Available online at www.sciencedirect.com
ScienceDirect
ELSEVIER
Desalination 202 (2007) 114–121
DESALINATION
www.elsevier.com/locate/desal

Simultaneous high-strength organic and nitrogen removal with combined anaerobic upflow bed filter and aerobic membrane bioreactor

Y.T. Ahn[a], S.T. Kang[b], S.R. Chae[c], C.Y. Lee[d], B.U. Bae[e], H.S. Shin[a]*

[a]*Department of Civil and Environmental Engineering, Korea Advanced Institute of Science & Technology, 373-1 Guseong-dong, Yuseong-gu, Daejeon 305-701, South Korea*
Tel. +82 42 869-3613; Fax +82 42 869-8460; email: hangshin@kaist.ac.kr
[b]*Department of Environmental Science and Engineering, Gwangju Institute of Science & Technology, Oryong-dong, Buk-gu, Gwangju 500-712, South Korea*
[c]*Department of Environmental Engineering, Graduate School of Engineering, Hokkaido University, Sapporo 060-8628, Japan*
[d]*Department of Civil Engineering, The University of Suwon, San 2-2, Wau-ri, Bongdam-eup, Hwaseong-si, Gyeonggi-do 445-743, South Korea*
[e]*Department of Environmental Engineering, Daejeon University, Yongun-dong, Dong-gu, Daejeon 300-716, South Korea*

Received 31 July 2005; accepted 23 December 2005

Abstract

Biological treatment of high-strength nitrogen wastewater by a combined anaerobic (upflow sludge bed filter, UBF)/aerobic (membrane bioreactor, MBR) system has been studied. This system exhibited high performance on the removal of organic matter and nitrogen simultaneously. Organic and nitrogen concentrations increased from 6,000 to 14,500 mg/L and 300 to 1,000 mg/L, respectively. At the internal recycle ratio of Q (Q is the influent flow rate), average removal efficiencies of organic and total nitrogen were found to be 99 and 46%, respectively with the relatively short HRT of 24 h. When operated with the insufficient alkalinity supply, the organic removal efficiency in anaerobic reactor reduced from 98 to 82%. At high influent ammonia concentration, ammonification which is the dissimilatory nitrate reduction to NH_4^+ was observed. In case of membrane fouling, transmembrane pressure (TMP) of the combined process was about 9 times higher than that of a unit MBR under same operation conditions. The reason of severe fouling in the combined system might be caused by increased extracellular polymeric substance (EPS) and

*Corresponding author.

Presented at the conference on Wastewater Reclamation and Reuse for Sustainability (WWRS2005), November 8–11, 2005, Jeju, Korea. Organized by the International Water Association (IWA) and the Gwangju Institute of Science and Technology (GIST).

doi:10.1016/j.desal.2005.12.046

hydrophobicity. EPS composition and SUVA were more sensitive parameters than surface charge and total EPS content, with respect to the change of internal recycle ratio 100–300%.

Keywords: UBF; MBR; Internal recycle rate; Membrane fouling; Hydrophobicity

1. Introduction

As the discharge regulation limits of total nitrogen to surface and ground stream become stringent, the removal of ammonia nitrogen to meet the discharge limits by nitrification and denitrification was necessary. The technologies usually applied for nutrient removals are based on a spatial or temporal sequence of different anaerobic and anoxic, aerobic steps [1].

The treatment of strong nitrogen wastewater with high organic matter content has been pursued in anaerobic biological reactors due to the economic and technical advantages. Furthermore, the methane produced in this reactor can be used as an alternative energy. For these advantages, anaerobic digestion has been widely applied for organic and solid removal. Since early 1990s, as an alternative complex system for simultaneous carbon and nitrogen removal, a direct integration of the denitrification and the anaerobic function in a single reactor has been proposed [2–5]. Various configurations of anaerobic and aerobic reactor system were applied for the treatment of high strength synthetic/real wastewater [6,7]. In aerobic reactors, nitrite and nitrate could be reduced completely with volatile fatty acids [2].

This study attempts to propose an innovative combined anaerobic/aerobic system for the treatment of wastewater containing high concentration of nitrogen. The performance of the combined system and the membrane fouling phenomena, which was one of the major obstacles in MBR coupled process were evaluated under various operating conditions [8,9].

2. Material and methods

2.1. Characteristics of the combined UBF/MBR system

As shown in Fig. 1, the anaerobic reactor (UBF) has an effective volume of 6.27 L and it is packed with ceramic media at the top layer. It was inoculated with granular sludge of 1 L taken from a brewery wastewater treatment plant. Influent was fed at the bottom of the reactor and the produced gas was collected in a gas collector. The temperature of the reactor was maintained at 35°C. The submerged MBR was operated at a constant permeate flux of 0.019 L/m^2/h under hydraulic retention time (HRT) of 1 day. As shown in Fig. 1, MBR has an effective volume of 6.5 L, in which a U-shaped hollow fiber membrane module was placed. The membrane was made of polypropylene having a nominal pore size of 0.4 μm and an effective filtration area of 0.07 m^2. For the easy build-up of nitrifying bacteria in the bioreactor, no sludge was discharged and dissolved oxygen concentration was

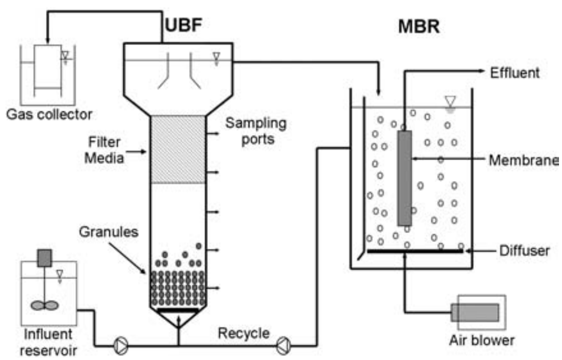

Fig. 1. Schematic diagram of the combined UBF/MBR system.

Table 1
Characteristics of the synthetic wastewater

Compound	Chemical formula	Molecular weight (g/mol)	Concentration (mg/L)
Glucose	$C_6H_{12}O_6$	180.0	14,500
Ammonium chloride	NH_4Cl	53.5	1000
Calcium chloride	$CaCl_2 \cdot 2H_2O$	147.0	0.368
Magnesium sulfate	$MgSO_4 \cdot 7H_2O$	246.5	5.07
Manganese chloride	$MnCl_2 \cdot 4H_2O$	197.9	0.275
Zinc sulfate	$ZnSO_4 \cdot 7H_2O$	287.5	0.44
Ferric chloride anhydrous	$FeCl_3$	162.2	1.45
Cupric sulfate	$CuSO_4 \cdot 5H_2O$	249.7	0.391
Cobalt chloride	$CoCl_2 \cdot 6H_2O$	237.9	0.42
Sodium molybdate dehydrate	$Na_2MoO_4 \cdot 2H_2O$	242.0	1.26
Yeast extract	–	–	30

maintained over 2.0 mg/L. For the comparison of membrane fouling, equal size of bioreactor was operated at the same operating condition.

Both reactors were connected in series with a recycling line from the MBR to the influent line of the UBF. The internal recycle ratio was 100–300% of influent flow rate for the denitrification of oxidized nitrogen.

2.2. Influent characteristics

UBF reactor was fed with the synthetic wastewater containing glucose and ammonia as summarized in Table 1. As shown in Table 2, the organic and nitrogen loading rate increased gradually. Maximum influent COD and nitrogen concentrations were 14,500 mg/L (7.2 kg COD/m^3/d) and 1,000 mg/L (0.5 kg NH_4-N/m^3/d), respectively.

2.3. Analytical methods

Suspended solids (SS), COD, TKN and NH_4-N concentrations were measured according to Standard Methods [10]. Concentrations of various ions in solution were analyzed using ion chromatography (DX-120, Dionex, USA). Total organic and inorganic carbons were determined by a TOC analyzer (DC-180, Dorhmann, Germany). The surface charge of microbial floc was determined by titration method. Polybrene and polyvinyl sulphate potassium (PVSK) were used as the cationic and anionic standards, respectively, in the titration method. A known volume of sludge

Table 2
Experimental conditions of UBF-MBR system

Phase	I	II	III	IV	V	VI	VII
Time (day)	1–18	19–35	36–47	48–58	59–73	74–80	81–89
COD (mg/L)	6000	7500	9750	11,250	14,500	14,500	14,500
NH_4^+-N (mg/L)	300	300	300	450	585	760	1000
COD/N ratio	20	25	32.5	25	24.8	19.1	14.5

sample was diluted with ultra-pure water and mixed with an excess amount of 0.001 N polybrene standard solutions. Standard solution of 0.001 N PVSK was used to titrate against the excess amount of polybrene using a few drops of toluidine blue as an indicator. An equal volume of polybrene diluted with the same amount of deionized distilled water was used as a blank. Then, the surface charge can then be determined from the following equation:

$$\text{Surface charge (meq./g VSS)} = \frac{(A-B)\times N\times 1000}{V\times M}$$

where A is mol of PVSK added to the sample, N normality of PVSK, B mL of PVS added to blank, V mL of sample used, and M g VSS/L.

Specific ultraviolet absorbance (SUVA) was used to estimate the hydrophobicity of supernatant. SUVA is the ratio of UV absorbance at 254 nm to dissolved organic carbon concentration. High SUVA indicates high degree of hydrophobicity due to its high aromaticity. The procedure of surface charge measurement was the same as described previously [8]. EPS was extracted from microbial floc by heat treatment [11]. The extracted solution was analyzed for total carbohydrate and proteins. The sum of carbohydrates and proteins represented the total amount of EPS, which are the dominant components typically found in extracted EPS [12,13]. Carbohydrates and proteins in EPS were determined according to the phenol–sulfuric acid method with glucose as a standard and Folin method with bovine serum albumin as a standard, respectively [14,15].

3. Results and discussion

3.1. Performance of the combined UBF/MBR system

Fig. 2 presents the performance of the organic and nitrogen removal under various operation conditions. During the experimental period, higher organic and nitrogen removal was possible under various loading rates. Average removal efficiencies of organic and total nitrogen were 99 and 47%, respectively at maximum COD_{Cr} of 14,500 mg/L and ammonia nitrogen of 1,000 mg/L (7.2 kg COD/m^3/d, 0.5 kg NH_4-N/m^3/d). In the anaerobic reactor, the average methane content of produced gas was 37–42%, which was smaller than the reported value from the conventional anaerobic treatment of wastewater due to the production of N_2 and additional CO_2.

Organic removal efficiency in anaerobic reactor was reduced from 98 to 82% when alkalinity decreased from 4,000 to 3,000 mg/L (as $CaCO_3$) for 40–64 days. Also ammonification, dissimilatory nitrate reduction to NH_4^+,

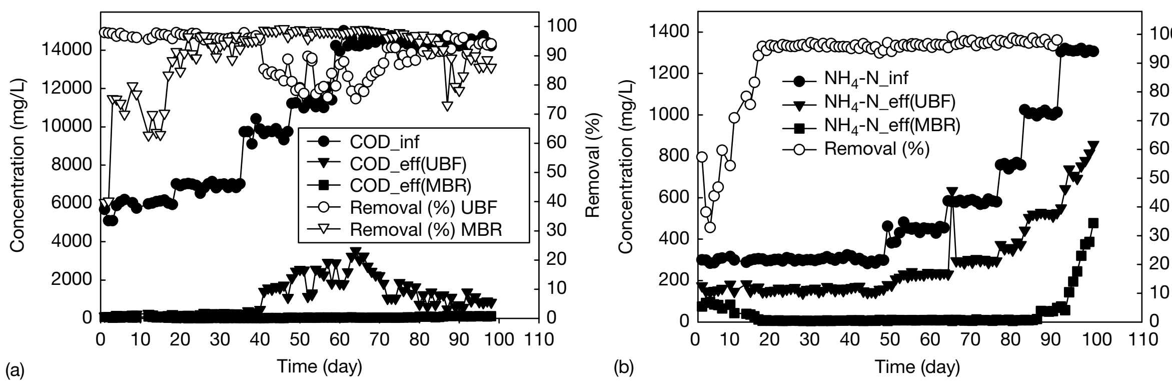

Fig. 2. Organic and nitrogen removal in the UBF-MBR system.

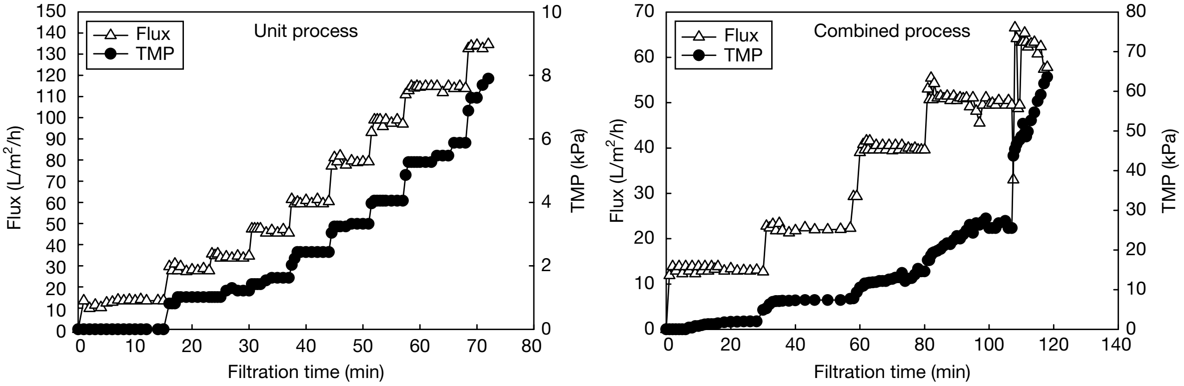

Fig. 3. Permeability of the unit MBR and the combined process sludge.

happened under higher influent ammonia of 585 mg/L. Despite of insufficient supply of alkalinity, effluent which is produced by membrane unit was quite stable. And organic removal efficiency was recovered as alkalinity increased to 4,000 mg/L again at 65 days.

3.2. Membrane fouling (sludge filtration test)

To compare the characteristics of membrane fouling, TMP was monitored at each permeate flux. As shown in Fig. 3, severer fouling was observed in the combined process. To maintain the same permeate flux of 39.6–45.5 L/m^2/h, the required TMP were 1.62 and 14.6 kPa for the unit MBR and the combined process, respectively. In case of the combined process sludge, it was difficult to maintain the flux over 66.53 L/m^2/h because of rotation speed limit of peristaltic pump.

There are various biological, physical and chemical factors affecting membrane fouling in the activated sludge. To elucidate the higher fouling tendency of combined process, the quantity of EPS was analyzed. EPS matrix is heterogeneous, in which polymeric materials such as carbohydrates, proteins, lipids and nucleic acids have been found. In this study, however, the sum of carbohydrates and proteins was considered to represent the EPS because these were the dominant components found in extracted EPS [12,13]. Fig. 4 shows the concentrations of carbohydrates and protein in microbial floc. The total EPS content of the combined process was 1.3–1.4 times higher (13.8–18.9 mg/g VSS) than that of the unit process. But there was no tendency in the ratio of protein to carbohydrate components.

As shown in Fig. 4, particle size distribution of MBR sludge was similar in both processes, also no remarkable tendency in sludge particle size was observed. To evaluate the surface properties of microbial floc and supernatant, hydrophobicity of supernatant and surface charge of microbial floc were measured (Fig. 5), which might affect membrane fouling. Sludge of the combined process has about twice higher in SUVA than that in the unit process. This result indicated that the formation of aromatic and larger molecular weight soluble organics in this combined system. As shown in Fig. 5, the surface charge of microbial floc showed similar value.

To compare the sensitivity of various parameters on the membrane fouling, internal recycle ratio was gradually increased from 100 to 300%. As shown in Table 3, the total amount of EPS on microbial floc were 65.1, 64.5 and 68.8 mg/g VSS at various internal recycle ratio of Q, $2Q$, and $3Q$, respectively. Even though there was only

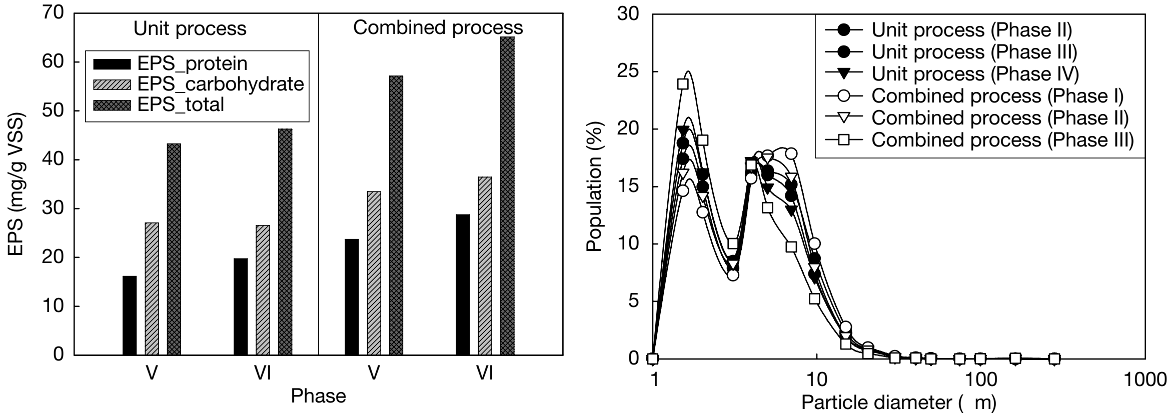

Fig. 4. EPS concentration and sludge particle size distribution.

small variation in total amount of EPS content, protein content decreased by 17% and carbohydrate content increased by 12% as the internal recycle ratio increased from 100 to 200%. With a high food to microorganism (F/M) ratio in aerobic reactor due to the higher COD concentration of UBF effluent, EPS carbohydrate content in sludge increased, which reflected the available carbon.

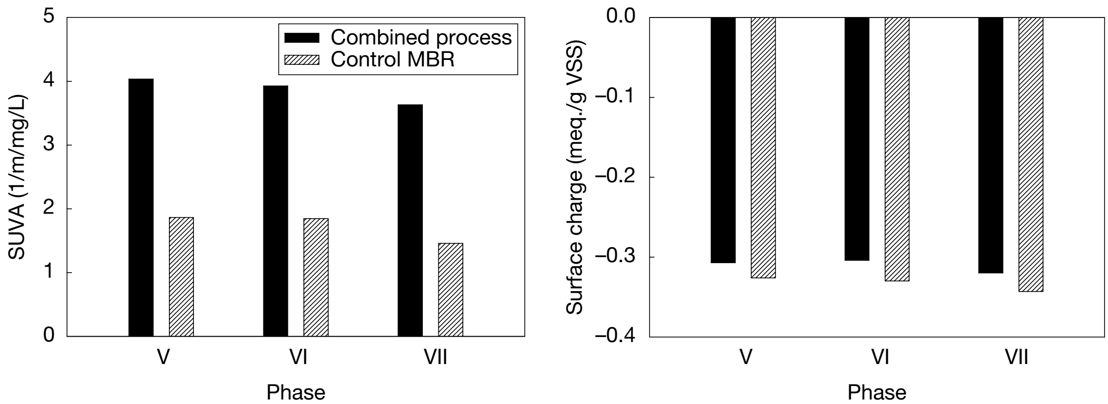

Fig. 5. SUVA of supernatant and surface charge of MBR sludge.

Table 3
Properties of microbial floc and supernatant at various recycle rates

Recycle ratio (%)	Specific UV absorbance (m^{-1} mg^{-1} L)	EPS (mg/g VSS)			Surface charge (meq./g VSS)
		Carbohydrate	Protein	Total	
100	2.81	36.4	28.7	65.1	–0.3211
200	2.94	40.7	23.8	64.5	–0.3182
300	3.12	44.4	24.4	68.8	–0.3179

Also sludge surface charge and hydrophobicity increased as the internal recycle rate increased from 100 to 300%. The difference of SUVA and surface charge between phase 1 and phase 3 were 11% (0.31 m^{-1} mg^{-1} L) and 1% (0.0032 meq./g VSS), respectively. It can be concluded that EPS composition and SUVA is more sensitive than hydrophobicity or total EPS content.

4. Conclusions

In this study using a combined anaerobic/aerobic (UBF/MBR) system for the treatment of strong nitrogen wastewater, following conclusions were obtained:

- Higher organic and total nitrogen removal (99 and 46%) were possible at various organic and nitrogen loading rates.
- Decreased alkalinity from 4,000 to 3,000 mg/L as ($CaCO_3$) affected organic removal efficiency and denitrification in anaerobic UBF reactor.
- Rapid TMP increase was observed at the combined process. And the TMP value of the combined system was nine times higher than that of unit process to obtain the same permeate flux.
- In case of combined process, the total contents of EPS were higher than that of unit process. And the supernatant of combined process MBR showed more hydrophilic characteristic. These characteristics of sludge would affect the severe membrane fouling in the combined process.
- EPS composition and SUVA was more sensitive parameter than surface charge and total EPS content, with respect to the change of recycle rate 100–300%.

Acknowledgements

This work was supported by Ministry of Environment as “The Eco-technopia 21 project” (grant no. 2004-07001-0084-0) and the NRL Program (grant no. M1-0203-00-0063).

References

[1] M.L. Lacalle, S. Villaverde, F. Fdz-Polanco and P.A. Garcia-Encina, Combined anaerobic/aerobic (UASB + UBAF) system for organic and nitrogen removal from a high strength industrial wastewater, Water Sci. Technol., 44 (2001) 255.
[2] J.C. Akunna, Denitrification in anaerobic digesters: a review of recent studies, Proceeding of 50th Industrial Waste Conference, Purdue Univ., 1995.
[3] D. Hanaki and C. Polprasert, Contribution of methanogenesis to denitrification with an upflow filter, J. WPCF, 61 (1989) 1604.
[4] M. Kuroda, H. Shima and Y. Sakakibara, A study on simultaneous treatment of organic matter and nitrate with a biofilm consisting of methane fermentative bacteria and denitrifying bacteria, Proc. Environ. Sanit. Eng. Res., 1988, p. 231.
[5] H.S. Shin, K.Y. Kim, C.Y. Lee, S.E. Oh and Y.C. Song, Simultaneous removal of carbon and nitrate in a single stage hybrid type reactor, Proc. of WEF Conf., New Orleans, USA, 1999.
[6] W.P. Barber and D.C. Stuckey, Nitrogen removal in a modified anaerobic baffled reactor (ABR): 1, Denitrification, Water Res., 34 (2000) 2413.
[7] N. Bernet, N. Delgenes, J.C. Akunna, J.P. Delgenes and R. Moletta, Combined anaerobic–aerobic SBR for the treatment of piggery wastewater, Water Res., 34 (2000) 611.
[8] W.T. Lee, S.T. Kang and H.S. Shin, Sludge characteristics and their contribution to microfiltration in submerged membrane bioreactors, J. Membr. Sci., 216 (2003) 217.
[9] T. Mukai, K. Takimoto, T. Kohno and M. Okada, Ultrafiltration behaviour of extracellular and metabolic products in activated sludge system with UF separation process, Water Res., 34 (2000) 902.
[10] APHA, AWWA, WPCF, Standard Methods for the Examination of Water and Wastewater, 20th edn., American Public Health Association, Washington, 1998.
[11] J.W. Morgan, C.F. Forster and L. Evison, A comparative study of the nature of biopolymers extracted from anaerobic and activated sludge, Water Res., 24 (1990) 743.
[12] R. Bura, M. Cheung, B. Liao, J. Finlayson, B.C. Lee, I.G. Droppo, G.G. Leppard and S.N. Liss, Composition of extracellular polymeric substances in the activated sludge floc matrix, Water Sci. Technol., 37 (1998) 325.

[13] B. Frølund, R. Palmgren, K. Keiding and P.H. Nielsen, Extraction of extracellular polymers from activated sludge using a cation exchange resin, Water Res., 30 (1996) 1749.

[14] M. Dubois, K.A. Gilles, J.K. Hamilton, P.A. Rebers and F. Smith, Colorimetric method for determination of sugars and related substances, Anal. Chem., 28 (1956) 265.

[15] O.H. Lowry, N.H. Rosebrough, A.L. Farr and R.J. Randall, Protein measurement with the Folin phenol reagent, J. Biol. Chem., 193 (1951) 265.