Biological nitrogen removal from plating wastewater by submerged membrane bioreactor packed with granular sulfur

Jinyoung Moon, Yongwoo Hwang, Junbeum Kim and Inho Kwak

ABSTRACT

Recent toughened water quality standards have necessitated improvements for existing sewer treatment facilities through advanced treatment processes. Therefore, an advanced treatment process that can be installed through simple modification of existing sewer treatment facilities needs to be developed. In this study, a new submerged membrane bioreactor process packed with granular sulfur (MBR-GS) was developed and operated to determine the biological nitrogen removal behaviors of plating wastewater containing a high concentration of NO₃⁻. Continuous denitrification was carried out at various nitrogen loading rates at 20°C using synthetic wastewater, which was comprised of NO₃⁻ and HCO₃⁻, and actual plating wastewater, which was collected from the effluent water of a plating company called ‘H Metals’. High-rate denitrification in synthetic plating wastewater was accomplished at 0.8 kg NO₃⁻-N/m³·day at a nitrogen loading rate of 0.9 kg NO₃⁻-N/m³·day. The denitrification rate further increased in actual plating wastewater to 0.91 kg NO₃⁻-N/m³·day at a nitrogen loading rate of 1.11 kg NO₃⁻-N/m³·day. Continuous filtration was maintained for up to 30 days without chemical cleaning with a transmembrane pressure in the range of 20 cmHg. Based on stoichiometry, SO₄²⁻ production and alkalinity consumption could be calculated theoretically. Experimental alkalinity consumption was lower than the theoretical value. This newly proposed MBR-GS process, capable of high-rate nitrogen removal by compulsive flux, is expected to be applicable as an alternative renovation technique for nitrogen treatment of plating wastewater as well as municipal wastewater with a low C/N ratio.

Key words | denitrification, granular sulfur, plating wastewater, stoichiometry, submerged membrane bioreactor

INTRODUCTION

Due to eutrophication and the phenomenon of red tides, regulatory standards concerning nutrient salts for effluent water have steadily become stricter, which has increased the need for the removal of nutrient salts (Wu et al. 2009). Biological nitrification and denitrification processes for sewage and wastewater treatment have been applied in numerous fields due to their economical and environmentally friendly properties compared to physical/chemical treatment processes (Yang & Zhang 1995; Baetens et al. 1999; Vela et al. 2015). Activated sludge process is the most representative type of process. Few sewage treatment facilities in Korea have been constructed with integrated advanced treatment processes from the beginning of the design phase, and most are operated based on standard activated sludge methods. However, recent toughened water quality standards have necessitated improvements for existing sewer treatment facilities through advanced treatment processes. Therefore, an advanced treatment process that can be installed through simple modification of existing sewer treatment facilities needs to be developed.

Among various types of factory wastewater, plating wastewater is a representative high-nitrogen concentration wastewater. Plating wastewater commonly contains highly toxic cyanide, cyanide complexes and metal ions, which makes treatment a complex problem, as well as high biological oxygen demand (BOD), chemical oxygen demand...
(COD), suspended solids (SS), total solids, color, and turbidity, all of which make wastewater treatment a complex problem (Kim et al. 2005; Upadhy 2006). However, the deficient removal processes currently applied to plating wastewater are incapable of meeting the regulation limits for the total nitrogen concentration of effluent water. In addition, most of the plating companies in Korea are small-scale operations and thus face difficulties in installing high-cost facilities for nitrogen removal. To overcome the problem of incomplete removal of organic matters and nitrogen from sewage and wastewaters, autotrophic denitrification (Batchelor & Lawrence 1989) using sulfur as an electron donor without the addition of organic matters has been studied. To date, numerous studies on autotrophic denitrification using sulfur have been conducted internationally (Sahinkaya & Dursun 2012; Souza & Foresti 2013; Van Doan et al. 2013; Ramanathan et al. 2014; Wan et al. 2014; Zhang et al. 2015) as well as by the Korean research society (Byun et al. 2000; Lee et al. 2000, 2005, 2004; Chu et al. 2002; Oh et al. 2002; Yoon et al. 2010; Yoo et al. 2012; Tian et al. 2013; Ahn & Bae 2014; Moon & Lee 2014). In order to renovate existing sewer treatment facilities, concurrent studies (Korea Ministry of Environment & Korea Environmental Management Corporation 2004) on nitrification and denitrification in an aeration tank have been conducted by installing granular sulfur (GS)-packed bed inside an aeration tank. These GS-packed denitrification processes offer advantages such as simple installation and low costs for additional installation and operation. However, they also suffer shortcomings because the inflow of nitrified fluid into the inner packed bed is dependent on the agitation force inside the aeration tank, which causes limited flux and consequently only a limited improvement of nitrogen removal efficiency. Further, when wastewater is treated, the media in the GS-packed bed can leak. This paper proposes the installation of a separation membrane module on the inside of a GS-packed bed to create a forced flux of nitrified fluid into the packed bed, which will improve the nitrogen removal efficiency via autotrophic denitrification as well as prevent sulfur leakage into the packed bed.

Therefore, the plating wastewater was selected for this study.

For this purpose, we developed a submerged membrane bioreactor packed with GS (MBR-GS), which combines the biological membrane method and the separation method of autotrophic denitrification using GS. We experimented using both synthetic wastewater and actual plating wastewater in an attempt to develop a highly efficient and commercially applicable nitrogen removal process, by maximizing the nitrogen removal rate, $\text{SO}_4^{2-}$ production quantity, and alkalinity usage quantity.

### EXPERIMENTAL EQUIPMENT AND METHODS

#### Reactor configuration

A schematic diagram of the MBR-GS reactor used in this study is shown in Figure 1. A porous, cylindrical shape case was installed inside a square reaction tank made of acrylic and the surrounding area was filled with GS by positioning a hollow-fiber module at the center. The volume size of the reactor was $21,025 \text{ cm}^3$ (width $29 \text{ cm} \times \text{length } 29 \text{ cm} \times \text{height } 25 \text{ cm}$). The MBR-GS reactor had a height of $25 \text{ cm}$ and an outer diameter of $20 \text{ cm}$, whereas the diameter of the hollow-fiber module installed on the inside was $5 \text{ cm}$. The hollow-fiber module was designed in the shape of an ‘I’ in accordance with the characteristics and shape of the reactor. The module was made of polyethylene, with a membrane area of $0.2 \text{ m}^2$ and an average pore size of $0.4 \mu\text{m}$. To investigate the characteristics of the submerged membrane separation process, a pump with proper capacity for suction was installed in the outflow portion. To

![Figure 1](https://iwaponline.com/wst/article-pdf/74/4/805/458925/wst074040805.pdf)

**Figure 1** | Schematic diagram of submerged membrane bioreactor packed with MBR-GS.
determine the fouling of the membrane, a pressure gauge was installed between the hollow-fiber module and the proper capacity pump. As the electron donor, a particle size of 3–6 mm was used, as this size has previously been proven to maximize denitrification efficiency (Koenig & Liu 1997; Koenig & Liu 2001).

**Experimental method**

As influent waters, synthetic wastewater, comprised mainly of NO₃-N and bicarbonate, and actual wastewater were used. The latter was the discharge water from a plating company, ‘H Metals’, with similar properties to those of the synthetic wastewater. Table 1 presents the properties of the influent water. Almost no SS, organic matter or ammonia was present in the plating wastewater. The wastewater contained mainly nitric nitrogen.

To investigate the effect of nitrogen concentration loading in the synthetic and plating wastewaters on biological nitrogen removal, the experiments were conducted at the same hydraulic loading, a constant temperature of 20 °C, an inflow of about 24 L/day and an empty bed contact time (EBCT) of 8 hours for the GS-packed bed. The specific operating conditions, in accordance with concentration loading, are shown in Table 2.

Synthetic wastewater with a high nitrogen concentration was used to verify the denitrification rate of MBR-GS. KNO₃ was used as the nitrogen source for the synthetic loading, are shown in Table 2. Loading of nitric nitrogen gradually increased during the denitrification experiment. A pump was used to force the suction and release of the treated water, with an hourly flow rate of about 5(L/m²·hr) through 1 m² unit area of the separation membrane. In this case, fouling was observed. Fouling can reduce membrane performance due to the deposition of suspended and dissolved solids on the membrane surface or pores (Koros *et al.* 1996). To reduce membrane fouling (contamination and fouling of membranes causes higher energy usage, a higher cleaning frequency and a shorter membrane lifespan), any residual solid matter left over after membrane filtration in the center area was regularly removed. In the case of the transmembrane pressure reaching 20 cmHg, chemical cleaning was carried out using 1 M hydrochloric acid (HCL).

The sample analysis of influent and effluent waters was performed based on the method of the American Public Health Association (APHA, AWWA & WEF 1998) and the water pollution process test (Korea Ministry of Environment 2004). A pH meter (Orion Model 250A) was used. Titration method was used for alkalinity and the measurements were taken by titration up to pH 4.3. Negative ions such as NO₃⁻, NO₂⁻ and SO₄²⁻ were analyzed after filtration through a 0.45 μm membrane by using ion chromatography (Dionex, DX-500) with a column (Transgenomic, ICSep ANSC) for negative ion analysis and an attached conductivity detector (Waters, 432 Conductivity Detector).

---

**Table 1 | Composition of the synthetic and plating wastewaters as influent**

<table>
<thead>
<tr>
<th>Items</th>
<th>Synthetic wastewater</th>
<th>Plating wastewater</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.7–8.5</td>
<td>8.1–8.4</td>
</tr>
<tr>
<td>Alkalinity (mg/L)</td>
<td>440–1,320</td>
<td>150–280</td>
</tr>
<tr>
<td>TSS (mg/L)</td>
<td>–</td>
<td>&lt;10</td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>–</td>
<td>350</td>
</tr>
<tr>
<td>BOD₅ (mg/L)</td>
<td>–</td>
<td>&lt;10</td>
</tr>
<tr>
<td>NH₄-N (mg/L)</td>
<td>–</td>
<td>&lt;1</td>
</tr>
<tr>
<td>NO₃-N (mg/L)</td>
<td>100–300</td>
<td>360–390</td>
</tr>
<tr>
<td>NO₂-N (mg/L)</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Total Kjeldahl nitrogen (mg/L)</td>
<td>–</td>
<td>&lt;1</td>
</tr>
<tr>
<td>SO₄²⁻ (mg/L)</td>
<td>10–20</td>
<td>12,000–14,000</td>
</tr>
</tbody>
</table>

---

**EXPERIMENTAL RESULTS AND DISCUSSION**

**Nitrogen removal**

To evaluate the possibility of biological removal of nitric nitrogen from plating wastewater by using the MBR-GS process a denitrification experiment was conducted using synthetic wastewater with increased influent loading. After experimental verification of the high denitrification capability of MBR-GS for the synthetic wastewater, the same process was applied to actual wastewater.
In accordance with nitrogen influx loading, the phases were separated, and the nitric nitrogen concentrations of the influent water and effluent waters, in each phase, are shown in Figure 2. In examining Phases I–IV, in which synthetic wastewater was applied, the average nitric nitrogen concentration of effluent water in Phase I was 5.5 mg/L, and the removal efficiency was about 95%. The average nitric nitrogen concentrations of the effluent water in Phases II and III were 6.4 mg/L and 10.3 mg/L, respectively. The accompanying removal efficiencies were almost constant at about 96% and 95%, respectively, despite the increase in influent water concentration loading. Although the removal efficiency decreased slightly to 92% in Phase IV, in which influx loading was increased, the denitrification efficiency remained high. This result verifies that GS more than sufficiently fulfilled its role as an electron donor in autotrophic denitrification.

Meanwhile, in examining Phases V–XII, in which actual plating wastewater was used, the average nitric nitrogen concentration in effluent water was below 10 mg/L with average removal efficiencies of 79, 82, 88 and 90% in Phases V, VI, VII, and VIII, respectively. Starting in Phase IX, the nitric nitrogen concentration in effluent water exceeded 10 mg/L. In Phase XII, with a plating wastewater percentage of 100%, the nitric nitrogen concentration in effluent water was 66 mg/L, indicating degradation in the quality of effluent water. Starting in Phase IX, the average removal efficiencies of nitric nitrogen in Phases IX, X, XI and XII were 90, 88, 87 and 82%, respectively. Here, the nitrogen removal efficiency was maximized when the nitric nitrogen concentration in the influent water was 100 mg/L. This result can be attributed to the fact that the sulfur-utilizing microorganisms in autotrophic denitrification were affected by toxic substances present in the introduced plating wastewater. After about 20 days of operation, the microorganisms had adapted to the toxic substances, and efficiency was reduced due to high loading, and after Phase VIII these effects were relatively less important.

Sulfur-utilizing autotrophic denitrification can be performed by denitrifying sulfur bacteria under autotrophic and heterotrophic conditions. The first study using this process was conducted by Beijerinck (1920). The autotrophic denitrification process involves the reduction of NO$_3^-$.
and/or NO₂ into N₂ using H₂ or sulfur compounds (S²⁻, S₂O³⁻, S₄O₆²⁻, SO₃²⁻) as electron donors, CO₂ and HCO₃⁻ as carbon sources, and sulfur-oxidizing bacteria (Beijerinck 1920; Koenig et al. 2005; Fernández et al. 2006). Driscoll (1976) reported that when thiosulfate and sulfide are used as electron donors, NO₃⁻ removal efficiency can reach 100%.

Further, Bisogni & Driscoll (1977) demonstrated the overall reaction equation for nitrite removal by autotrophic denitrification using thiosulfate and sulfide.

The rate of nitric nitrogen influx loading and the rate of removal during the operation of the MBR-GS process are shown in Figure 3. The influx loading graph showed almost no difference compared to the removal rate graph from Phase I, which was the experimental period of applying synthetic wastewater application, through Phase III.

However, in Phase IV, in which influx loading of 0.90 kg NO₃⁻-N/m³·day was applied, the gap started to increase slightly. Meanwhile, the influx loading during the experimental period when plating wastewater was applied ranged from 0.06 kg NO₃⁻-N/m³·day up to 1.11 kg NO₃⁻-N/m³·day, and the difference between the influx loading rate and nitrogen removal rate increased slightly as compared to the period of synthetic wastewater application.

The correlation between the denitrification and the influx loading, is shown in Figure 4. The denitrification rates are presented in terms of average values of influx loading, by phases. For synthetic wastewater, the rate increased from an initial stage influx loading of 0.3 kg NO₃⁻-N/m³·day to a maximum of 0.9 kg NO₃⁻-N/m³·day, and the accompanying removal rate increased to about 0.8 kg NO₃⁻-N/m³·day. The removal
efficiency remained above 95% up to an influx loading of 0.7 kg NO₃-N/m³·day, after which it gradually decreased as the loading increased. This result is similar to that of a previous study (Koenig & Liu 1997) on a sulfur-packed bed reactor (SPBR), which reported a maximum removal rate of 0.7 kg NO₃-N/m³·day. Nevertheless, in our study, based on the possible increase in removal rate even at influx loadings above 0.9 kg NO₃-N/m³·day, we surmised that the removal rate could increase beyond 1.0 kg NO₃-N/m³·day. Meanwhile, in the case of actual plating wastewater, at an influx loading of 1.11 kg NO₃-N/m³·day, the maximum removal rate was 0.91 kg NO₃-N/m³·day.

The SO₄²⁻ concentration in Phase XII, which was the application period of 100% plating wastewater, was about 13,000 mg/L. This result is 2.5 times higher than the 5,000 mg/L SO₄²⁻ concentration which influenced denitrification efficiency as reported by Claus & Kutzner (1985). Despite the expected inhibitory effects due to the high SO₄²⁻ concentration inside the reactor tank at 100% plating wastewater, no such inhibitory phenomenon was observed. However, the nitrogen removal rate was reduced due to increased influx loading. In their denitrification experiment after immersing GS in an aeration tank, Chu et al. (2002) reported a nitrogen removal rate of 0.59 kg NO₃-N/m³·day, which was somewhat lower than the result of our experiment. This difference can be attributed to the fluid not flowing freely into the GS-packed bed. In other words, a forced flux of nitrified fluid was induced in the MBR-GS process inside the GS-packed bed, which increased the chance of contact between the GS and nitric nitrogen. This resulted in a highly efficient nitrogen removal rate of 0.91 kg NO₃-N/m³·day, which was about two times higher than that of existing studies.

Change in alkalinity and sulfur ions

To act as a buffering agent for pH, which was reduced during the autotrophic denitrification reaction using GS, the alkalinity of the influent water was supplemented in the form of HCO₃⁻. Consequently, as shown in Figure 5, the pH of the influent water was maintained at above 8.0 throughout the entire experiment. However, the pH of the effluent water was reduced due to loss of alkalinity during the autotrophic denitrification reaction, i.e., the pH was reduced due to generation of hydrogen ions. The pH difference between the influent and effluent waters was higher in synthetic wastewater than in plating wastewater since actual wastewater, which is similar to plating wastewater, contains various ions that can supplement changes in pH in the influent water, unlike synthetic wastewater.

Changes in the alkalinity of the influent and effluent waters during the experiment are shown in Figure 6. When applying synthetic wastewater, the alkalinity of the influent water was adjusted in accordance with nitrogen influx loading, by phase, from about 500 mg/L to 1,200 mg/L. As a result, although the alkalinity of the influent water showed a slight increase according to the loading increase as well as a range of 200 mg/L to 400 mg/L, sufficient alkalinity needed for the denitrification reaction was achieved. Meanwhile, the alkalinity of the effluent water of the plating wastewater was initially about 200 mg/L, which was less than that needed for denitrification. Therefore, sodium bicarbonate was used to artificially supplement the alkalinity for denitrification of the plating wastewater. As influx loading increased, more alkalinity was consumed; however, excess alkalinity was present in the effluent water due to the sufficient supply of alkalinity. In the real wastewater, there exist several ions that can

![Figure 5](https://iwaponline.com/wst/article-pdf/74/4/805/458925/wst074040805.pdf)  
**Figure 5** | Changes in influent and effluent pH levels.  

Downloaded from https://iwaponline.com/wst/article-pdf/74/4/805/458925/wst074040805.pdf by guest
buffer the pH reduction during sulfur-utilizing autotrophic denitrification. Therefore, we think that the alkalinity of the real wastewater is sufficient. However, in the case of full-scale application of MBR-GS, we should take extra steps for alkalinity supplementation after analysis of wastewater characteristics.

The SO$_4^{2-}$ concentrations of the influent and effluent waters during the experiment are shown in Figure 7. The autotrophic microorganisms, which use GS, oxidize sulfur compounds into SO$_4^{2-}$ at the same time when returning oxidized nitric nitrogen into N$_2$. The SO$_4^{2-}$ concentrations of the influent water during the application of synthetic wastewater were below 20 mg/L in all phases, and the SO$_4^{2-}$ concentrations of effluent water increased proportionally to the quantity of nitric nitrogen removal as influx loading increased. When plating wastewater was applied, due to the high SO$_4^{2-}$ concentration contained in the influent water, SO$_4^{2-}$ concentrations in the effluent water increased in accordance with the plating wastewater percentage. In addition, as loading increased, the difference between the experimental measured SO$_4^{2-}$ concentrations and the calculated theoretical concentrations gradually increased. As a result, the quantity in Phase XII was about 1.36 times greater (3,660 mg SO$_4^{2-}$/L) than the theoretical concentration level (2,690 mg SO$_4^{2-}$/L). The SO$_4^{2-}$ concentration that occurs during denitrification using GS is directly linked to the amount of alkaline inputted during the treatment process; therefore, it acts as an important factor for determining operating costs. It is thus very important to accurately determine the consumption amount, denitrification amount and generated amount of SO$_4^{2-}$, as it would greatly assist in the design of actual process and operation.

As shown in Equation (1), in the denitrification reaction using GS, SO$_4^{2-}$ was generated proportionally in accordance with NO$_3^{-}$-N that is eliminated through the stoichiometric equation. In prior experiments, Batchelor & Lawrence (1978) proposed the following stoichiometric equation (Equation (1)). The generation ratio of sulfur ions via the proposed stoichiometric equation could be calculated as 7.54 g SO$_4^{2-}$/g NO$_3^{-}$-N. In the case of typical microorganisms, i.e., the equation of C$_5$H$_7$O$_2$N for the biological reaction seen in the stoichiometric equation, differences
are shown against the measured equations (Rittmann & McCarty 2000). In a study by Kleerebezem & Mendez (2002), who recently reviewed the thermodynamic efficiency of denitrification using GS, the molecular equation of *Thiobacillus denitrificans* could be expressed as \( \text{CH}_{1.8}\text{O}_{0.5}\text{N}_{0.2} \):

\[
\text{NO}_3^- + 1.1\text{S} + 0.76\text{H}_2\text{O} + 0.4\text{CO}_2 + 0.08\text{NH}_4^+ \\
\rightarrow 0.08\text{C}_6\text{H}_7\text{O}_2\text{N} + 0.5\text{N}_2 + 1.1\text{SO}_4^{2-} + 1.28\text{H}^+ 
\] (1)

Figure 8 shows the quantities of \( \text{SO}_4^{2-} \) generated as well as the alkalinity consumed for each gram of \( \text{NO}_3^-\)-N removed, expressed in terms of the average values for each phase. By using the above stoichiometric equation, the theoretical and actual values for the quantity of generated \( \text{SO}_4^{2-} \) were compared and examined. For synthetic wastewater, the initial difference was about 20%. As the operation of MBR-GS progressed, the quantity of generated \( \text{SO}_4^{2-} \) approached the theoretical level. Here, when the initial influx of \( \text{NO}_3^-\)-N was low, the large difference from the theoretical value can be explained by *Thiobacillus thiooxidans* oxidizing sulfur, using over 8 mg/L of dissolved oxygen present in the influent water (Lampe & Zhang 1999). Meanwhile, in the application of plating wastewater, the generated \( \text{SO}_4^{2-} \) ratio was 11.9 on average, which was about 30% higher than the theoretical value, and it showed a gradual increasing trend as the plating wastewater percentage increased. These results cannot be sufficiently explained by the sulfur oxidation reaction due to dissolved oxygen, which suggests the action of another generation mechanism. In general, when applying plating wastewater, oxidizing agents such as hydrogen peroxide, potassium permanganate, and chlorine are injected to remove any toxic chemicals such as cyanide present in the wastewater. The presence of residual oxidation materials after such treatment (Han et al. 1998) can be considered to have resulted in further oxidization of the GS inside the reaction tank.

In examining the consumed quantity of alkalinity in accordance with the \( \text{NO}_3^-\)-N removal quantity, average alkalinity values of 5.2 g/gN and 2.6 g/gN were consumed when applying synthetic and plating wastewaters, respectively. This result supports the possibility of additional oxidation of GS by the residual oxidation materials when plating wastewater was applied. Meanwhile, the differences between these values and the theoretical alkalinity-consumed quantity of 4.92 g/gN were due to the fact that although the measured alkalinity-consumed quantities were based on the total alkalinity, which was measured up to pH 4.5, the typical theoretical alkalinity-consumed quantities were limited to only generated \( \text{H}^+ \) ion and consumed-\( \text{HCO}_3^- \) quantities. According to the reaction equation, at the time of the autotrophic denitrification reaction using GS, \( \text{SO}_4^{2-} \) was generated in addition to \( \text{H}^+ \) while \( \text{CO}_2, \text{NO}_3^- \), \( \text{H}_2\text{S} \), and \( \text{HS}^- \) were consumed. As these substances exert buffering effects on pH (Stumn & Morgan 1996), when the actual wastewater was applied, the alkalinity-consumed quantities for the influent and effluent waters were lower than the theoretical values up to pH 4.5.

**Membrane pressure change and cleaning**

After denitrification, membrane filtration was conducted in order to remove any residual solids in the reaction fluid. In order to maintain constant flux over time, a suction-type constant-speed filtration operation was carried out. In general, membrane fouling is weighted over the operational period, which leads to an increase in pressure. In normal operations, when the pressure has reached a certain point,
the separation membrane’s filtration capacity needs to be restored by membrane cleaning. Figure 9 shows the changes in pressure over the experimental period. During the experiment, the membrane was chemically cleaned using 1 M HCL after disassembling the hollow-fiber module when the transmembrane pressure reached about 20 cmHg, as the amount of influent through the membrane decreased dramatically after approaching a pressure of about 20 cmHg. In the first operation, it took about 40 days for the transmembrane pressure to reach 20 cmHg. Although the separation membrane showed a filtration capacity similar to that in the initial stage after cleaning, the time to reach 20 cmHg was slightly reduced to about 35 days. If the MBR-GS process is applied to wastewater treatment facilities in Korea, the microorganism concentrations inside the biological reaction tank will increase due to heterotrophic microorganisms that consume organic matter, which in turn will proportionally increase the transmembrane pressure. Therefore, prior to applying MBR-GS to wastewater treatment, additional studies will be required on membrane issues that arise due to the presence of high-concentration solids.

CONCLUSIONS

In this study, MBR-GS was used to examine the biological removal characteristics of nitric nitrogen at high concentrations contained in plating wastewater. The experimental results supported the following conclusions.

1. High denitrification rates of 0.8 and 0.91 kg NO$_3^-$-N/m$^3$-day were achieved from synthetic wastewater, comprised of NO$_3^-$-N and bicarbonate, and from plating wastewater, under influx loadings of 0.9 and 1.11 kg NO$_3^-$-N/m$^3$-day, respectively.

2. In the GS-packed bed of MBR-GS, even at SO$_4^{2-}$ concentration above 17,000 mg/L, a normal biological denitrification reaction using GS was possible without any inhibitory phenomena due to the high SO$_4^{2-}$ concentration.

3. Based on the stoichiometry for the autotrophic denitrification reaction using GS, calculated using the microorganism molecular formula CH$_{1.8}$O$_{0.5}$N$_{0.2}$S$_{0.005}$, and a theoretical generation coefficient of 0.086, 4.92 g of alkalinity was consumed while 8.15 g of SO$_4^{2-}$ was generated during the removal of 1 g of NO$_3^-$-N.

4. In the continuous experiment using synthetic and plating wastewaters, 3.2 g and 2.6 g of alkalinity were consumed during the removal of 1 g of NO$_3^-$-N, respectively. These values were lower than the theoretical values, which can be attributed to the pH buffering action of the various ions present in the actual wastewater.

5. The theoretical SO$_4^{2-}$ concentration of 8.15 g/gN generated in the continuous experiment was almost attained in the synthetic wastewater experiment, compared to 11.9 g/gN in the plating wastewater experiment.

6. Use of MBR-GS for more than 30 days resulted in continuous operation at a transmembrane pressure below 20 cmHg without any chemical cleaning.

REFERENCES


APHA, AWWA & WEF 1998 Standard Methods for the Examination of Water and Wastewater. 20th edn. American
Public Health Association/American Water Works Association/Water Environment Federation, Washington, DC, USA.


Driscoll, C. T. 1976 Use of Thiosulfate and Sulfide as Electron Donor in Autotrophic Denitrification. MS thesis, Department of Civil and Environmental Engineering, Cornell University, Ithaca, NY, USA.


Korea Ministry of Environment & Korea Environmental Management Corporation 2004 *Collection of Excellent Case Studies of Improvement Methods for the Operation of Sewer Treatment Facilities*, Korea Ministry of Environment, Sejong-si, South Korea, pp. 29–35.


First received 26 January 2016; accepted in revised form 19 May 2016. Available online 1 June 2016