

WASTEWATER TREATMENT USING COMBINATION OF MBR EQUIPPED WITH NON-WOVEN FABRIC FILTER AND OYSTER-ZEOLITE COLUMN

Yoo-Jin Jung, Hyun-Woong Koh*, Won-Tae Shin**, and Nak-Chang Sung***,†

Division of TMDL Policy, National Institute of Environmental Research, Incheon,
South Korea 404-708

*R&D Center, XXIEN Co., Ltd. Busan, South Korea 604-838

**Marine Environmental Division, Ministry of Marine Affairs and Fisheries Seoul,
South Korea 110-793

***Department of Environmental Engineering, Dong-A University Busan, South Korea 604-714
(received March 2005, accepted October 2005)

Abstract : A combination of the submerged membrane activated-sludge bioreactor(SMABR) equipped with non-woven fabric filter and oyster-zeolite (OZ) packed-bed adsorption column was studied to evaluate the advanced tertiary treatment of nitrogen and phosphorous. The non-woven filter module was submerged in the MBR and aeration was operated intermittently for an optimal wastewater treatment performance. Artificial wastewater with COD_{cr} of 220 mg/L, total nitrogen (T-N) of 45 mg/L, and total phosphorous (T-P) of 6 mg/L was used in this study. MLSS was maintained about 4,000 ~ 5,000 mg/L throughout the experiments. The experiments were performed for 100-day with periodic non-woven filter washing. The results showed that COD_{cr} could be effectively removed in SMABR alone with over 94% removal efficiency. However, T-N and T-P removal efficiency was slightly lower than expected with SMABR alone. The permeate from SMABR was then passed through the OZ column for tertiary nutrients removal. The final effluent analysis confirmed that nutrients could be additionally removed resulting in over 87% and 46 % removal efficiencies for T-N and T-P, respectively. The results of this study suggest that the waste oyster-shell can be effectively reclaimed as an adsorbent in advanced tertiary wastewater treatment processes in combination with SMABR equipped with non-woven fabric filter.

Key Words : MBR, SMABR, Non-woven fabric filter, Tertiary treatment, Oyster-shell, Zeolite

INTRODUCTION

As a result of the presence of nitrogen, phosphorous, and carbon compounds in effluents and run-offs, serious pollution problems currently exist that could affect human health. Consequently, the governmental wastewater discharge regulations became more stringent than ever

before requiring higher standards of discharge water quality from wastewater treatment plants. To solve these problems, a biological method of wastewater treatment has been studied intensively. One advancement in biological wastewater treatment was the introduction of membrane bioreactors (MBRs).

The use of membrane in biological wastewater treatment processes was first reported in the 1970s claiming several advantages over conventional treatment methods.¹⁾ Since then, MBRs have been studied extensively for the

† Corresponding author
E-mail: ncsung@donga.ac.kr
Tel: 051-200-7681, Fax: 051-200-7675

optimization of wastewater treatment processes. The advantages of adopting membrane in activated sludge processes (ASPs) include the elimination of settling tanks which occupy significant plant space and process holdup time, relatively small sludge production, and the removal of bacteria and viruses to a great extent as well as carbon and nutrients.²⁻⁵⁾

However, the use of expensive microfiltration and/or ultrafiltration modules occupies significant capital cost making MBRs less compatible to conventional ASP. To solve this problem, less expensive membrane materials were studied.^{6,7)} The non-woven fabric filter is possible candidate for use in MBR system. This study explored the use of less expensive non-woven fabric filter module in place of microfiltration module.

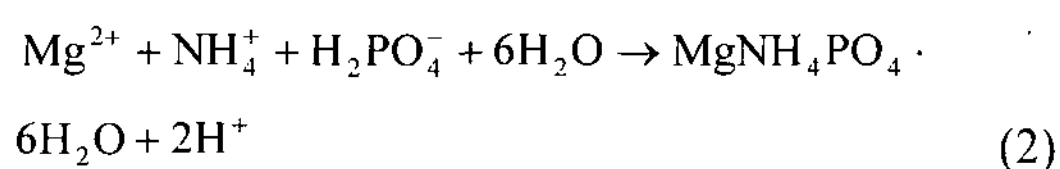
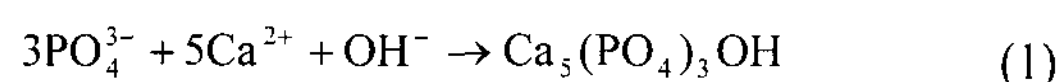
It is reported that MBRs can provide a certain degree of nutrients removal. However, it is desired to incorporate advanced treatment methods to achieve an acceptable level of nutrients in the effluents. Lesjean et al.⁸⁾ showed nutrients removal using a biological phosphorous removal process incorporating a conventional treatment plant. Côté et al.⁹⁾ showed high nitrogen removal using a long sludge age. However, they failed to achieve the same degree of phosphorous removal. The high degree of nitrogen removal in MBRs can be attributed to the simultaneous nitrification and denitrification due to zoning inside the reactor. Many literature reports showed that nitrogen removal can be maximized using intermittent aeration inside the MBR for maintaining aerobic and anoxic periods.^{10,11)} Recent study using staged MBR reactor design and intermittent aeration demonstrated high nutrient removal.¹²⁾ Many design modification of MBR to improve nutrient removal can be found in the literature.

In this study, the crushed oyster shell-zeolite (OZ) packed-bed adsorption column was introduced for advanced nutrient removal from the permeate. The column was packed with half crushed oyster-shells and half zeolite. The crushed oyster-shell is used as an adsorbent for phosphorous removal in this work. Zeolite is

widely used for the ammonia removal from wastewater treatment by ion exchange.¹³⁾ Zeolites owe their unique ion exchange properties to their structural characteristics. They possess a framework structure enclosing cavities occupied by cations which are weakly held to the structure to compensate for the charge imbalance created by the substitution of Al^{+3} for Si^{+4} in the basic tetrahedral structure. Many studies revealed that the use of zeolite is a promising method for ammonia removal.^{14,15)}

Oyster, *Crassostrea gigas*, is a major maricultural product at the southern coast of S. Korea. Waste oyster-shell is the result of mass production of oysters and imposes a significant environmental challenge to the maricultural community. Consequently, efforts were focused on the reuse and recycle of the waste oyster-shells. Yoon et al.¹⁶⁾ reviewed the chemical-mechanical characteristics of crushed oyster-shells, which is the same type of oyster used in this study. According to them, approximately 96% of an oyster-shell is comprised of $CaCO_3$. Thus, it is expected that crushed oyster-shells may be used as a seed material for hydroxyapatite crystallization.

In conventional activated sludge processes, the phosphorous removal was about 10~30%.¹⁷⁾ MBR showed a similar treatment performance for phosphorous removal. Hence, many methods of phosphorous removal based on biological treatment have been developed. Crystallization of phosphorous in the form of hydroxyapatite or struvite is gaining popularity among other phosphorous removal technologies due to less sludge production compared to chemical precipitation. The formation of hydroxyapatite and struvite is described by Eqs. (1) and (2), respectively:^{17,18)}



As we can see from these equations,

crystallization of hydroxyapatite and struvite needs addition of calcium and magnesium, respectively, in the system. Using naturally occurred calcium and magnesium in the system, the crystallization is expected to be successful.

The objective of this work is to investigate the feasibility of a submerged membrane activated-sludge bioreactor (SMABR) equipped with non-woven fabric filter followed with an oyster-zeolite packed column for advanced phosphorous and nitrogen removal. The result of this work may lead to the use of a less expensive membrane module and an alternate waste oyster-shell utilization process.

MATERIALS AND METHODS

The experimental setup is comprised of an activated sludge bioreactor, in which a non-woven fabric filter module was submerged, and an oyster-zeolite packed adsorption column as shown in Figure 1 and Figure 2(a). The influent was introduced into a 40-L SMABR with a feeding pump. An air diffuser was set up at the bottom of the SMABR to promote aerobic conditions in the system and to prevent or reduce fouling of the non-woven. An agitator was employed for the complete mixing of the influent and sludge. The influent was synthesized in the laboratory to maintain uniform composition throughout the experiments. The chemical composition of synthetic wastewater is shown in Table 1. The chemical composition was blended under the formulation of local wastewater treatment plant design guideline. The concentrated synthetic wastewater was then diluted to a desired concentration before being reused in the experiments. The influent had the

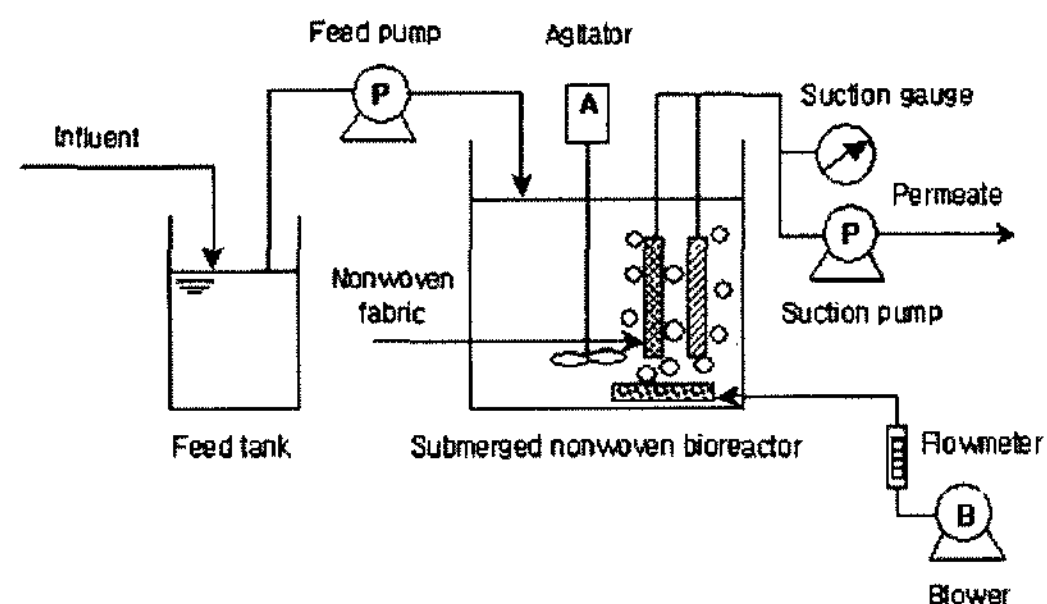


Figure 1. Schematic diagram of submerged membrane activated-sludge bioreactor (SMABR).

following characteristics: $COD_{cr} = 220$ mg/L, Total Nitrogen (T-N) = 40 mg/L, and Total Phosphorous (T-P) = 5 mg/L. The mixed liquor suspended solids (MLSS) in the reactor was maintained in the range of 4,000~5,000 mg/L. The hydraulic retention time (HRT) was maintained at 10 hr and there was no sludge withdrawal during the experiments. The aeration was operated at an intermittent mode. The use of intermittent aeration can be found in various literature reports.^{10,11)}

The two stage packed-bed adsorption column was connected to the SMABR permeate tank. The schematic of the packed-bed column is shown in Figure 2(a). The packed-bed column has dimensions of 9 cm in diameter and 200 cm in height with an effective packing height of 150 cm. The packing materials were crushed oyster-shell and natural zeolite. The column packed with these materials is called oyster-zeolite (OZ) column in this study. Oyster and zeolite were packed at a 1:1 ratio. To examine the performance of the OZ column, adsorption experiments were operated using a two-stage column system. The effluents were named as effluent 1 and effluent 2 after passing through columns 1 and column 2, respectively. The concen-

Table 1. The chemical composition of synthetic wastewater

Chemicals	Concentration (mg/L)	Chemicals	Concentration (mg/L)
Glucose	120.0	MgSO ₄ ·7H ₂ O	24.0
Peptone	90.0	MnSO ₄ ·5H ₂ O	2.16
Yeast extract	12.0	FeCl ₃ ·6H ₂ O	0.12
NH ₄ Cl	96.0	CaCl ₂ ·2H ₂ O	2.4
KH ₂ PO ₄	17.0	NaHCO ₃	300

trations of COD, T-P, T-N and other parameters were measured for effluent 1 and effluent 2.

The submerged non-woven module was adopted in this study. The non-woven has the following features: (1) plate and frame type filter module (2) operation in outside-in filtration mode, and (3) aeration in an intermittent mode to avoid sludge build-up. The characteristics of the non-woven module are reported in Table 2. The module has the dimension of W160×H250×D7.5 mm. The non-woven module was obtained from Korea Non-Woven Tech Co., LTD. (Model PP-100) and has effective area of 0.05 m².

The permeate from the SMABR was sent to the OZ column for tertiary treatment, as shown in Figure 2(a). Both raw oyster-shell and natural zeolite were washed with distilled water and dried naturally. Then, they were evenly crushed

with a ball mill and sieved using a # 100 mesh. The mean particle diameter of packing materials was 4.76-mm. The materials were then stored in a desiccator before experiments to prevent adsorption of water vapor. The natural zeolite was obtained from Wang Chemical Co. (Pohang, Korea) and its properties can be found in the literature.^{13,19)} Table 3 shows the characteristics of the natural zeolite used in this work.

The Freundlich adsorption isotherm data for the zeolite and crushed oyster-shell with respect to ammonium ion in Table 4 and shown in Figure 2(b). The Freundlich isotherm is expressed as:

$$q = KC_e^{1/n} \tag{3}$$

where q is the amount adsorbed per unit mass of adsorbent, K and n are empirical constants

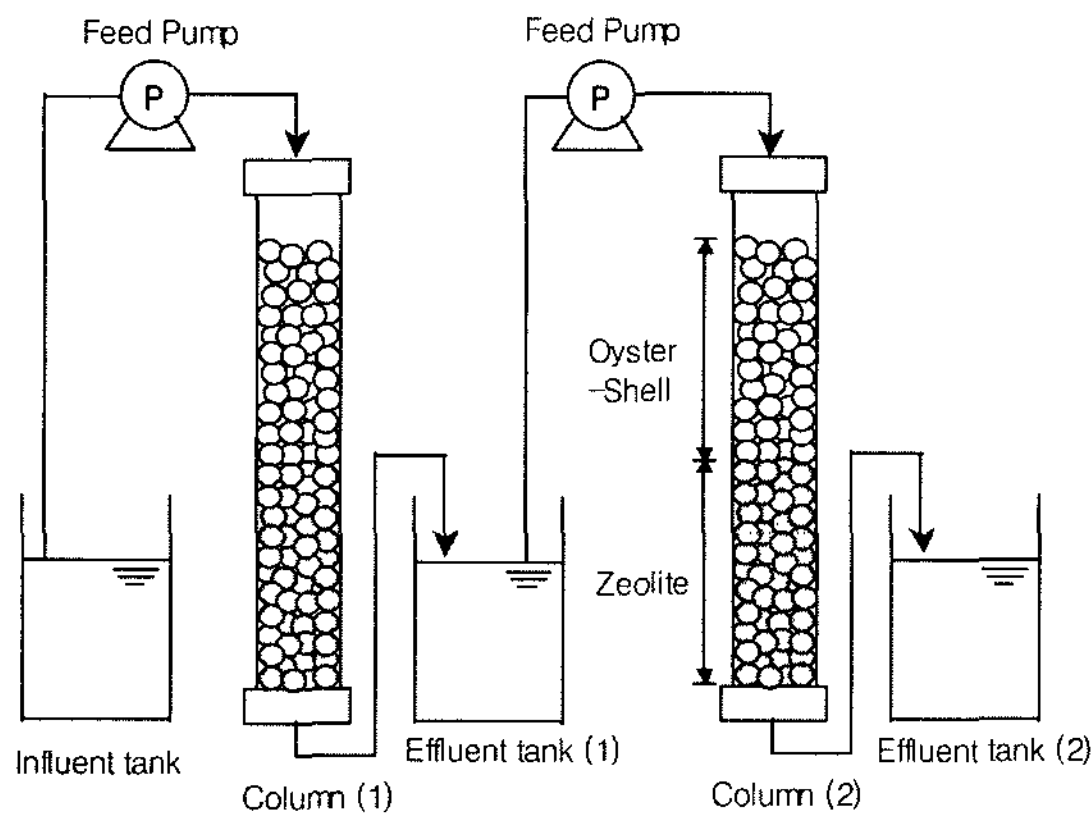


Figure 2(a). Schematic diagram of two-staged OZ adsorption columns.

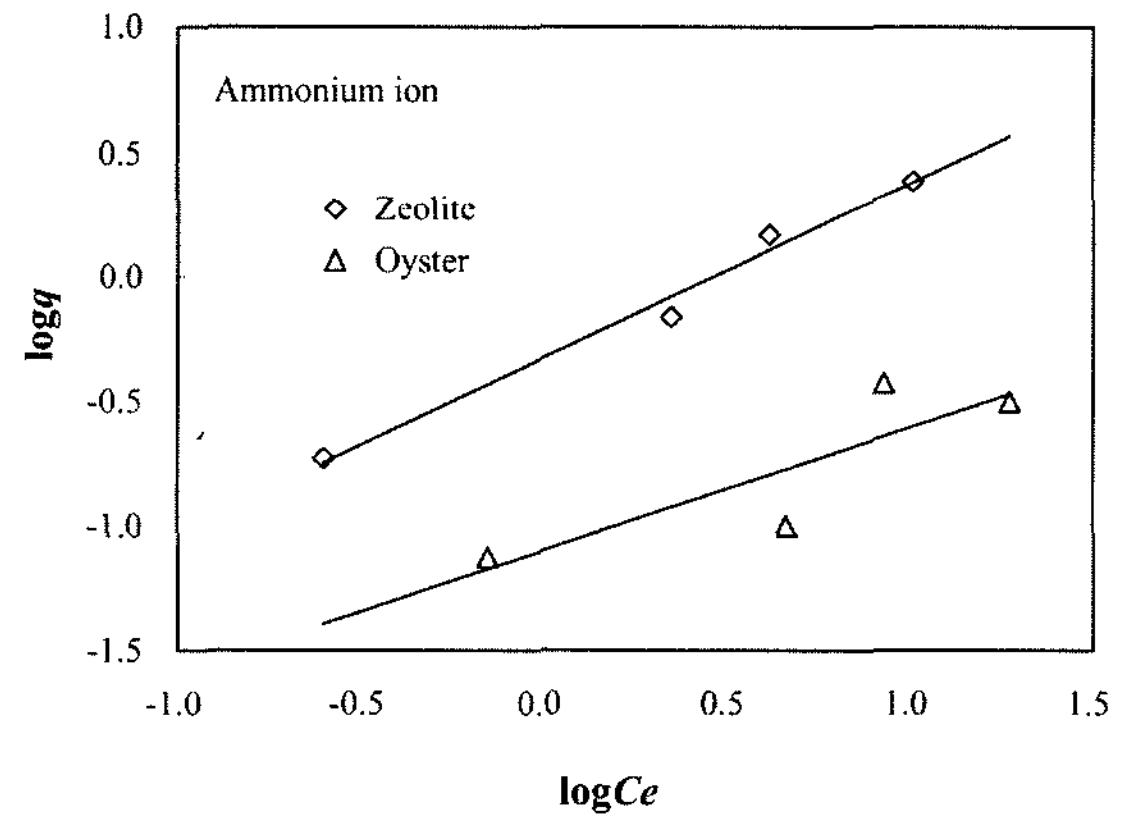


Figure 2(b). The Freundlich isotherm information of the crushed oyster-shell and zeolite for ammonium ion.

Table 2. Standard physical properties of non-woven fabric

Weight (g/m ²)	Thickness (mm)	Tensile strength (N/5cm)		Elongation (%)	
		MD	CD	MD	CD
100	0.61	240	160	170	170

Table 3. Characteristics of natural zeolite used in this work

Particle size (mm)	pH	CEC (cmol/kg)	Exchangeable cations (cmol/kg)			
			K	Ca	Mg	Na
22	8.5	100	9.4	12.7	1.9	25.1

Table 4. Freundlich isotherm data for zeolite and crushed oyster-shell

adsorbent	K	1/n
Zeolite	0.48	0.70
Oyster-shell	0.08	0.49

RESULTS

Two sets of experiments, short-term and long-term experiments, were conducted to study the feasibility of the OZ column bioreactor. Short-term experiments were operated for 10-day to obtain the experimental conditions necessary for long-term experiments. Once the operating parameters were determined, long-term experiments operated for 100-day were performed for the simulation of actual treatment plant conditions. The OZ column experiments were performed along with long-term experiments for tertiary nutrients removal.

Short-term Experiments

In short-term experiments, the operating parameters such as suction interval and aeration interval, were determined based on the findings of COD_{cr}, T-P, and T-N measurements of effluents for 10-day. To obtain the optimum aeration interval cycle, three cycles were tested: (a) 60-min aeration and 60-min non-aeration (60/60) cycle, (b) 120/60 cycle, and (c) 120/120 cycle. The air-flow rate was maintained at 12 L/min. During the short-term experiments, the suction flux was maintained at 20 L/m²·h and the MLSS was approximately 4,000~5,000 mg/L.

Some showed that intermittent suction of permeate has more advantages, such as lower trans-membrane pressure and less clogging, than continuous suction.²¹⁾ Figure 3 shows the pressure variation inside the filter module when operating with different suction intervals (SI). Two suction intervals were examined: (a) 5-min suction and 1-min pause (5/1) and (b) 10-min suction and 2-min pause (10/2). In this figure, the 5/1 cycle showed a stiff pressure increase after 60-hrs of operation, while the 10/2 cycle showed stable increase during the same period

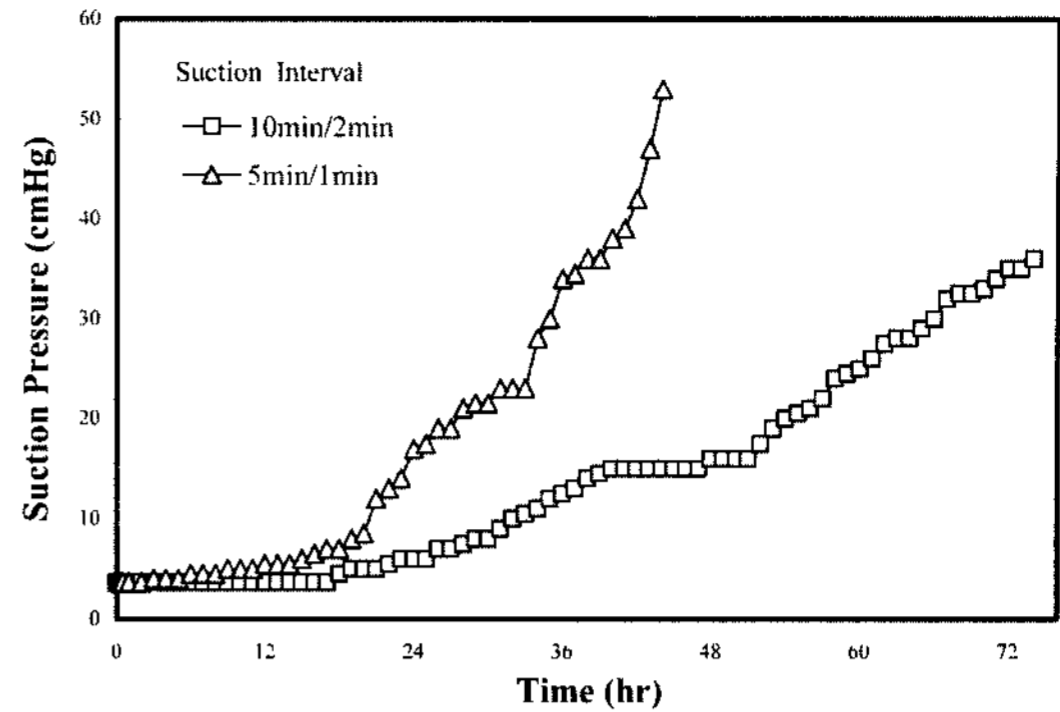


Figure 3. Suction pressure variation with intermittent suction time.

of operation.

Figure 4 shows the suspended solids (SS) removal with non-woven fabric filter module. It is shown that the filter module can successfully remove the SS after 12 hr, maintaining SS of less than 10 mg/L. This result suggested that non-woven fabric filter should be operated after cake layer is built on the surface of the filter module.

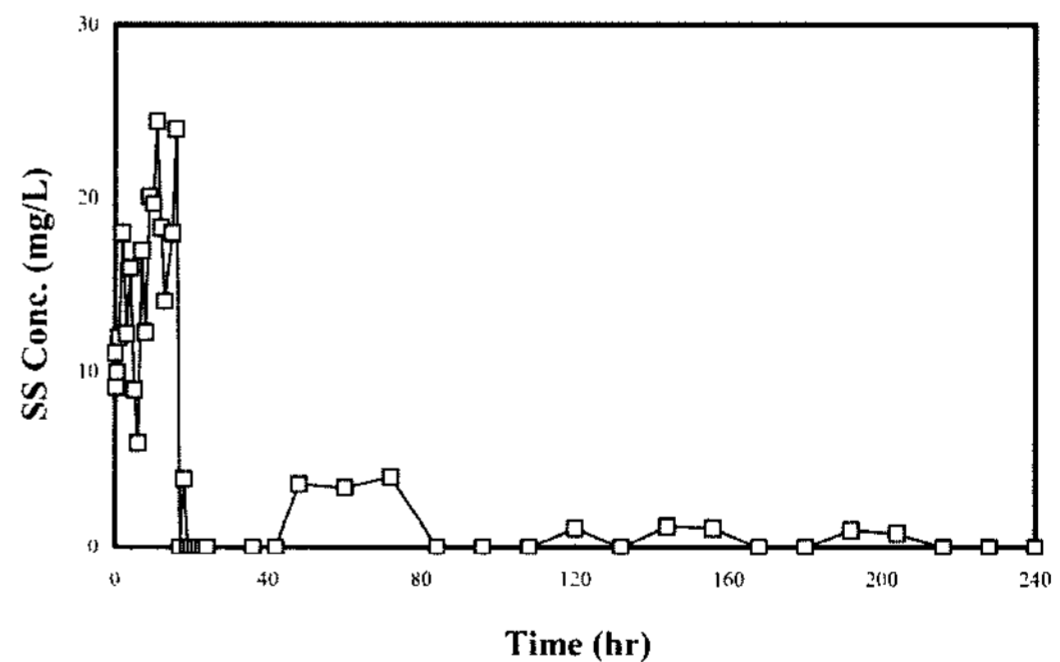


Figure 4. SS removal using non-woven fabric filter module.

While maintaining a SI of 10/2 cycle, the nutrient removal was examined to determine the optimum aeration interval (AI) cycle. Figures 5(a), 5(b), and 5(c) show the COD_{cr}, T-N, and T-P concentration variations, respectively, during the short-term experiments. Although there was not much variation in COD_{cr} removal, the T-N removal was about 45% higher with 120/120 AI cycle than continuous aeration as shown in Figure 5(b). Thus, the 120/120 AI cycle was selected for the long-term experiments.

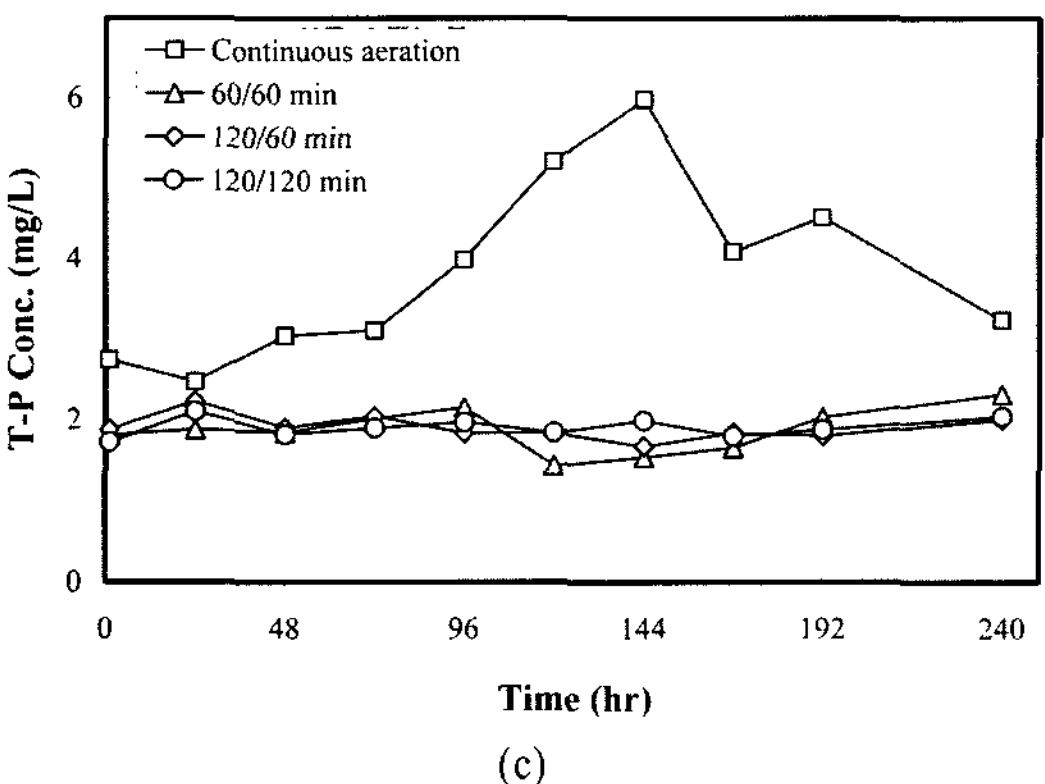
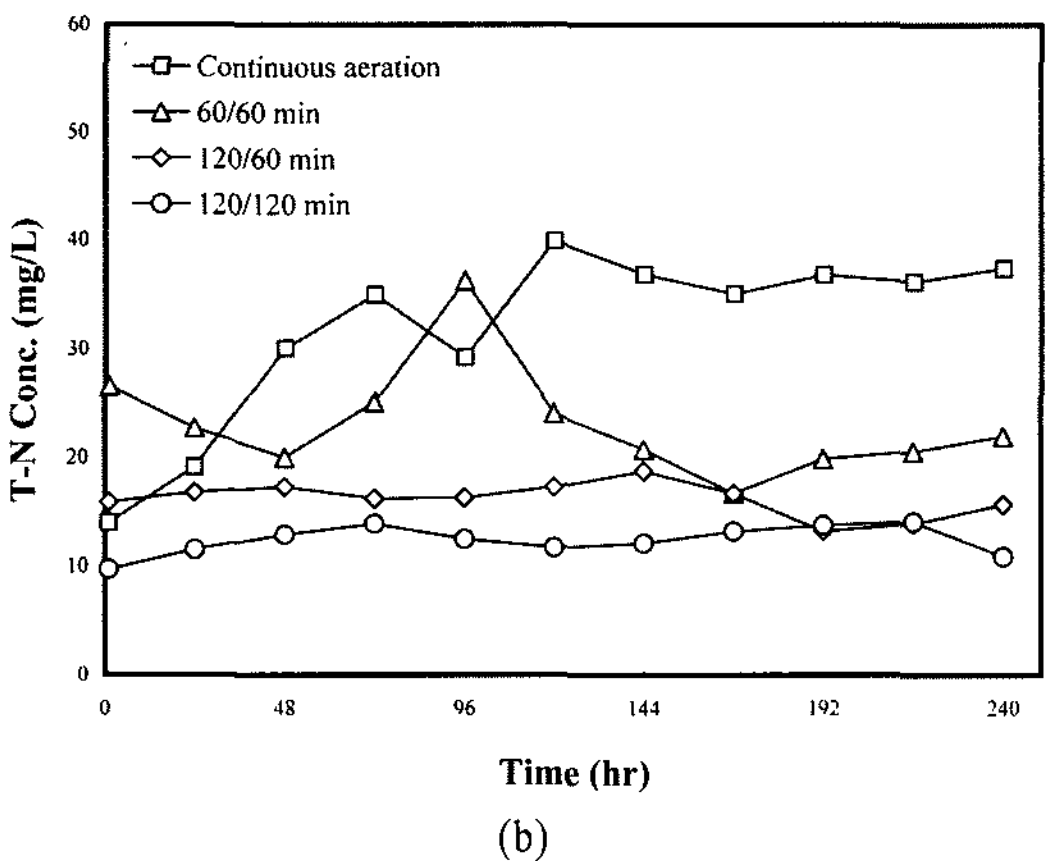
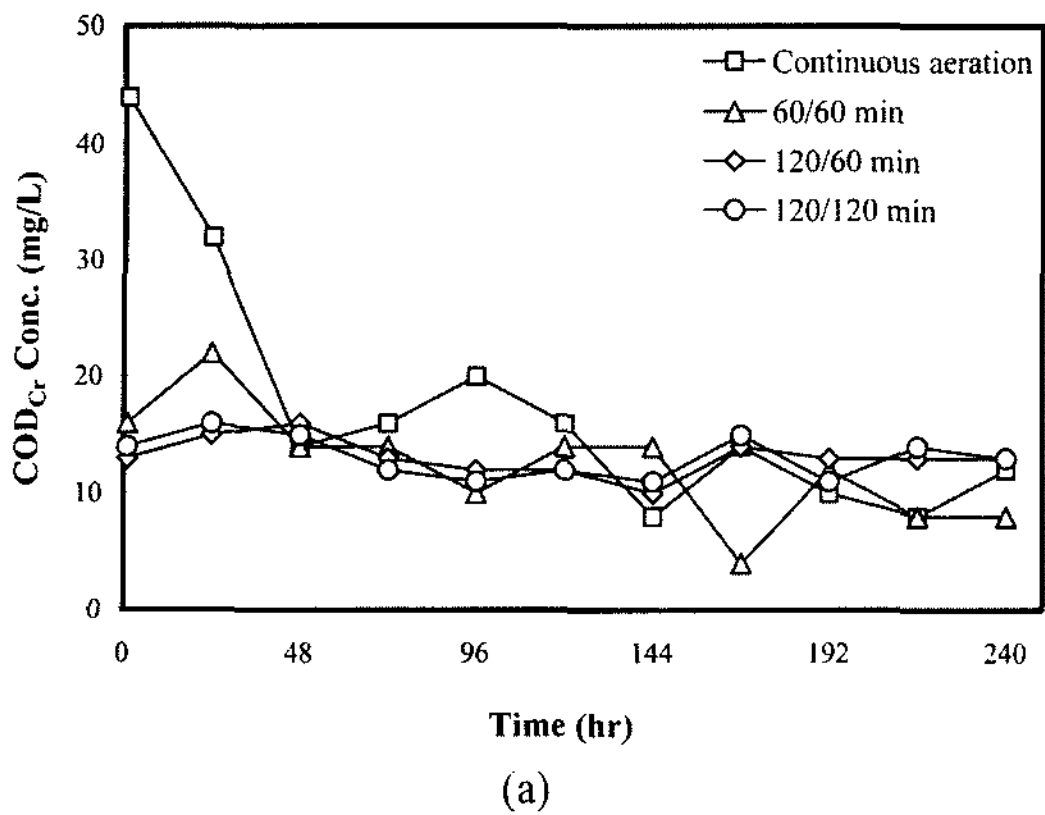


Figure 5. Effluent concentration variation with aeration/non-aeration operation; for (a) COD_{cr} , (b) T-N, (c) T-P.

Long-term Experiments

The optimum operating conditions obtained from the 10-day experiments were used throughout the continuous experiments. The operating conditions were as follows: MLSS is 4,000~5,000 mg/L, permeate flux is 20 LMH, suction/

pause interval is 10 min/2 min (10/2), and aeration/non-aeration interval is 120 min/120 min (120/120). The introduction of influent to the bioreactor was performed during a nonaeration period while mixing of MLSS was continuously operated for a uniform distribution of the influent. The experiments were continued for 100-day using the submerged microfiltration non-woven. There was no sludge removal during the experiments.

During the experimental period, the microfiltration module was cleaned with a sponge washer to prevent excessive pressure build-up by removing cake and gel layers on the surface of the non-woven. The sponge washing was performed every 20-day. For a 40-day period, the non-woven was cleaned with 0.1% NaOCl along with sponge washing to prevent pore clogging.

The change in TMP was measured during the 100-day experiments. The critical flux is defined as the flux at which cake deposition starts to be detectable. According to their findings, the non-woven used in this work should have similar critical flux as found in other literature reports. The change in TMP is shown in Figure 6. As shown in this figure, the pressure did not exceed over 20-cm Hg for a 20-day cycle due to sponge washing and chemical washing. Hence, withdrawal of permeate from bioreactor was continuously performed without changing of non-woven module.

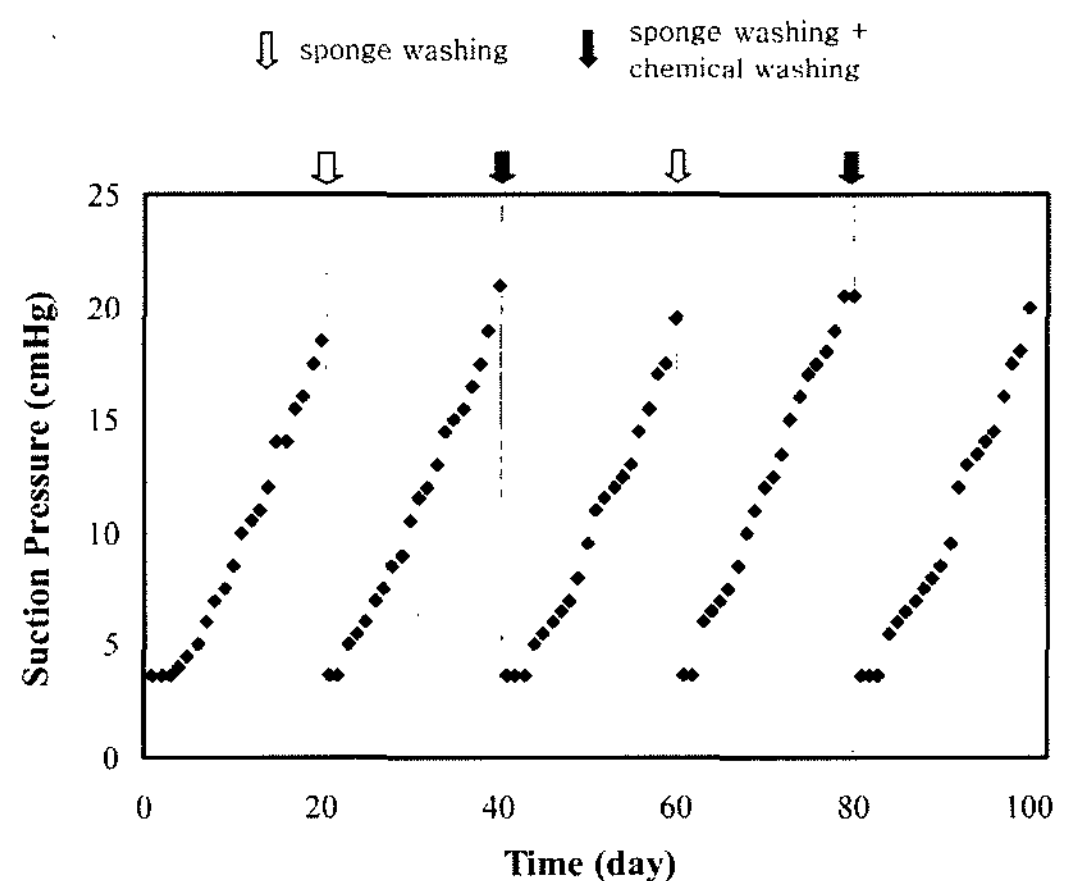
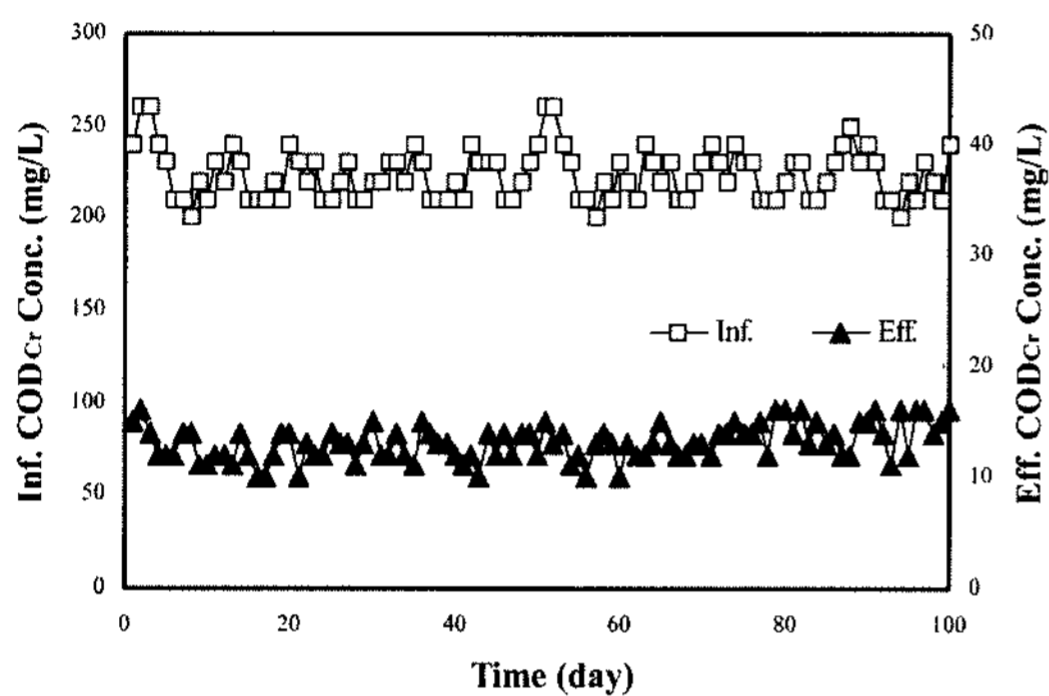
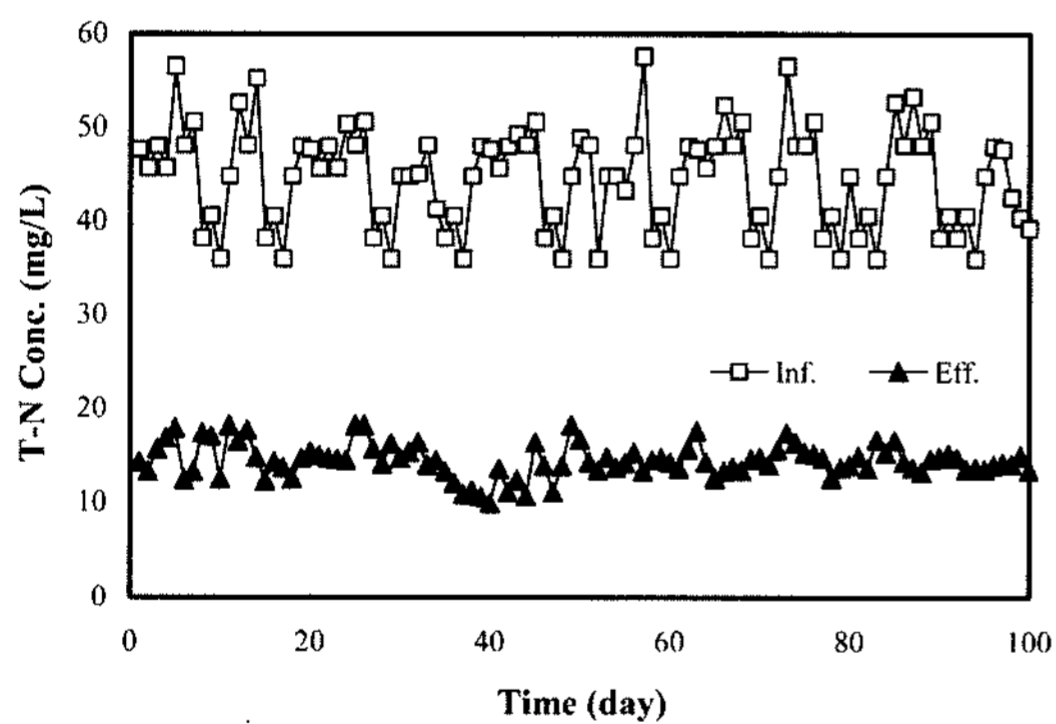


Figure 6. Suction pressure variation in SMABR.

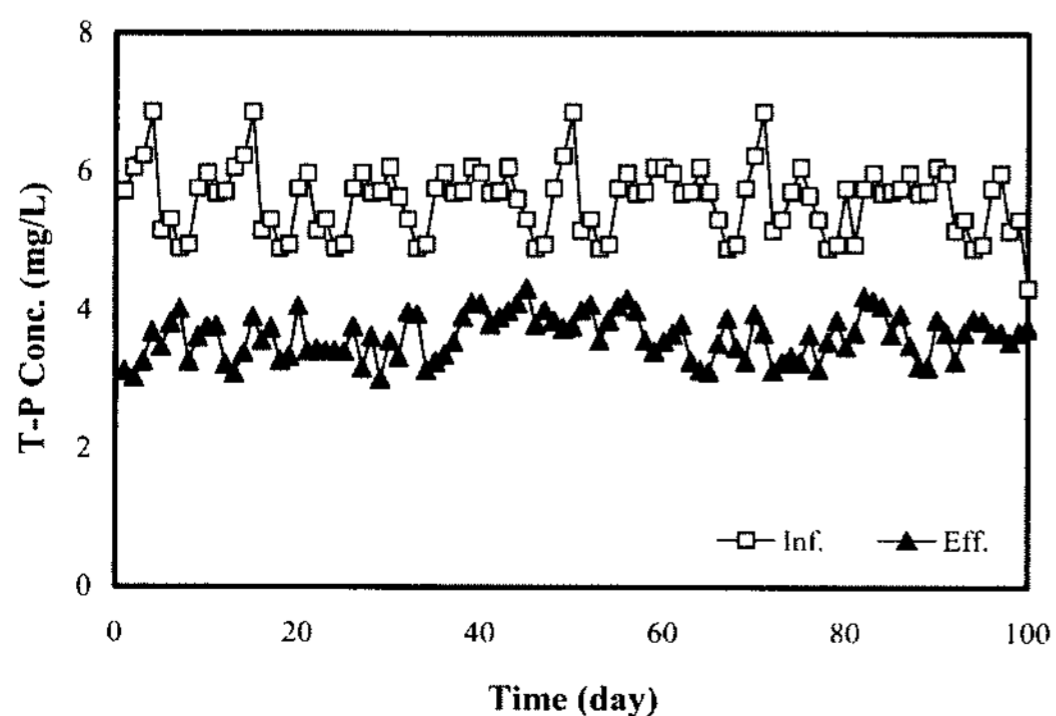
The permeate from the non-woven bioreactor was analyzed for COD_{cr} , T-N, and T-P concentrations. Figure 7(a) shows the variation of COD_{cr} concentration in the bioreactor. The influent had a mean COD_{cr} concentration of 223.6 mg/L. The permeate mean COD_{cr} concentration was 13.1 mg/L for a 100-day period showing a COD_{cr} removal efficiency of over 94%. The performance of stable COD_{cr} removal



(a)



(b)



(c)

Figure 7. Effluent concentration variation in SMABR; for (a) COD_{cr} , (b) T-N, (c) T-P.

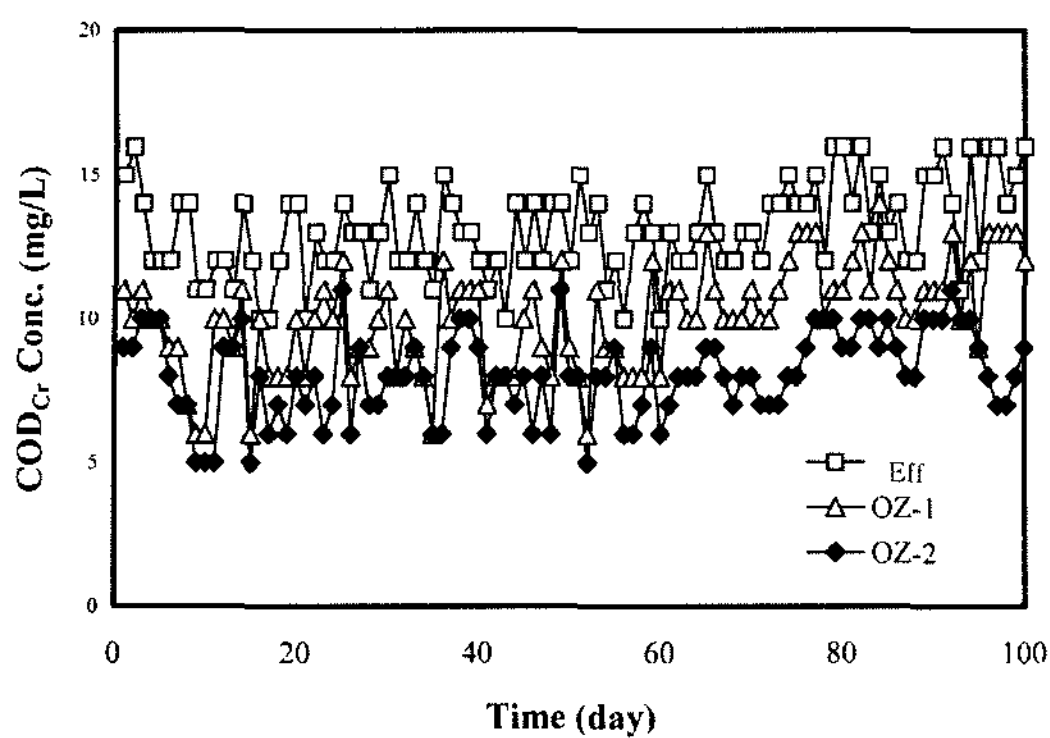
can be attributed to the microorganisms in the MLSS and microfiltration. The large organic compounds were converted to small organic compounds by microorganisms. The resulting smaller compounds were then sieved from non-woven or adsorbed by the cake and gel layer on the non-woven surface.

Figure 7(b) illustrates the change in T-N concentration in the bioreactor. As shown in this figure, the T-N concentration in the permeate is very stable, suggesting a reliable performance of the non-woven bioreactor. The T-N concentration in the influent was 44.6 mg/L and the mean permeate T-N concentration was 14.5 mg/L, yielding a removal efficiency of approximately 67.5%. The T-P removal in the non-woven bioreactor is shown in Figure 7(c). As this figure suggests, the phosphorus removal efficiency was 35.7% and the average effluent concentration was 3.6 mg/L.

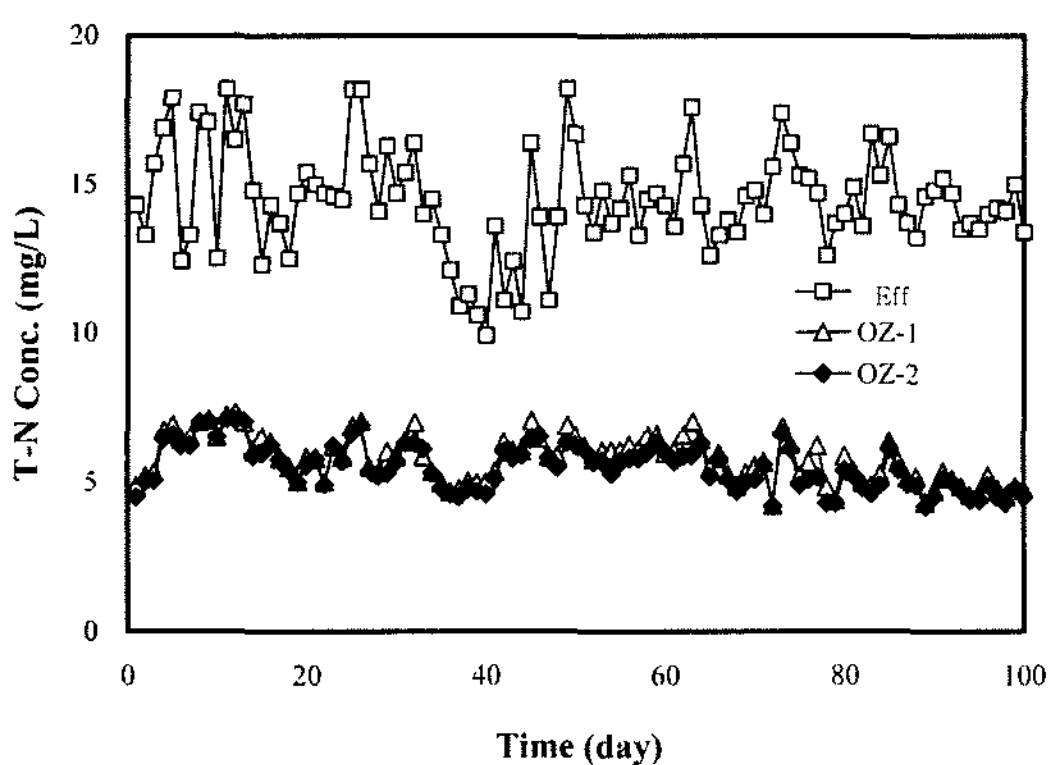
Oyster-zeolite(OZ) Column Adsorption Experiments

As we can see from Figure 7(c), about 36% of total T-P can be removed using SMABR alone. To cope with more stringent governmental discharge water regulations, it is necessary to enhance water quality by means of tertiary treatment. In this study, OZ adsorption columns were used for advanced nutrient removal. The effluent from the SMABR was introduced into OZ columns as shown in Figure 2(a). This study is the first report of the use of oyster-zeolite columns for advance nutrient removal.

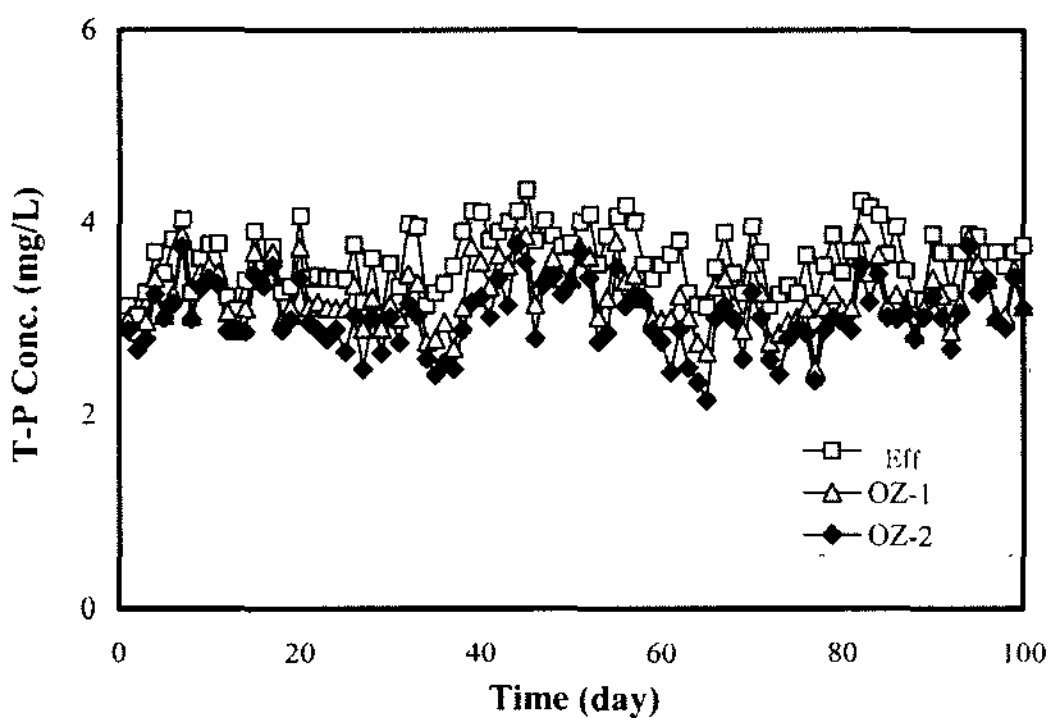
Figures 8(a), 8(b), and 8(c) show the COD_{cr} , T-N, and T-P concentrations, respectively, at the exit of the OZ columns. As expected, the OZ column adsorption has a small effect on removing COD_{cr} . COD_{cr} concentration already satisfied the discharge water quality regulations after SMABR. OZ columns showed the biggest effect on T-N removal reaching less than 5 mg/L T-N concentration after two stages. However, it is found that the second OZ column (OZ 2) has almost no removal effect on T-N treatment. It can be assumed that the available



(a)



(b)



(c)

Figure 8. Effluent concentration variation in OZ adsorption columns; for (a) COD_{cr} , (b) T-N, (c) T-P.

T-N can be sufficiently removed by the 1st OZ column. The T-P concentration after the OZ columns showed that the extended removal of T-P can be possible with OZ columns. The removal efficiency was about 11% after the two stages of OZ columns. Overall, 96%, 88%, and 46% of COD_{cr} , T-N, and T-P, respectively, can

be removed using SMABR and a series of two OZ columns.

DISCUSSION

Short Term Experiments

With the short-term experiments which were conducted for 10-day, the operation parameters were determined. The operation parameters determined in these experiments were suction/pause interval (SI) of 10 min/2 min(10/2) and aeration/non-aeration interval(AI) of 120 min/120 min(120/120) based on the findings of figures 5(a), 5(b), and 5(c).

The use of intermittent suction and aeration provide clogging prevention and simultaneous nitrification and denitrification in the SMABR. Although there is literature¹²⁾ showing the reactor design modification to improve nutrients removal, the manipulation of aeration can provide certain degree of nutrients removal without change of reactor configuration.

Long-term Experiments

With the long-term experiments, it was found that the T-N removal was relatively lower than other reported in the literature.²⁰⁾ One possible reason for this deviation can be attributed to low $COD/T-N$ ratio due to artificial wastewater composition. It was reported that the $COD_{cr}/T-N$ ratio should be more than 10 to achieve nitrogen removal efficiency over 80%. The $COD/T-N$ ratio used in this study found to be 2.3. The untreated ammonia in the SMABR can be effectively removed in the OZ column followed with the SMABR.

The removal efficiency of phosphorous was slightly lower than the normal activated sludge reactor. The reason for the lower phosphorous removal efficiency can be attributed to the absence of aged sludge withdrawal. It is known that phosphorous over-fed sludge should be removed periodically for optimum phosphorous removal. The untreated effluent phosphorous can be effectively captured in the OZ column.

Overall, the performance of SMABR is

reasonable compare to the traditional activated sludge processes with harsh environments set during the experiments, e.g., low COD/T-N ratio and no sludge withdrawal.

With the results of the long-term experiments, it can be inferred that the non-woven fabric filter module can be successfully replace the more expensive microfiltration module without sacrificing the effluents quality.

Oyster-zeolite(OZ) Column Adsorption Experiments

As shown in Figure 9, the data clearly showed that the second column barely functioning in the removal of T-P. This means that the first column is sufficient for the removal of phosphorous. It can be inferred from the results that *available* phosphorous for adsorption was captured in the first adsorption column. The second column confirmed the treatment performance of the crushed oyster-shell adsorption column.

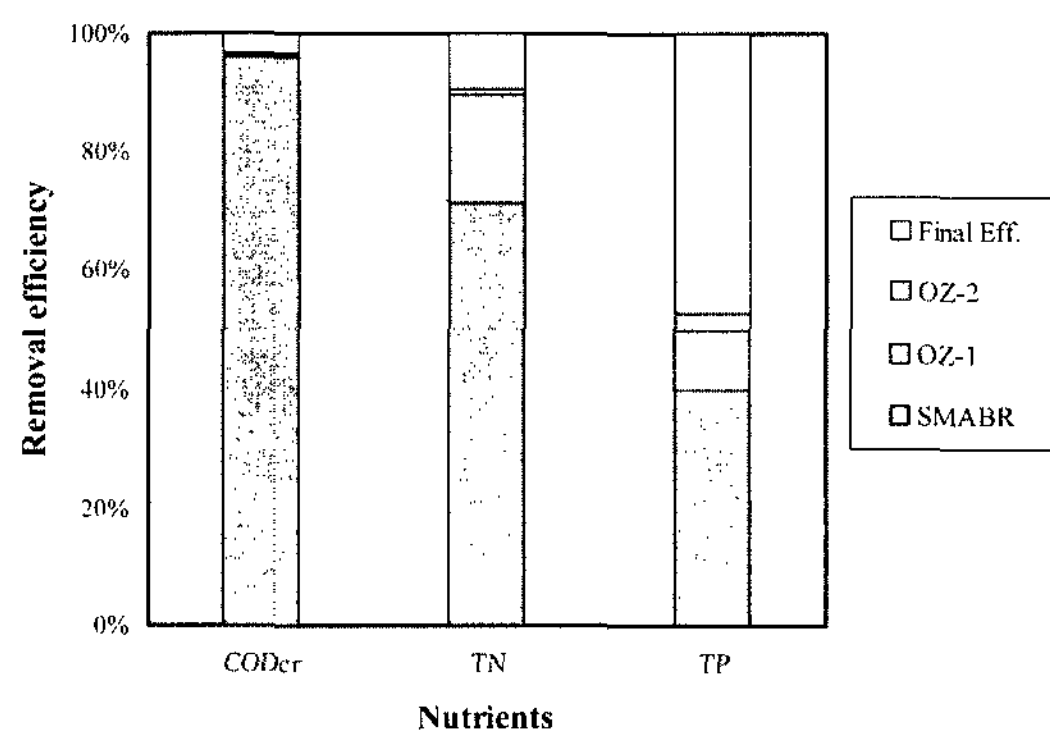


Figure 9. Comparison of removal efficiency using combined SMABR with OZ adsorption columns.

CONCLUSIONS

This study presents the research effort to incorporate crushed oyster shell-zeolite adsorption for advanced nutrients removal with a SMABR equipped with non-woven fabric filter module. The experiments were performed for 100-day to imitate the actual treatment facility. The results showed that the SMABR alone can

remove up to 94% of COD_{cr}. However, the nitrogen and phosphorous removal efficiencies were 67.5% and 35.7%, respectively, due to harsh operating environments suggesting the need of tertiary nutrients removal. Thus, the effluent of SMABR was then introduced into a series of two oyster-zeolite adsorption columns for advanced nutrient removal. Using OZ adsorption columns, T-N and T-P can be further removed to a satisfactory level of discharge concentrations. The results of this study demonstrated a possible substitute of expensive microfiltration membrane modules for less expensive non-woven fabric filter modules. Also, this work provided a possible waste oyster-shell utilization in South Korea.

REFERENCES

1. Bouhabila, E. H., Aïm, R. B., and Buisson, H., "Microfiltration of activated sludge using submerged membrane with air bubbling (application to wastewater treatment)," *Desalination*, **118**, 315-322 (1998).
2. Vaid, A., Kopp, C., Johnson, W., and Fane, A. G., "Integrated waste water treatment by coupled bioreactor and membrane system," *Desalination*, **83**, 137-143 (1991).
3. S. Chaize and A. Huyard, "Membrane bioreactor on domestic wastewater treatment sludge production and modeling approach," *Wat. Sci. Tech.*, **23**, 1591-1600 (1991).
4. Rosenberger, S., Krüger, U., Witzig, R., Manz, W., Szewzyk, U., and Kraume, M., "Performance of a bioreactor with submerged membranes for aerobic treatment of municipal waste water," *Wat. Res.*, **36**, 413-420 (2002).
5. Lee, Y., Cho, J., Seo, Y., Lee, J. W., and Ahn, K.-H., "Modeling of submerged membrane bioreactor process for wastewater treatment," *Desalination*, **146**, 451-457 (2002).
6. Chang, I.-S., Gander, M., Jefferson, B., and Judd, S.J., "Low-cost membranes for use in a submerged MBR," *Proc. Safety Env. Protection: Trans. Inst. Chem. Eng. Pt. B*,

- 79, 183-188 (2001).
7. Gander, M.A., Jefferson, B., and Judd, S.J., "Membrane bioreactors for use in small wastewater treatment plants: membrane materials and effluent quality," *Wat. Sci. Tech.*, **41**, 205-211 (2000).
 8. Lesjean, B., Gnirss, R., and Adams, C., "Process configurations adapted to membrane bioreactors for enhanced biological phosphorous and nitrogen removal," *Desalination*, **149**, 217-224 (2002).
 9. Côté, P., Buisson, H., Pound, C., and Arakaki, G., "Immersed membrane activated sludge for the reuse of municipal wastewater," *Desalination*, **113**, 189-196 (1997).
 10. Hasar, H., Kinaci, C., Unulü, A., and İpek, U., "Role of intermittent aeration in domestic wastewater treatment by submerged membrane activated sludge system," *Desalination*, **142**, 287-293 (2001).
 11. Chang, I.-S., and Judd, S.J., "Air sparging of a submerged MBR for municipal wastewater treatment," *Proc. Biochem.*, **37**, 915-920 (2002).
 12. Zhang, D., Lu, P., Long, T., and Verstraete, W., "The integration of methanogenesis with simultaneous nitrification and denitrification in a membrane bioreactor," *Process Biochem.*, **40**, 541-547 (2005).
 13. Milan, Z., Sánchez, E., Weiland, P., de Las Pozas, C., Borja, R., Mayari, R., and Roviroso, N., "Ammonia removal from anaerobically treated piggery manure by ion exchange in columns packed with homoionic zeolite," *Chem. Eng. J.*, **66**, 65-71 (1997).
 14. Borja, R., Sánchez, E., Weiland, P., and Travieso, L., "Effect of the clay mineral zeolite on ammonia inhibition of anaerobic thermophilic reactors treating cattle manure," *Env. Technol.*, **14**, 891-896 (1993).
 15. Borja, R., Sánchez, E., Weiland, P., Travieso, L., and Martin, A., "Kinetics of anaerobic digestion of cow manure with biomass immobilized on zeolite," *Chem. Eng. J. and Biochem. Eng. J.*, **54**(1), B9-B14 (1994).
 16. Yoon, G.-L., Kim, B.-T., Kim, B.-O., and Han, S.-H., "Chemical-mechanical characteristics of crushed oyster-shell," *Waste Manag.*, **23**, 825-834 (2003).
 17. Jang, H. and Kang, S.-H., "Phosphorus removal using cow bone in hydroxyapatite crystallization," *Wat. Res.*, **36**, 1324-1330 (2002).
 18. Lee, S. I., Weon, S. Y., Lee, C. W., and Koopman, B., "Removal of nitrogen and phosphate from wastewater by addition of bittern," *Chemosphere*, **51**, 265-271 (2003).
 19. Mondale, K. D., Carland, R. M., and plan, F. F., "The comparative ion exchange capacities of natural sedimentary and synthetic zeolites," *Min. Eng.*, **8**, 535-548 (1995).
 20. AWWA, APHA, Standard Methods for The Examination of Water and Wastewater, 17th ed., Washington, DC, USA (1989).
 21. Araki, H., Koga, K., Kusuda, T., and Awaya, Y., "Intermittent aeration for nitrogen removal in small oxidation ditches," *Wat. Sci. Tech.*, **22**, 131-138 (1990).