Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2014.940392

56 (2015) 565–573
October

Taylor & Francis
Taylor & Francis Group

Study and engineering application of an MBR in treating cold-rolled steel wastewater

Nien-Hsin Kao[a,*], Ming-Chien Su[b], Wen-Chun Huang[c]

[a]*Department of Environmental Engineering, Kun Shan University, No. 195, Kunda Road, Yong Kang District, Tainan City 710, Taiwan, Tel. +886 6 2050494; Fax: +886 6 2050540; email: kaon@mail.ksu.edu.tw*
[b]*Department of Natural Resources and Environmental Studies, National Dong Hwa University, No. 1, Sec.2, Da Hsueh Rd., Shoufeng, Hualien 97401, Taiwan, Tel. +886 3 8633331; Fax: +886 3 8633339; email: mcsu@mail.ndhu.edu.tw*
[c]*M.S. Department of Environmental Engineering, Kun Shan University, No. 195, Kunda Road, Yong Kang District, Tainan City 710, Taiwan, Tel. +886 6 2050494; Fax: +886 6 2050540; email: abney@ms36.hinet.net*

Received 5 January 2014; Accepted 26 June 2014

ABSTRACT

The pickling process in virgin steel manufacturing generates a great deal of oily wastewater in the metals industry. During this process, the coated rolling oil needs to be removed by washing the surface of the steel with acid and alkaline solutions. High chemical oxygen demand (COD), oil, grease, and emulsified oil-in-water pollutants are the key characteristics of the wastewater. Chemical consumption in breaking emulsified wastewater and waste sludge are the main problems in traditional treatment methods. To improve treatment efficiency and reduce chemical usage, a membrane system was applied into the existing wastewater treatment process. The objective of this study is to build an engineering scale membrane bioreactor (MBR) system with a treatment capacity of 1,500 m^3/d based on the attained optimum operating parameters in the field study. To assure the success of an actual MBR system being able to be used to treat the oily wastewater, two stages of pilot experiments were conducted. The results showed that the effluent quality of the pilot MBR system for grease concentration, turbidity, and COD were under 10 mg/L, less than 1 NTU, and lower than 100 mg/L, respectively. Based on the results, an actual full size MBR system was constructed and had reduced the costs of chemicals, daily operation, sludge treatment and disposal.

Keywords: MBR (membrane bioreactor); Cold-rolled steel wastewater; Oil-in-water

1. Introduction

The application of membranes in treating oily wastewater on a small scale was first reported in late 1990, where a membrane was used to treat various kinds of wastewater such as that discharged from alkaline/acidic cleaners, machine coolants, petroleum industries, and the reported primary sources of oily wastewater generated by the aluminum and steel industries [1]. The traditional treatment method for oil-in-water wastewater uses chemicals to break down emulsified oil followed by coagulation and physical separation; however, chemical consumption and the large amount of waste sludge were the accompanying problems. Generally, wastewater generated from the

*Corresponding author.

steel industry often exists in a form like an oil–water mixture and due to necessity; the emulsified oil has been popularly used in the manufacturing process. Spent cutting-oils in the steel cold-rolling process might have a smaller size of droplets of less than 20 μm, containing inorganic particles, surfactants, and other organic compounds that complicate the treatment process [1,2]. A membrane unit is then introduced into the treatment process in treating oily or heavy metal wastewater due to the fact that no chemicals are needed in physically breaking down the emulsified oil or separating heavy metals by forcing wastewater to flow through an appropriate pore-sized membrane [1–4]. However, those were limitations in the early stages such as problems with the engineering scale-up and fouling: thus, a variety of hybrid membrane processes have been developed. The application of powdered activated carbon into a membrane bioreactor (MBR) system to remove toxic compounds and the combination of ozonation to remove pharmaceutical wastewater are the reported cases of the hybrid process [5–7]. Steel industries are still generating great amounts of oily wastewater and to treat this oil-in-water waste is a necessary process. A pilot scale of electro-sorption technology, the destabilization of emulsion by adding natural minerals, and a combination of hybrid system gas-energy-management, electrochemical catalytic oxidation, and MBR have been reported in treating the oily wastewater [8–10]. A detailed review of membrane research in North America and a variety of membrane material applications or studies of a pilot scale MBR and comparisons with conventional activated sludge systems in treating micropollutants have also been reported [11–18]. However, an MBR treating capacity greater than 2000 m^3/d has been reported in Europe and is usually applied in treating and reusing municipal wastewater [19]. In treating oil-in-water waste, there have been rarely reported cases of an engineering scale up or a pilot MBR study applied to an actual treatment process.

In our study, a series of experiments were conducted using a pilot scale to attain the optimum operating parameters in treating the emulsified oil wastewater that was discharged from a steel industry and finally, an MBR system with treatment capacity of 1,500 m^3/d was built and put into operation. In our case, the influent wastewater to the MBR was pre-treated by the existing chemical coagulation treatment unit followed by a settling tank in the steel plant. Generally, the wastewater constituent inflow to the MBR had chemical oxygen demand (COD) concentrations of between 1,000 and 1,300 mg/L and grease contents of 50–80 mg/L. However, for the steel industry, the current three major limited standards (in mg/L) in the discharged effluent for grease, COD, and SS are 10, 100, and 30, respectively. Thus, an MBR system was planned to support the conventional treatment units to reduce the costs of operation, chemical and wasted sludge disposal, and meet the current regulatory terms of compliance.

2. Material and methods

To assure the success of an actual MBR system being used to treat the oily wastewater, a consequent two-stage pilot study was conducted during a four month period with one year needed for the construction and verification of a full-sized MBR system. The primary stage was the pilot MBR treatability study followed by a second stage of confirmation of the optimum operating parameters with the results adopted as the design data in an engineering application. In the first stage, an MBR pilot reactor with a treatment capacity of 40 L/d was used to treat the discharged effluent from an existing chemical coagulation unit within an operating process in treating cold-rolled steel plant wastewater. Fig. 1 shows the schematic of the MBR reactor which contains the main 30 L (effective volume 25 L) plexiglass tank and the four pieces of PTFE (Polytetrafluoroethylene) N-MBR® flat sheet membrane with dimensions of 15 cm (L) × 10 cm (W) for each and a

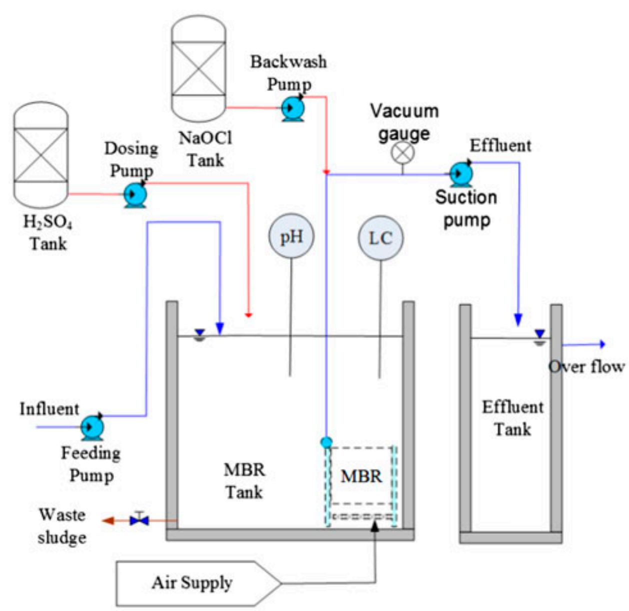

Fig. 1. Schematic diagram of the MBR pilot reactor in the first stage study.

pore size of 0.3 μm. The auxiliary devices for the reactor included one electromagnetic diaphragm inflow pump (Tacmina, PZD-32) and three peristaltic pumps (Master flex, 77921, 77921-40 and 77200-12) for controlling outflow, backwash, and pH (within 6.8–7.8) adjustment. Maintaining a stable water level was achieved and measured using an ultrasonic level sensor (Ho-Shie, LU-27) accompanied with the adjustment of the influent rate, monitoring of negative transmembrane pressure (TMP), and measurement of discharge flow. The discharge flow from the system was measured twice daily and the average hourly flux was calculated. The MBR module was operated using an intermittent mode that was discharged for 10 min followed by a 2 min idle. Daily cleaning of the MBR was conducted using a backwash flow rate of 5 L/m^2 and 50 ppm of NaOCl for 10 min followed by a 20 min idle to prevent fouling problems and to achieve the optimum and stable flux conditions. Seeded activated sludge for the MBR was taken from the existing steel wastewater treatment plant with an initial concentration (MLVSS) of 3,000 mg/L. The initial operating parameters for F/M ratio, volume loading, and HRT were set at 0.15–0.18 kg COD/kg MLVSS-d, 0.40–0.55 kg COD/m^3 d and 60 h, respectively. Due to the low SS concentration in the permeation flux, the turbidity quality was used to monitor the flow. The turbidity meter (Merck, Turbiquant® 1100 IR) was regularly calibrated using a standard solution with concentrations between 0.2 and 1,000 NTU. A Merck dichromate solution analysis kit with a spectrometer (Merck, Spectroquant® NOVA 60) was used to determine the COD. The n-hexane Soxhlet extraction method (NIEA W505.51C) was used to determine the grease content in the wastewater. The MLSS and MLVSS in the MBR were analyzed using the standard suspended solid determination method (NIEA W210.58A) [20].

3. Results and discussion

3.1. Pilot MBR study

During the study, the clear color changed from the original dark brown to a steady yellow orange and healthy activated sludge flocs were observed which indicated the advantaged micro-organism was the dominant population in the reactor and suitable for degrading the target compounds. Fig. 2(a) shows the variation of biomass concentration which indicated that the micro-organism stably increased as the inflow rate increased while the ratio (MLVSS/MLSS) was maintained at around 0.85 in the final stage, which is a good ratio for treating this kind of oily wastewater. The figure indicates that the MLVSS was increased from 8,000 mg/L to the designed 10,000 mg/L when raising the inflow rate from 50 to 60 L/d after day 80 while the calculated sludge age was about 50 d. Fig. 2(b) shows the fluctuations of influent COD which were around 950–1,300 mg/L while the treated-effluent COD could only be reduced to about 430 mg/L with a treatment efficiency of only 61% at day 30 with no nutrients added to the reactor. To achieve a better efficiency, urea and phosphate were added to the system and maintained a ratio of COD/N/P at 200/5/1. The COD removal efficiency was dramatically increased to 83% after 15 d of nutrient dosing and reached 93% at day 48 with the effluent COD under the regulatory limit concentration, which is 100 mg/L. Grease and SS were the other pollutant compounds that needed to be removed in the wastewater and Fig. 2(c) shows the inflow grease concentrations into the MBR were around 50–80 mg/L. It should be noted that due to the confidentiality of the cold-rolled process, no specified grease compounds, constituent, or brands were informed.

Initially, the HRT was set at 60 h to provide an incubation environment for the micro-organisms to degrade the grease compound with the removal efficiency reaching 95% at day 41. Eventually, the effluent grease concentration was under 10 mg/L with removal efficiency up to 95% at a set 10 h HRT. Similarly, the influent turbidity was reduced from influent concentration of 120–250 NTU to less than 1 NTU in the effluent. The major operation parameters of the MBR system are shown in Fig. 3(a) which indicated that HRT, Flux, and TMP ratios were gradually adjusted to fit the respective conditions in each step. At the beginning, to test the membrane, the operated flux was maintained between 3 and 7 L/m^2 h where the observed TMP was around 6–13 cmHg. After day 80, when a good biomass ratio (MLSS/MLVSS) was achieved, the observed TMP was still maintained below 30 cmHg with no reduced outflow rate. The outflow of the MBR system was operated in a sporadic cycle and the total amount of effluent was measured twice daily. However, at day 91, the observed TMP had dramatically increased to over 40 cmHg when the operated average hourly flux was set at 21 L/m^2 h and a reduction of outflow was observed. To stabilize the system and avoid membrane damage, we installed one more piece of membrane to reduce the TMP and the discharged flux. Finally, the calculated averaged hourly flux was 16.7 L/m^2 h. In the end, the best removal efficiency of pollutants was

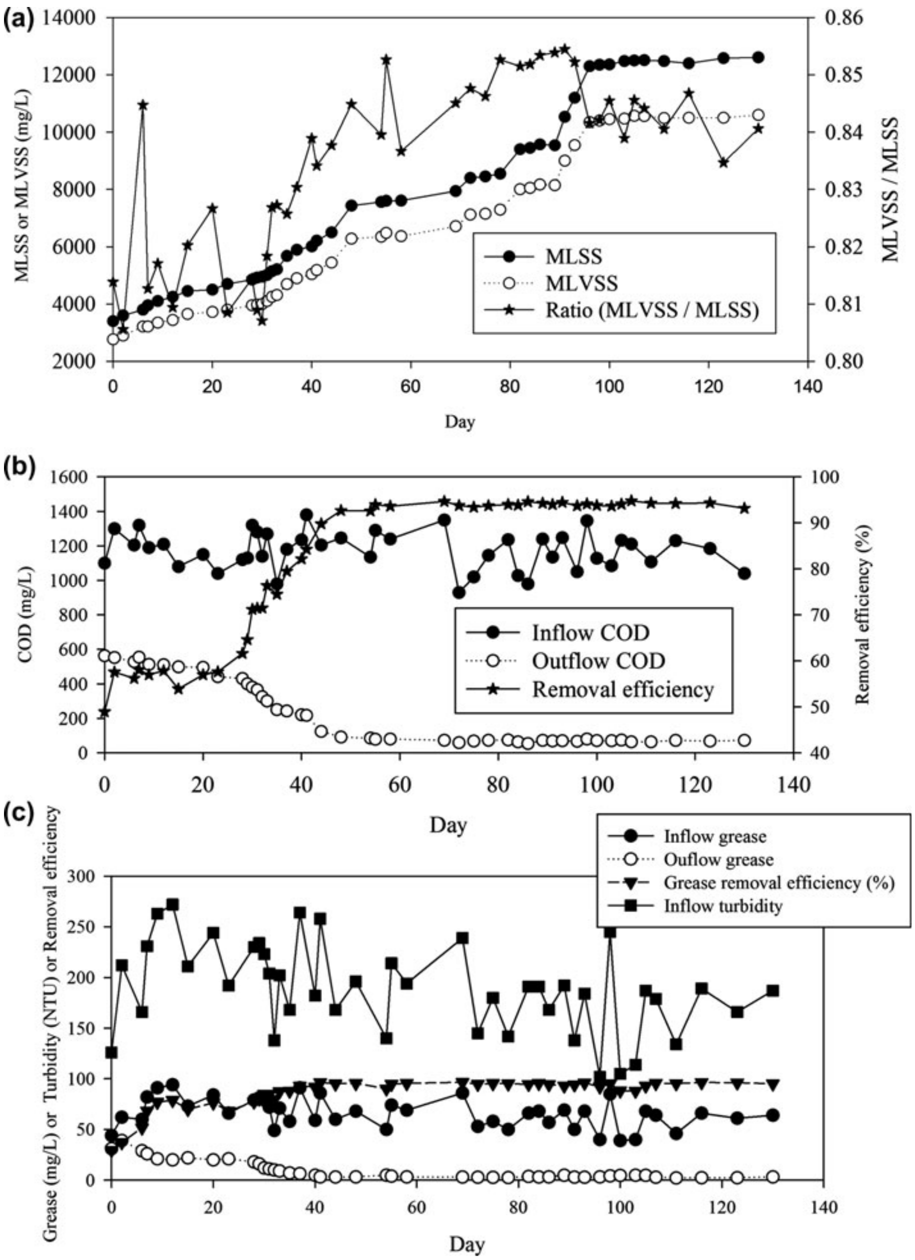

Fig. 2. Variation of concentrations in the MBR system (a) Biomass (b) COD (c) Grease.

achieved as shown in Fig. 3(b) which indicated the operating parameters for flux, F/M ratio, and COD loading.

In conclusion, Figs. 2 and 3 show the results of the first-stage study with the findings of appropriate operating parameters for MLVSS, averaged hourly flux, F/M ratio, HRT, and TMP set at 10,500 mg/L, 16.7 L/m^2 h, 0.2 ± 0.05 kg COD/kg MLVSS-d, 10 h, and 30 cmHg, respectively. There were reported operating conditions for submerged MBR in treating municipal wastewater, which listed parameters for MLSS, long-term operation flux, F/M ratio, HRT, and TMP were 5–25 g/L, 15–30 L/m^2 h, $\leq$ 0.2 kg COD/kg MLSS-d, 1–9 h, and 20 kPa, respectively [19]. Compared with these reported parameters, our study shows the results are acceptable and can be applied in treating industrial wastewater. In this stage, the applied pilot MBR unit was proved to be efficient in treating the oily wastewater with only the necessary nutrients added to the bioreactor and

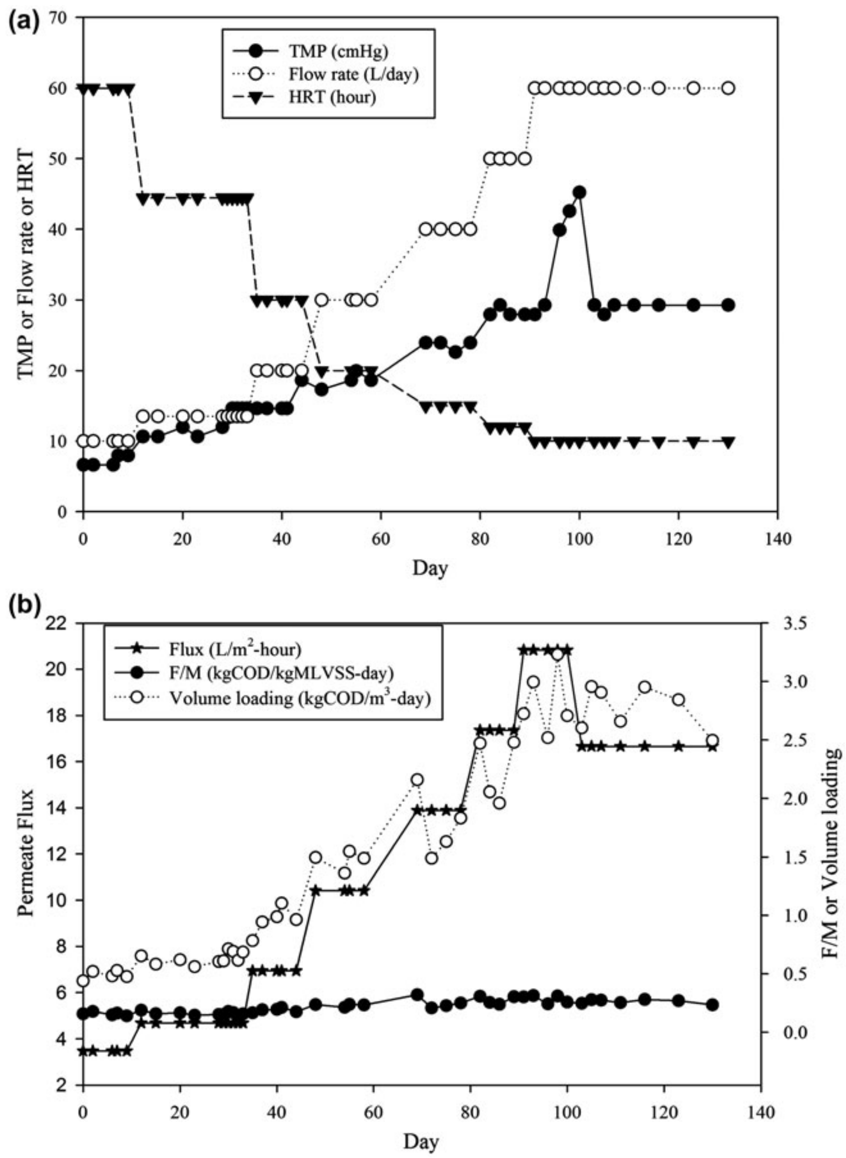

Fig. 3. Variation of major operation parameters in the MBR system (a) TMP (b) Permeate flux.

no other chemicals needed in breaking down the pollutants. From a long-term perspective, the study also supports that an MBR system can be a reduced cost method if compared with the conventional activated sludge system or other methods that use chemicals in breaking down emulsified oily wastewater.

3.2. Confirmation of optimum parameters

In an MBR system, the membrane fouling problem will induce unstable permeation flux, irregular TMP and consequently results in damage to the membrane. Thus, the next step was to confirm the proper flux flow and the regularity of the backwash frequency for an actual engineering scale system. The second stage of the study was conducted to confirm the optimum operating conditions before those studied parameters in the previous stage were applied into the engineering design. Fig. 4 shows the two sets of experimental modules which were used to confirm the permeation flux and backwash operating parameters. These identical MBR modules were equipped with necessary piping, gauges, water pumps, and air pumps. Each module was set at different operating parameters to compare the results. Firstly, we tested the stability of flux for these four modules in different sporadic cycles without backwash in all cycles as

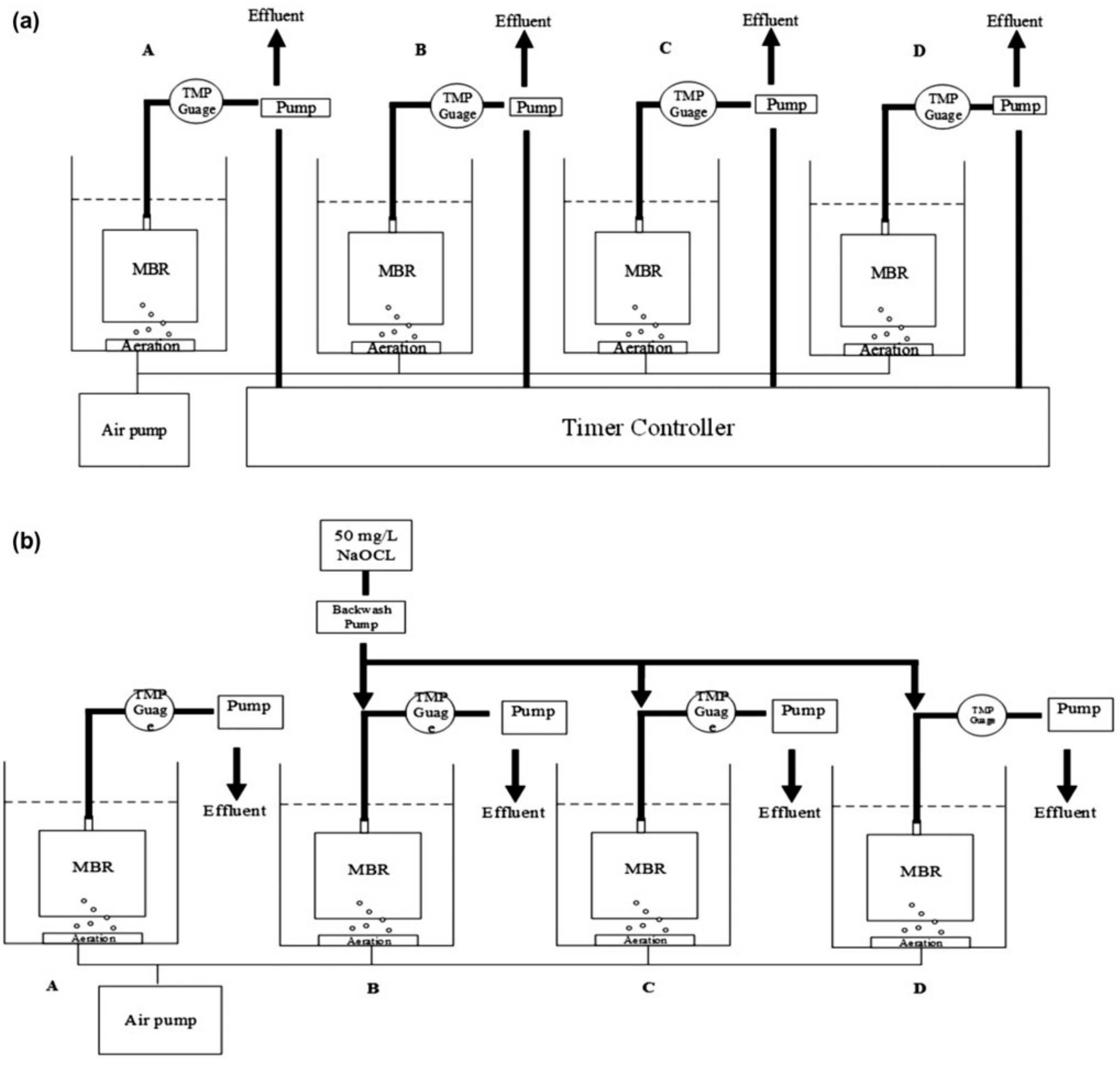

Fig. 4. Schematic diagram of identical MBR modules for the second stage study (a) Permeate flux test (b) Backwash test.

Table 1
Operating parameters for the second-stage flux test

Module	*A*	*B*	*C*	*D*
Common operating parameters				
Membrane area (m^2): one piece 10 cm × 10cm, double side	0.02			
MLVSS (mg/L)	10,500			
F/*M* (kg COD/kg MLVSS-d)	0.24			
Air flow rate (Membrane exterior) (L/m^2 min)	10			
Individual operating parameters				
(a) Discharge time (min)	5	10	15	20
(b) Idle time (min)	2	2	2	2
*Calculated required discharge flux(L/m^2 h): $\left[16.7 \times \frac{(a+b)}{a}\right]$	23.4	20.1	18.9	18.3

*16.7 is the attained average hourly flux in the first-stage study.

shown in Fig. 4(a). Table 1 lists the common operating parameters, which were attained in the previous stage and the individual sporadic cycle parameters for this experiment.

To match the attained average hourly flux of 16.7 L/m^{2}h in the first stage, the instantaneous discharge flux needed to be calculated to make up the loss of idle time in these sporadic cycles. Table 1 shows the calculated required initial discharged flux for each module. To test the limitations of the membrane, the experiment was conducted continuously for 14 d to study the effects of biofilm accumulation on the membrane. Fig. 5(a) shows that compared with the other three modules, module *B* had the least increment of the TMP and the most stable permeation flux during this two-week period. The tested sporadic cycle agreed with the optimum parameters of the MBR system in the first stage which was a 10 min discharge followed by 2 min idle. Fig. 4(b) shows another set of experiments,

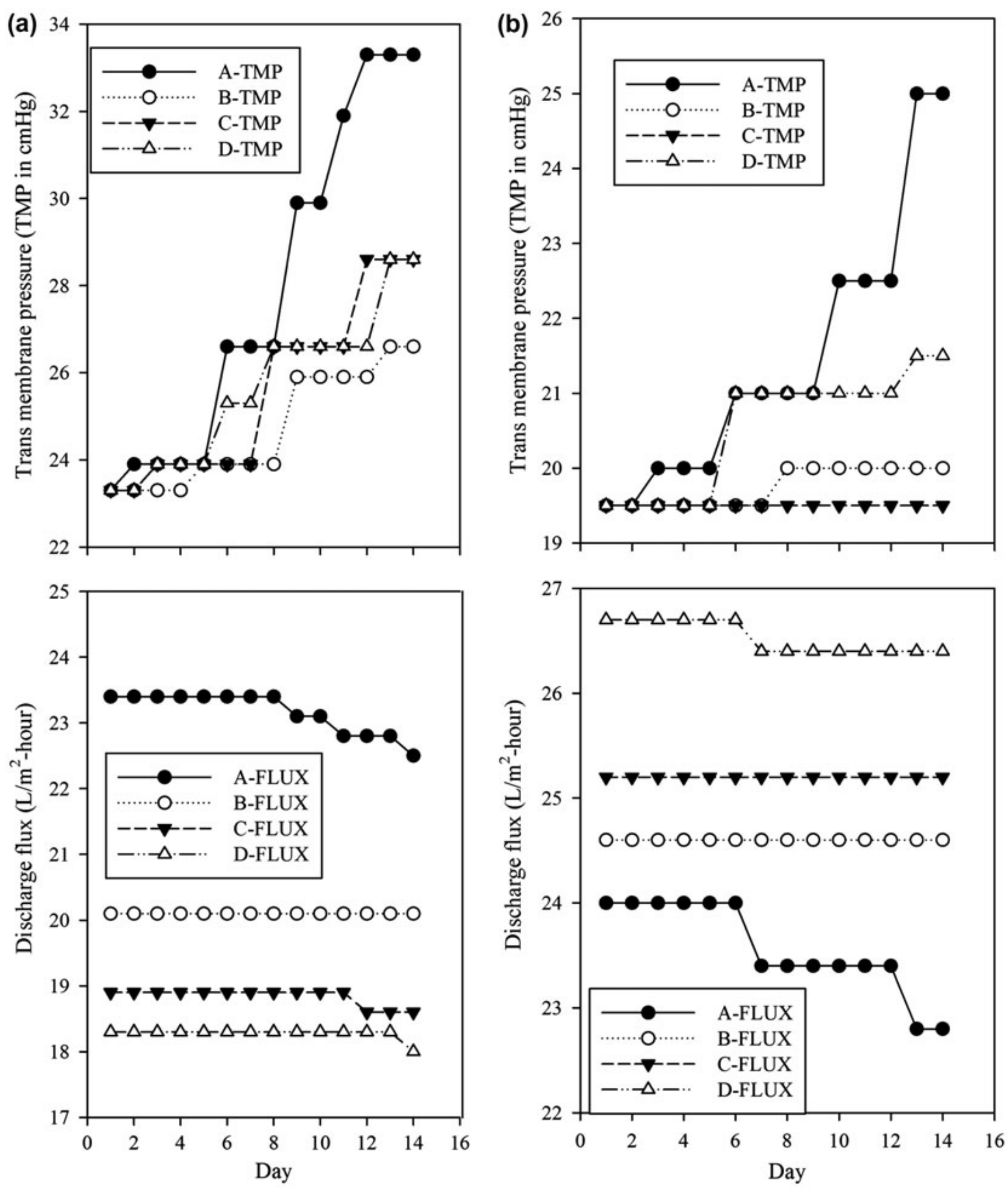

Fig. 5. Comparison of TMP and flux in the second stage study (a) Permeate flux (b) Backwash.

which was conducted to study the effect of the backwash cycle, using 50 ppm of NaOCl solution to attain a proper backwash frequency. Table 2 lists the common and individual operating parameters for this experiment. The designed discharge flux was set at 20 L/m^{2}h and thus, to make up for the loss of idle time for the discharge and backwash cycles, the operated instantaneous discharge flux was calculated as listed in the Table. Fig. 5(b) shows that module *C* had the most stable TMP followed by module *B*, which indicated that twice or once daily backwashes were acceptable; however overuse of the NaOCl solution is disadvantageous to an MBR system.

Thus, daily washing is more preferable in an actual operation. In contrast to that the results of no backwash in module *A* and too much backwash in module *D* caused an unstable TMP due to the plugging problem in the membrane and the high-instantaneous discharge flux to make up for the wasted idle time. Fig. 5(b) also indicates that modules *B* and *C* had a more stable flux rather than the diminished flux in modules *A* and *D*. Finally, the results in this stage confirmed that the optimum operating parameters were acceptable and practicable in an engineering application.

3.3. Engineering planning

To be more practical, a preliminary engineering planning is suggested based on the principles of the pilot study and in one year period, the MBR system was constructed and has been operating until the present day. Based on the designed treatment capacity of 1,500 m^3/d, a total of 20 sets of suspended flat MBR modules with pore size of 0.3 μm are equally divided into four tanks while the total effective volume of the

Table 2
Operating parameters for the second-stage backwash test

Module Common operating parameters	*A*	*B*	*C*	*D*
Membrane area (m^2): one piece 10 cm × 10 cm, double side	0.02			
MLVSS (mg/L)	10,500			
F/*M* (kg COD/kg MLVSS-d)	0.24			
Air flow rate (Membrane exterior) (L/m^2 min)	10			
Designed discharge flux (L/m^2 h)	20			
Sporadic cycle: discharge (min)/idle (min):	10/2			
Calculated daily discharge time (min): $\left[1440 \times \frac{(10)}{(10+2)}\right]$	1200			
Individual operating parameters				
Backwash (min)/Idle time (min):Terminated discharge time: 30 min/wash	10/20			
(a) Backwash frequency (wash/d)	0	1	2	4
Calculated required discharge flux(L/m^2 h): $\left[20 \times \frac{(1440)}{(1200-30\times a)}\right]$	24.0	24.6	25.2	26.7

Table 3
Preliminary engineering planning parameters

Main operation parameters				
Wastewater	COD	SS	Grease	pH
Influent (mg/L)	≤1,300	≤100	≤100	6–8
Effluent (mg/L)	≤80	≤1	≤5	6–8
Membrane module: rigid frame with 3D structure (PTFE outer layer/PET inner layer)	Flux (L/m^2 h)	MLVSS (mg/L)	HRT (h)	*F*/*M* (kg COD/kg MLVSS-d)
	15.0	10,000	10	0.2 ± 0.05
Estimated operating costs (based on local conditions, in NT$/d)				
(a) Electricity (system requirement 2,955 kw/h at 2.2 NT$/kwh)				6,500
(b) Chemical consumption (NaOCl and pH adjustment)				536
(c) Manpower				2,250
(d) Materials depletion (equipment and membrane at 2%/year)				450
(e) Wasted sludge disposal fee (2.5 NT$/kg at moisture 85%)				5,200
*Calculated unit cost (NT$/m^3): (a + b + c + d + e)/1,500				9.96

*1,500 is the designed treatment capacity (in m^3/d).

reactor is 750 m^3. The preliminary planning included all the necessary engineering elements for the practicable MBR system; such as an RC structure for reactors, pH adjustment, cleaning tank for membrane, membrane modules, piping/pumping system, and a control system. Table 3 summarizes the suggested planning operation parameters; however, considering the actual filed conditions, the suggested discharge flux is set at 15 L/m^2h, which is 90% of the attained parameter in the first stage. The estimated operating costs and the calculated daily operating cost is about 9.96 NT$/d (or 0.32 $/d) which should be acceptable if compared with conventional treatment methods.

4. Conclusions

Based on the study, an appropriated engineering scale of the PTFE MBR system was designed and reached the objective of physically breaking down the emulsified oil wastewater and degrading the unrevealed pollutants in the wastewater. The treatability study of emulsified oil wastewater for a cold-rolled steel plant in regard to high COD and unspecified grease compounds was conducted and attained a set of optimum operating parameters for an engineering scale up. The concluded operating parameters for MLVSS, averaged hourly flux, F/M ratio, HRT, and TMP were set at 10,500 mg/L, 16.7 L/m^2h, 0.2 ± 0.05 kg COD/kg MLVSS-d, 10 h, and 30 cmHg, respectively. To date, an MBR system with treatment capacity of 1,500 m^3/d has been built and put into operation based on these design principles. Compared with conventional treatment methods, the MBR system has reduced the costs of chemicals, daily operation, and sludge treatment and disposal.

References

[1] M. Cheryan, N. Rajagopalan, Membrane processing of oily streams, Wastewater treatment and waste reduction, J. Membr. Sci. 151 (1998) 13–28.

[2] J.M. Benito, G. Ríos, E. Ortea, E. Fernández, A. Cambiella, C. Pazos, J. Coca, Design and construction of a modular pilot plant for the treatment of oil-containing wastewaters, Desalination 147 (2002) 5–10.

[3] V. Mavrov, T. Erwe, C. Blöcher, H. Chmiel, Study of new integrated processes combining adsorption, membrane separation and flotation for heavy metal removal from wastewater, Desalination 157 (2003) 97–104.

[4] M.A. Barakat, New trends in removing heavy metals from industrial wastewater, Arabian J. Chem. 4 (2011) 361–377.

[5] N. Lesage, M. Sperandio, C. Cabassud, Study of a hybrid process: Adsorption on activated carbon/membrane bioreactor for the treatment of an industrial wastewater, Chem. Eng. Process. 47 (2008) 303–307.

[6] G. Mascolo, G. Laera, A. Pollice, D. Cassano, A. Pinto, C. Salerno, A. Lopez, Effective organics degradation from pharmaceutical wastewater by an integrated process including membrane bioreactor and ozonation, Chemosphere 78 (2010) 1100–1109.

[7] Y. Satyawali, M. Balakrishnan, Effect of PAC addition on sludge properties in an MBR treating high strength wastewater, Water Res. 43 (2009) 1577–1588.

[8] Y.H. Zhang, F.X. Gan, M. Li, D.H. Wang, Z.M. Huang, Y.P. Gao, Treatment of reused comprehensive wastewater in iron and steel industry with electrosorption technology, J. Iron Steel Res. Int. 18(6) (2011) 37–42.

[9] S. Yuan, M. Tong, G. Wu, Destabilization of emulsions by natural minerals, J. Hazard. Mater. 192 (2011) 1882–1885.

[10] Y.H. Zhang, F.X. Gan, M. Li, J. Li, S.Q. Li, S.H. Wu, New integrated processes for treating cold-rolling mill emulsion wastewater, J. Iron Steel Res. Int. 17(6) (2010) 32–35.

[11] W. Yang, N. Cicek, J. Ilg, State-of-the-art of membrane bioreactors: Worldwide research and commercial applications in North America, J. Membr. Sci. 270 (2006) 201–211.

[12] S. Weiss, T. Reemtsma, Membrane bioreactors for municipal wastewater treatment - A viable option to reduce the amount of polar pollutants discharged into surface waters? Water Res. 42 (2008) 3837–3847.

[13] B. Bienati, A. Bottino, G. Capannelli, A. Comite, Characterization and performance of different types of hollow fibre membranes in a laboratory-scale MBR for the treatment of industrial wastewater, Desalination 231 (2008) 133–140.

[14] J. Arévalo, L.M. Ruiz, J.A. Parada-Albarracín, D.M. González-Pérez, J. Pérez, B. Moreno, M.A. Gómez, Wastewater reuse after treatment by MBR. Microfiltration or ultrafiltration? Desalination 299 (2012) 22–27.

[15] E. Sahar, I. David, Y. Gelman, H. Chikurel, A. Aharoni, R. Messalem, A. Brenner, The use of RO to remove emerging micropollutants following CAS/UF or MBR treatment of municipal wastewater, Desalination 273 (2011) 142–147.

[16] A. Carucci, S. Milia, G. Cappai, A. Muntoni, A direct comparison amongst different technologies (aerobic granular sludge, SBR and MBR) for the treatment of wastewater contaminated by 4-chlorophenol, J. Hazard. Mater. 177 (2010) 1119–1125.

[17] P.K. Tewari, R.K. Singh, V.S. Batra, M. Balakrishnan, Membrane bioreactor (MBR) for wastewater treatment: Filtration performance evaluation of low cost polymeric and ceramic membranes, Sep. Purif. Technol. 71 (2010) 200–204.

[18] J.J. Qin, M.H. Oo, G. Tao, K.A. Kekre, Feasibility study on petrochemical wastewater treatment and reuse using submerged MBR, J. Membr. Sci. 293 (2007) 161–166.

[19] T. Melin, B. Jefferson, D. Bixio, C. Thoeye, W. De Wilde, J. De Koning, J. van der Graaf, T. Wintgens, Membrane bioreactor technology for wastewater treatment and reuse, Desalination 187 (2006) 271–282.

[20] Environmental Analysis Laboratory, EPA, Executive Yuan, Taiwan, R.O.C. Accessed May 28, 2013 Available from: http://www.niea.gov.tw/analysis/method/ListMethod.asp?methodtype=WATER.