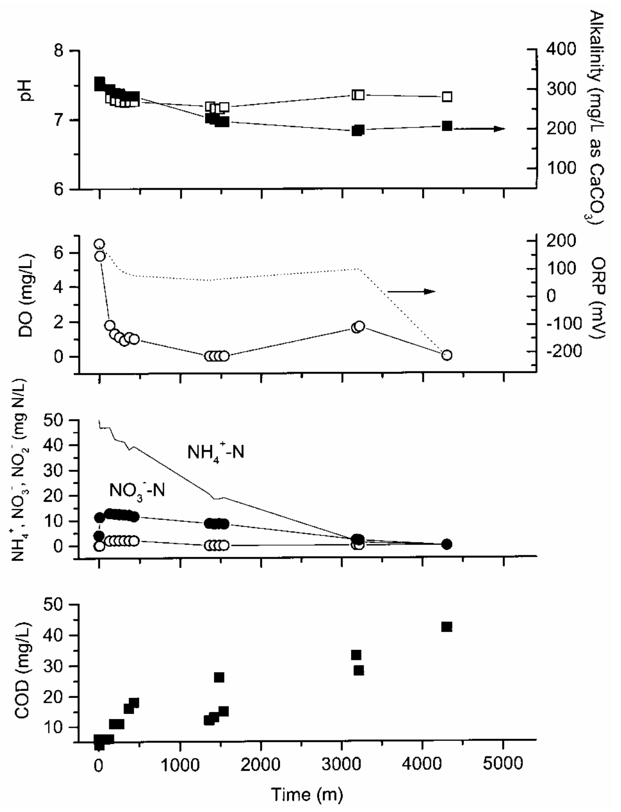

Fig. 7. pH/Alkalinity, DO/ORP, nitrate/nitrite and residual COD profiles in the double-membrane bioreactor (methanol concentration in the denitrifying biofilm is 14 g/L as COD).

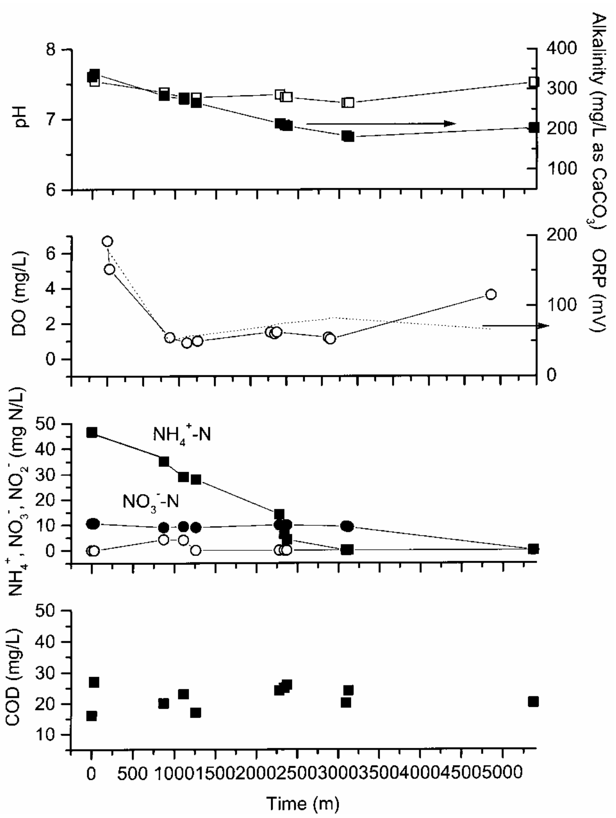

Fig. 8. pH/Alkalinity, DO/ORP, nitrate/nitrite and residual COD profiles in the double-membrane bioreactor (methanol concentration in the denitrifying biofilm is 7 g/L as COD).

rate [14], alkalinity will be supplied to the bulk phase more quickly.

Alkalinity Balance

Since the nitrification and denitrification occur simultaneously in the same tank, the alkalinity produced during denitrification can supplied to the demand for nitrification on the PSB module. The alkalinity consumption during nitrification was calculated that 3.15 g of alkalinity (as $CaCO_3$) is consumed for removing 1 g of ammonium-nitrogen while the methanol concentration is 30 g/L as COD in the denitrification module illustrated in Fig. 6 (run 1, Table 1). Figure 7 and Fig. 8 (run 2 and run 3, Table 1) show 3.25 and 4.51 g of alkalinity (as $CaCO_3$) are consumed for removing 1 g of ammonium-nitrogen while the methanol concentration are 14 and 7 g/L as COD in the denitrification module, respectively. Since theoretical ratio is 7.14 g of alkalinity (as $CaCO_3$) are consumed for nitrifying 1 g of ammonium-nitrogen, and 3.57 g of alkalinity (as $CaCO_3$) are yielded per denitrifying 1 g of nitrate-nitrogen. Theoretically the alkalinity demand for removing 1 g of total nitrogen (simultaneous nitrification and denitrification) is 3.57(= 7.14 -3.57) g as $CaCO_3$. Thus suggesting the denitrifying rates are faster than nitrifying rate at run 1 and run 2 (Table 1) due to the alkalinity consumption (as $CaCO_3$) for removing 1 g of ammonium-nitrogen are lower than 3.57, the theoretical value for removing 1 g of total nitrogen (simultaneous nitrification and denitrification). Those results are supported by the nitrate accumulation against the reaction time in Fig. 6 and Fig. 7. Similarly the denitrifying rate is slower than nitrifying rate on run 3 (Table 1) due to the alkalinity consumption (as $CaCO_3$) for removing 1 g of ammonium-nitrogen is greater than 3.57, and the nitrate concentration decreased with time in Fig. 8.

In a simultaneously nitrifying and denitrifying bioreactor, the operations will shift to complex when the nitrifying and denitrifying rates very imbalance. While the nitrifying rates are greater than denitrifying rates, the nitrate or nitrite will accumulate in the bioreactor and the alkalinity demand should be concerned. Otherwise, while the denitrifying rates are greater then nitrifying rates, the COD breakthrough will occur due to the nitrate exhausted. Adjusting the methanol concentration in the MFSB module will not only change the denitrifying rates but also change the alkalinity yield, that provide a alternative approach for operating this new system.

CONCLUSIONS

This study presents the effect of a denitrifying biofilm on nitrification in a novel nitrogen-removal system. The nitrification rates in this system were found to be higher than those in the nitrification-only reactor. Under alkalinity limiting conditions, the system obtained a higher nitrification rate when the MFSB module was fed with a denser methanol. In contrast, the system obtained a lower nitrification rate when the MFSB was fed with a lower methanol under sufficient amounts of alkalinity. It can be concluded that the maximum nitrification rate can be obtained by adjusting the methanol concentration under different alkalinity conditions. Besides the advantages of saving space and alkalinity requirement, this system also offers a more flexible operation.

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同時硝化脫硝之雙薄膜系統中脫硝生物膜對硝化反應之影響

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關鍵詞：硝化、脫硝、薄膜生物反應槽、薄膜式基質添加生物反應槽 (MFSB)

摘　　要

本研究群先前曾開發一新式薄膜反應系統，該生物薄膜反應系統爲一雙薄膜之同時硝化脫硝反應系統，可在單一反應槽體中，同時完成硝化脫硝反應。本研究目的在探討該反應系統中，同時存在之硝化生物膜以及脫硝生物膜彼此間之相互反應，期能更能瞭解該生物反應系統之特性。研究結果發現，與單槽硝化反應槽相較之下，脫硝生物膜對於硝化生物膜之硝化速率有明顯之促進作用。在鹼度限制的條件之下，供應高濃度甲醇（碳源）的脫硝生物膜可有效促進系統整體之硝化速率。而在鹼度充裕的條件之下，脫硝端所供應的甲醇濃度高低則對系統硝化速率影響不大。由於本雙薄膜系統的特性是硝化、脫硝生物膜皆在一無機、無氧的條件下同時進行硝化、脫硝反應，因此，脫硝生物膜所產生的鹼度可適度補充硝化反應所需之鹼度。結果指出，脫硝生物薄膜端所添加的甲醇濃度不僅影響脫硝速率，亦會影響硝化速率。故控制脫硝之甲醇濃度將可迅速且具彈性地進行本雙薄膜反應系統之操作。