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A Submerged Membrane Bioreactor with Anoxic-oxic Recycle for the Treatment of High-strength Nitrogen Wastewater

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Abstract : Using the hollow fiber membrane module in a lab-scale membrane bioreactor, the anoxic-oxic (AO) process for nitrogen removal was operated for about one year. For the influent wastewater containing 1,200-1,400 mg l^{-1} of CODcr and 200-310 mg l^{-1} of nitrogen, this process achieved a high quality effluent of less than 30 mgCOD liter^{-1} and 50 mgN liter^{-1}. The removal rate of organics was above 98% at a loading rate larger than 2.5 kgCOD m^{-3} d^{-1}. When the internal recycle from the oxic to the anoxic reactor changed from 200 to 600% for the influent flow rate, the nitrogen removal rate increased from about 70 to 90% at a loading rate of 0.4 kgT-N m^{-3} d^{-1}. The initial increase of transmembrane pressure (TMP) was observed after a 4-month operation while maintaining the flux and MLSS concentration at 7-9 l m^{-2} h^{-1} and 6,000-14,000 mg l^{-1}, respectively. The TMP could be maintained below 15 cmHg for an 8-month operation. The chemical cleaning with an acid followed by an immersion in an alkali solution gave better cleaning result with the membrane operated for 10 month rather than that only by an alkali immersion.

Keywords : *submerged membrane bioreactor, nitrogen removal, anoxic-oxic process, hollow fiber membrane*

1. Introduction

Recently, there are growing interests in removing nitrogen from wastewater in order to reduce the effect of algae bloom in the receiving water. An activated sludge process, which is used most widely in Korea, is fairly efficient in terms of organic removal. However, this method is not suitable for removing nutrients from the wastewater stream. The removal of nitrogen and/or phosphorous can be achieved using Bardenpho, A/O, A^2/O, UCT, and VIP processes. While many studies using above processes have been performed for the nutrient removal, those are mainly concentrated on the treatment of a low-strength wastewater such as municipal sewage. A high concentration of nitrogen is contained in many industrial wastewaters, for example, tannery, food processing and chemical wastewaters. The design and operational experiences for the above mentioned processes, which has been operated mainly for sewage treatment, can not be easily applied for the treatment of high-strength nitrogen wastewater. Moreover, the treatment efficiency in terms of a reactor volume is relatively low because those processes are based on the continuous stirred tank reactors and the gravitational settling tanks

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of low efficiency.

Microorganisms responsible for nitrogen removal typically have a slow growth rate and are very sensitive to the changes of their surrounding environment such as pH and temperature. With the conventional processes (i.e. activated sludge process), a difficulty may arise in maintaining high concentration of biomass in order to accommodate for the slow-growing bacteria. The use of a membrane allows controlling the sludge retention time (SRT) by providing a complete solid/liquid separation. Hence a better nitrogen removal efficiency can be achieved by maintaining a high concentration of slow-growing bacteria, which can especially affect on the treatment of high-strength nitrogen wastewater.

A membrane technology has been introduced for a solid-liquid separation in a biological wastewater treatment system from 1960s. The advantages of membrane processes include the minimum sludge wastage by maintaining a low food-to-microorganism (F/M) ratio and the reduction of plant size due to a higher biomass concentration in the reactor. Several studies related with membrane bioreactor (MBR) system have succeeded to obtain high degree of treatment in terms of organic and/or nitrogen removal [1-10]. In terms of nitrogen removal, operation through the inclusion of a separate anoxic zone is common in current nutrient removal processes although intermittent aeration systems have also been developed in MBR systems [4-6]. Using intermittent aeration method, various removal efficiency of nitrogen was reported in a side-stream MBR treating synthetic wastewater [4]. More than 75% nitrogen removal occurred in operational conditions, in which the BOD/TKN ratio of the influent was higher than 12.1 and the TKN loading was lower than 0.12 g g^{-1} d^{-1}. The nitrogen removal through a separate anoxic reactor has also been reported in MBR systems [9-10], but the quantitative data on the variables such as the size of anoxic reactor and the percentage of internal recycle are not fully available. Moreover, many studies have been carried out with a low-loaded nitrogen waste water around 0.1-0.2 kg m^{-3} d^{-1}, which may not fully demonstrate the high volumetric efficiency of the membrane bioreactor for nitrogen wastewater treatment.

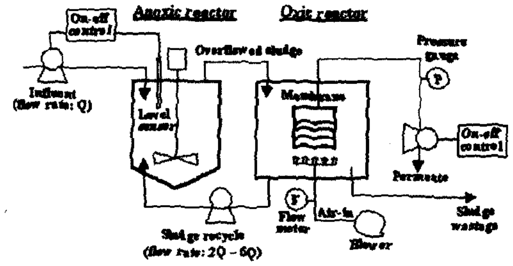

Fig. 1. Scheme of submerged membrane bioreactor system.

In this study, a submerged membrane bioreactor composed of hollow fiber membrane module was investigated to obtain the design parameter for membrane bioreactor system applied to the treatment of highly loaded nitrogen wastewater. A synthetic wastewater was used throughout this study to vary the nitrogen concentration in the influent. Also, the long-term performance of membrane, which is most important factor for the evaluation of process economics, was studied including various washing methods of fouled membrane. During the operation, the variation of sludge volume index (SVI) was also monitored how the sludge settlability might affect the membrane performance.

2. Materials and Methods

2.1. Experimental System

The process scheme of membrane bioreactor system is shown in Figure 1. The system consists of two reactors; an anoxic and an aerated oxic reactor with submerged hollow fiber membrane module. The two reactors had a total operating volume of 20 liter. The hollow fiber membranes (hydrophilized polyethylene, pore size of 0.1 mm, Mitsubishi Rayon Co. Ltd., Japan) were brought together in a so-called membrane module, which had the filtration area of 0.2 m^2. The membrane module was installed vertically inside the oxic reactor and connected to a suction

Table 1. Operation Conditions of Hollow Fiber Membrane Bioreactor System

Anoxic reactor volume (l)	5 - 12
Oxic reactor volume (l)	8 - 15
HRT in whole system (hr)	11 - 15
SRT (d)	20 - 30
Recycle ratio from oxic to anoxic reactor over influent flow rate (Q)	2Q - 6Q
Air flow rate into oxic reactor (L/min)	15 - 20
Mode of suction pump	Intermittent suction
MLSS (mg/L)	6,000 - 14,000
Temperature (°C)	20 - 27

pump. The pressure gauge was installed in order to monitor the variation of the transmembrane pressure between the membrane module and a suction pump. To maintain a constant level in the reactors, a peristaltic pump providing influent wastewater and a level sensor were used in an anoxic reactor. By gravity, the overflowed sludge was led to the oxic reactor and recirculated with a peristatic pump to the anoxic reactor. The air was supplied to an oxic reactor through the diffuser below the submerged membrane module, which was made from a 2 cm diameter tube with 3 mm openings so that the coarse bubble would be produced. The air functions in supplying the required oxygen to the microorganisms and providing the cleaning mechanism for the membrane surface.

2.2. Operating Conditions and Analytical Methods

Since the intermittent suction showed better performance than the continuous suction in maintaining the stable flux for a long period of time [2], the permeate was extracted by a suction pump under intermittent operation in a 10-min cycle; 8-min on and 2-min off. Table 1 shows the summary of the operating conditions during the experimental period. The sludge retention time (SRT) and sludge concentration (MLSS) were controlled by the intermittent wasting of the excess sludge. After MLSS was measured in a daily sample, excess sludge was intentionally wasted twice a week from the oxic reactor so that a MLSS concentration might be maintained around 12,000 mg l^{-1}. The SRT was calculated from the total mass of the sludge in both

Table 2. Composition of Synthetic Wastewater (basis: COD 1,200 mg/L, T-N 310 mg/L)

Component	Concentration (mg/L)
Glucose	808
Glutamic acid	345
CH_3COONH_4	265
$NaHCO_3$	750 - 2,000
NH_4Cl	888
KH_2PO_4	60
K_2HPO_4	80
$MgSO_4.7H_2O$	33
$MnSO_4.H_2O$	10
$FeCl_3.6H_2O$	3
$CaCl_2.2H_2O$	20
NaCl	25

anoxic/oxic reactor divided by the average wasting rate of the sludge [4]. The sludge used in this study was collected from a municipal wastewater treatment plant and was acclimated with the synthetic wastewater for about one month. The hydraulic retention time (HRT) of the whole process was determined by regulating the permeate flux of the membrane. The recycle ratio over influent flow rate and the volumetric ratio between anoxic/oxic reactors were varied in order to study the effect of operating conditions on the nitrogen removal. During the operation from the 180th day, the ratio of oxic over anoxic reactor volume varied arbitrarily at 8:12, 10:10, 12:8 and 15:5. Dissolved oxygen (DO) in the oxic reactor was not controlled in this system since the air flow rate was fixed in the range of 15-20 l min^{-1}. Synthetic wastewater with the composition shown in Table 2 was used in this study. The chemical oxygen demand (COD) and nitrogen

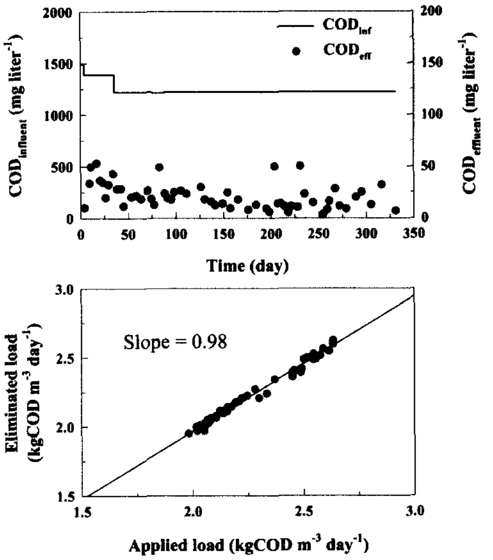

Fig. 2. COD concentration profile and average removal rate of COD.

concentrations were adjusted by changing the concentrations of glucose and NH_4Cl. $NaHCO_3$ was added for the pH buffering. Analysis of the influent and the treated water was conducted using standard procedures: COD (dichromate method), BOD (Winkler azide method), TKN (Macro-Kjeldahl method), NH_4-N (Nesslerization method by reading absorbance at 425 nm), NO_3-N (ultraviolet spectrophotometric screening method at 220 nm as described in the Standard Methods [11]). The temperature, pH, air and wastewater flow rates and mixed liquor suspended solids concentrations were monitored in a daily sample.

3. Results and Discussion

3.1. COD Removal Performance

Figure 2 shows the variation of influent/effluent COD concentrations and COD loading in the membrane bioreactor during the period. Regardless of the changes in the operation condition shown in Table 1, an excellent performance for COD removal was observed. There was no significant variation in effluent CODs with the changes such as hydraulic retention time (HRT), sludge retention time (SRT), MLSS concentration, and temperature. Since the submerged membrane herein form an absolute barrier to solids and bacteria and retain them in the reactor, suspended solids (SS) were not detected in the effluent almost perfectly. Most of the COD concentration in the effluent was less than 30 mg l^{-1} as shown in Figure 2 and the effluent BOD was lower than 3 mg l^{-1} (data not shown here). The high quality effluent, obtained from the membrane bioreactor as a single step process, is suitable for a direct water reuse or the feed for the reverse osmosis operation. Traditionally, the process for wastewater reuse requires the multiple treatment steps with significant capital investment and high operating cost. This resulted in a process that limited a number of applications.

From the slope of the applied COD load versus the eliminating load, the average COD removal rate of 98% was obtained, and maintained until we achieved the higher load of more than 2.5 kg m^{-3} d^{-1}. For the conventional aerobic wastewater treatment process, the maximum load is considered to be 0.3-0.6 kg m^{-3} d^{-1} [12]. Moreover, since the submerged membrane can be easily installed in the existing bioreactor, the existing bioreactor can be upgraded to treat five times more wastewater without new bioreactor construction.

3.2. Variation of Sludge Concentration and Settleability

The treatment capacity of a biological system is determined mainly by the amount of biomass involved in the process. As shown in Figure 3, the stable COD removal at a higher loading was possible due to a higher biomass concentration compared with the conventional process. The MLSS concentration of more than 10,000 mg l^{-1} could be stably maintained and the ratio of volatile SS to total SS was in the range of 0.8-0.9. While high solid concentration causes settling process, solid-liquid separation, of gravity settling systems to fail in a conventional process, the submerged membrane herein was able to operate without any operational problems for about one year. Yamamoto et al. [2,5] reported

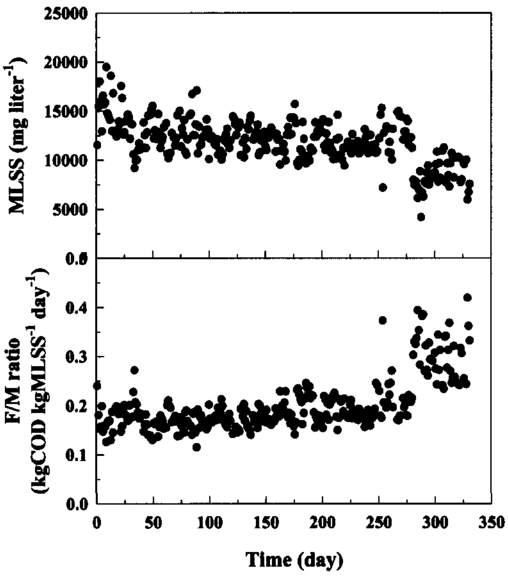

Fig. 3. Variation of MLSS and F/M ratio.

that the critical MLSS concentration corresponding to long-term stable operation would probably lie between 30,000 and 40,000 mg l^{-1} for tannery and domestic wastewater. In this study, MLSS was maintained below the half of that critical MLSS concentration. While the operation of the conventional activated sludge process is based on the sludge settleability, SRT, and sludge return ratio from the clarifier to the bioreactor, the membrane bioreactor process can be successfully operated with a proper control of MLSS in the bioreactor. During the whole period, the excess sludge was intermittently wasted to maintain MLSS concentration less than 15,000 mg l^{-1}. The SRT, which is determined from the wasting ratio of sludge, was in the range of 20-30 days. Maintaining a high SRT in the bioreactor allows for sludge digestion in the same reactor, which resulted in a low sludge yield of 0.2-0.3 kgVSS $kgBOD^{-1}$ in this study.

After about a 9-month operation, the MLSS was reduced to about 8,000 mg l^{-1} in order to study the fluctuation of operational parameters on the treatment efficiency and membrane performance. The reduction of MLSS resulted in the increase of F/M ratio up to 0.4 as shown in

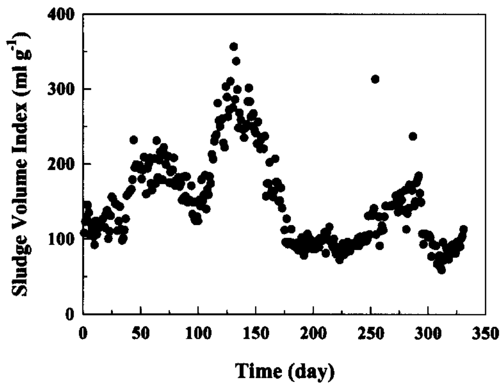

Fig. 4. Variation of sludge volume index in an oxic reactor.

Figure 3. Regardless of MLSS variation, the treatment efficiency and the operational performance of membrane was not significantly changed and therefore the stability of this membrane bioreactor process was verified.

Figure 4 shows the variation of sludge volume index (SVI), which was monitored to study the effect of sludge condition on the long-term performance of membrane. Over the whole period, SVI value fluctuated from about 60 to 350, which means the variation of sludge settleability. Since the SVI of 50-150 is a normal value for the successful operation of gravitational settler, the fluctuation of SVI shown in this study can lead to an operational failure in a conventional process. The result of this study shows that the membrane bioreactor process is a flexible process which is not affected by sludge settleability.

3.3. Nitrogen Removal Performance

Figure 5 shows the nitrogen removal efficiency under the variation of anoxic/oxic recycle ratio. A high concentration of nitrogen from 200 to 310 mg l^{-1} was fed to the membrane bioreactor. In terms of volumetric load, 0.6 kgT-N m^{-3} d^{-1} was maintained during the initial 30 days, but the removal efficiency of nitrogen was not stabilized as shown in Figure 5. After then, the nitrogen load was decreased to 0.4 kgT-N m^{-3} d^{-1} by lowering the influent nitrogen concentration. Over the whole period, a low level of effluent NH_3-N

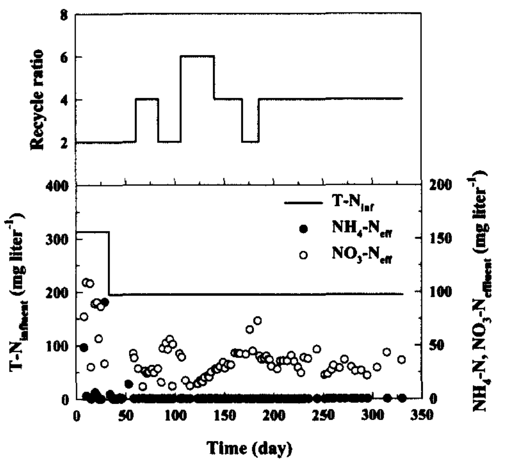

Fig. 5. Nitrogen concentration profile according to the recycle ratio over the influent flow rate.

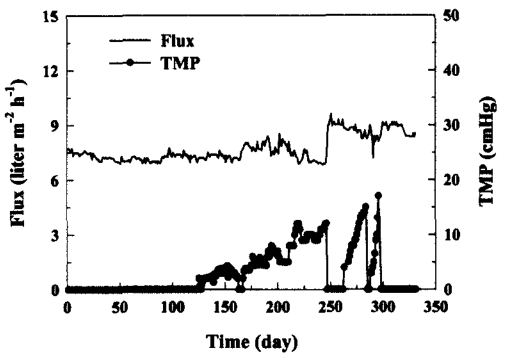

Fig. 6. Variation of flux and transmembrane pressure during experimental period.

below 1 mg l^{-1} suggested that the nitrification was very satisfactory in this system. In order to optimize the operating parameter for denitrification of nitrate, the recycle ratio from the oxic to anoxic reactor was varied from 2 to 6 times the influent flow rate. As the recycle ratio increased from 2 to 6, the average removal efficiency of nitrogen also increased from about 70 to 90% on average. The effluent NO_3-N was varied from 10-50 mg l^{-1} according to the change of the recycle ratio. From the 180th day, the ratio of oxic over anoxic reactor volume varied arbitrarily at 8:12, 10:10, 12:8 and 15:5 with maintaining the total reactor volume at 20 liter, but there was no significant change in nitrogen removal as well as nitrification efficiency. At 8,000 mg l^{-1} MLSS from the 280th day of operation, the nitrogen removal efficiency did not significantly decrease compared with the former period of operation at a higher MLSS. This may be due to the increase of organics for denitrification in anoxic reactor, which can balance the effect of decreased MLSS on denitrification.

3.4. Variation in Flux and Transmem-Brane Pressure

Figure 6 shows profiles for the flux and transmembrane pressure during the operation. The increase in the transmembrane pressure was observed from 125 days and increased steadily to about 15 cmHg. The flux was almost constant for the first 160 days of operation, being at 7.3 to 8 L m^{-2} h^{-1}. As the transmembrane pressure increased (after 170 days), the flux fluctuated ranging between 8.3 to 7 L m^{-2} h^{-1}. Unlike the externally circulated membranes that are housed in pressure vessels and require a positive pressure, the submerged membrane operates under a slight vacuum to draw water through the membrane. With only a slight negative pressure applied to the membrane, the energy requirement associated with the production of water is reduced. Membrane fouling is also reduced, as contaminants are not forced into the membrane pores under high pressure. Considering the variation of the sludge condition as shown in Figure 4, the membrane used in this study showed that the membrane bioreactor process was a stable process regardless of the sludge settleability, which is a main factor for the successful operation of the conventional gravitational settler.

Membrane cleaning was conducted on 247th, 284th and 296th days. During this period, the flux increased to 9.5 l m^{-2} h^{-1}, and the fouling was accelerated. To assess the different cleaning regimes, only NaOCl was used for the first cleaning and the combination of NaOCl and NaOH was used in the second cleaning. Finally, the combination of oxalic acid, NaOCl and NaOH was used for the third cleaning process. The increase of TMP was observed within 20 days after the first cleaning. The second cleaning was also not efficient in preventing the membrane fouling. However, we used the third cleaning process. The membrane fouling was not observed until the last day of this operation. This result signifies the importance of the cleaning method and also suggests that the oxalic acid provides an efficient cleaning of the membrane. In addition, the membrane fouled not only by microorganisms and the organic substances but also by the inorganic substances contained in the wastewater.

From this study, the operation of the submerged membrane bioreactor could be sustained for more than 250 days without any cleaning. However, the effect of the sludge condition on the membrane fouling and the transmembrane pressure could not be fully investigated because of long operation time due to the anti-fouling property of the submerged membrane used in this study under the normal MBR operation.

4. Conclusion

A lab-scale submerged membrane bioreactor equipped with a hollow fiber module for nitrogen removal was operated with an average MLSS of 12,000 mg l^{-1} and 13 hr HRT. The submerged membrane bioreactor produced a high quality effluent in terms of COD and NH_3-N. Moreover, SS in the effluent was not even detected. The removal rate of nitrogen was improved by the increase of recycle ratio from oxic to anoxic reactor. However, the variation of retention time and MLSS did not significantly affect on the nitrogen removal efficiency. The flux was maintained about at 8 L m^{-2} h^{-1} level for 4 months without TMP increase. TMP appeared to be only 15 cmHg after the continuous operation of 8 months. When the fouled membrane was washed with the acid and the base, the sign of TMP increase of a membrane was not shown even after 50 more days.

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