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Pharmaceutical wastewater treatment by membrane bioreactor process – a case study in southern Taiwan

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Abstracts

A pilot-scale study of pharmaceutical wastewater treatment by a membrane bioreactor (MBR) process in southern Taiwan is presented in this paper. A 10 m^3/day capacity MBR plant consisting of an aeration tank and a membrane bioreactor was installed to remove organic matter (measured in terms of chemical oxygen demand (COD)). The performance of the MBR was monitored for a period of 140 days. The removal of COD was on average over 95%. The effluent did not contain any suspended solids. During the 140 days of operation, manual cleaning was carried out twice and chemical cleaning was carried out once. A natural logarithmic evolution of the viscosity with TSS concentration was observed. The results of SEM and EDX demonstrated that the fouling on the membrane outer surface was mainly due to microorganisms and/or the sludge physiological properties. The results indicated that the MBR system has potential as a means of treating high-strength and fluctuating strength wastewater with consistent performance.

Keywords: Membrane bioreactor; Pharmaceutical wastewater; Viscosity; Scanning electron microscope

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1. Introduction

The existence of pharmaceutical substances in the aquatic environment and their possible effects on living organisms are a growing concern [1].

The treatment of pharmaceutical wastewater to the desired effluent standards has always been difficult due to the wide variety of the products that are produced in a drug manufacturing plant.

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Variable wastewater composition and fluctuations in pollutant concentrations cannot be treated by conventional treatment plants. Activated sludge process is a well-known process for removing various organic contaminants and organic carbon. However, the substances synthesized by pharmaceutical industries are organic chemicals that are structurally complex and resistant to biological degradation [2].

The use of membrane bioreactor (MBR) in wastewater treatment is becoming increasingly important, because they offer several advantages, i.e. high biodegradation efficiency, smaller footprint and less sludge production [3].

Recent literature shows that MBR can be effective in removing these emerging contaminants. During the last three years research results were published in this particular area, reflecting the growing number of MBR applications for treatment of specific chemical compounds, such as pharmaceuticals, fragrances and endocrine disrupting compounds. However, various aspects of practical applications still received little or no attention to date [4,5] and the application of the MBR in treatment of pharmaceutical wastewater is still in its infancy. While there are many similarities in the design parameters for municipal plants, industrial plants show considerable variations in design, control and operational performance.

This paper presents the results of a pilot-scale MBR performance used in the treatment of pharmaceutical wastewater in Southern Taiwan Science Park (STSP).

2. Materials and methods

2.1. Experimental setup and operation

Fig. 1 shows the MBR plant constructed to treat wastewater from a pharmaceutical company. The company is located at Southern Taiwan Science Park (STSP). Regulation requires the COD of the wastewater should be reduced to below 450 mg/L in order to be discharged into a tertiary treatment plant in the STSP Administration which has an effluent COD limit of 50 mg/L.

The system consisted of two tanks with a total volume of 20 m^3. The first tank is a biological tank (10 m^3) and the second tank has a dual

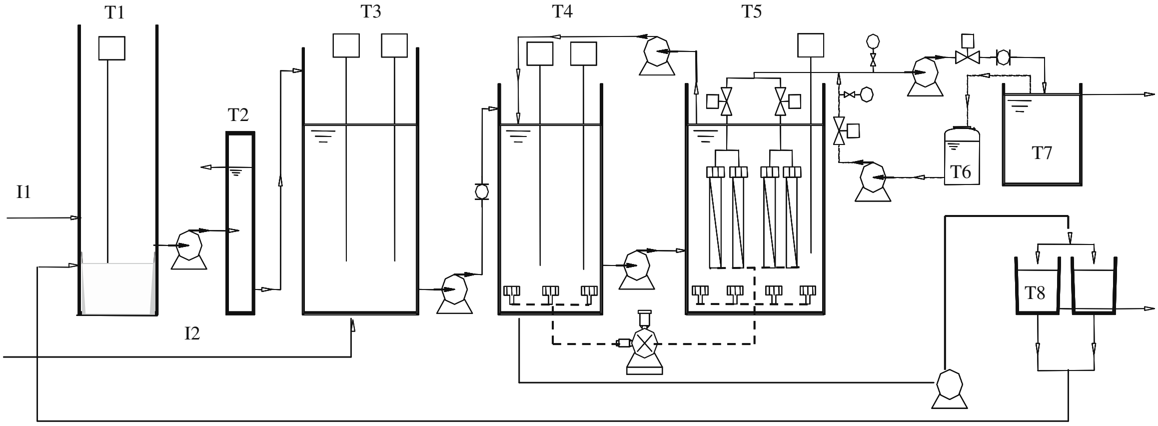


Fig. 1. Schematic diagram of the MBR system for pharmaceutical wastewater treatment. I1: influent from pharmaceutical manufacturing processes; I2: influent from septic tank effluent; T1: wet well; T2: solvent–liquid separation; T3: equalization tank; T4: biological tank; T5: membrane bioreactor; T6: backwash tank; T7: effluent tank; T8: sludge drying bed.

Table 1
Characteristics of hollow fiber membrane

Characteristic parameter	Membrane module
Material	PVDF
Internal/outer diameter (μm)	650/1000
Wall thickness (μm)	180
Pore size (μm)	0.1
Specific membrane area (m^2/g)	12.1
Fiber length (cm)	90
Number of the hollow fibers	4220

function of biological reaction with solid–liquid separation. The hollow fibre membrane used in this plant was manufactured by MOTIMO Company in China. Table 1 shows the characteristics of the membrane. The hollow fiber membrane was immersed in the membrane tank, where the air was supplied at the bottom of the membrane units to supply of oxygen for biological treatment and to create a turbulence which helps reduce membrane fouling.

The membranes were operated at an intermediate suction and were backwashed periodically using permeate. Prior to day 40 of operation, several operating modes including the suction–relaxation and coarse bubble aeration duration were evaluated with the aim of reducing the fouling of membranes. On day 41, the operation mode was fixed as follow: during the continuous operation mode, the suction pump was stopped for 30 s after 4 min of filtration to allow membrane relaxation. Two modules of membrane were employed in the second tank to alternatively accommodate the pumping and relaxation mode exchange operating mode. For each membrane, 54 min of membrane operation (12 cycles of suction–relaxation) was followed by 6 min of backwash by permeate.

After 30 days of seeding and start-up, the MBR plant was monitored continuously for 140 days. The HRT of the aerobic tank and MBR tank were set at the same value of 24 h. The re-circulation rate of the mixed liquor was set at 500% of the average influent flow rate. The operating parameters are shown in Table 2.

Table 2
MBR pilot plant operating conditions

Item	Value/range
Design flow	$10\ m^3\ d^{-1}$
Biological tank volume	$10\ m^3$
Membrane tank volume	$10\ m^3$
Aerobic tank HRT	24 h
Membrane tank HRT	24 h
SRT	>40 days
Mixed liquor recycle ratio	5
pH range	6–8
Temperature	16–28°C
F:M ratio of biological tank (kg COD kg ML $VSS^{-1}\ d^{-1}$)	0.014–0.65
F:M ratio of membrane tank (kg COD kg ML $VSS^{-1}\ d^{-1}$)	0.003–0.079
Volumetric loading rate of biological tank (kg COD $m^{-3}day^{-1}$)	0.099–6.844
Volumetric loading rate of membrane tank (kg COD $m^{-3}day^{-1}$)	0.011–0.408
Membrane surface area	$24\ m^2$
Flux ($m^3\ m^{-2}\ d^{-1}$)	0.384–1.536

2.2. Wastewater characteristics

The influent to the MBR system consisted of real pharmaceutical manufacturing wastewater and septic tank effluent. The plant has intermittent and fluctuating wastewater flow with variable wastewater composition depending on the production regime. The characteristics of the wastewater are indicated in Table 3.

2.3. Control, analysis and monitoring

DO, pH, ORP, temperature and flow rates were recorded daily using the in-line controllers. Dissolved oxygen (DO) was monitored with a DO analyzer and maintained higher than 3.0 mg/L

Table 3
Characteristics of the raw wastewater

Characteristic items	Range
Temperature (°C)	18.5–25.1
pH	6.6–9.4
SS (mg/L)	60–360
COD_{Cr} (mg/L)	800–11800
BOD_5 (mg/L)	100–6350
Conductivity (µs/cm)	518–2840

in the aerobic and membrane tanks. The influent and effluent of each tank were sampled two to three times per week. The analysis including chemical oxygen demand (COD), biochemical oxygen demand (BOD), mixed liquid suspended solids (MLSS), mixed liquid volatile suspended solids (MLVSS) and turbidity were performed in accordance with the standard methods (APHA, 1993) and the corresponding instrument instruction manuals. The mixed liquor viscosity was measured by a TVC-5 type viscometer (Toki Sangyo Co. Ltd., Japan).

The surface morphologies of the nascent and fouled membranes were characterized by scanning electron microscope (SEM) and energy dispersive X-ray analyzer (EDX) with a Hitachi S-3000 system. The samples were fixed with 4.0% glutaraldehyde in 0.1M phosphate buffer at pH 7.2 and dehydrated with ethanol, gold-coated by a sputter and observed in SEM.

3. Results and discussion

3.1. Performance of MBR system

Fig. 2 illustrates the influent and effluent quality of the MBR in terms of COD. COD effluent was remarkably stable and with a highest removal efficiency of 96%. This result may be attributed to the mass loading in MBR tank which was generally low and in the range of 0.003–0.079^{-1}. Moreover, COD organic loading to the biological tank was in the range of 0.099–6.844 kg COD m^{-3} day^{-1} and 0.011–0.408 kg COD m^{-3} day^{-1} to the membrane tank.

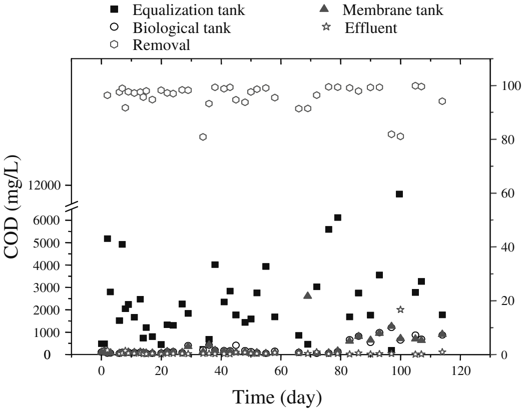


Fig. 2. Variations and removal of COD.

Besides, it was found that an additional 5% COD removal was observed in the membrane effluent compared to that in the final membrane tank.

Fig. 3 demonstrates the process performance on BOD_5 removal. As shown in Fig. 3, the influent concentration of BOD_5 fluctuated. However, BOD_5 concentrations in the effluent were at, or close to, the laboratory detection limits. The average BOD removal was more than 99% and the highest BOD removal efficiency of 100% was achieved.

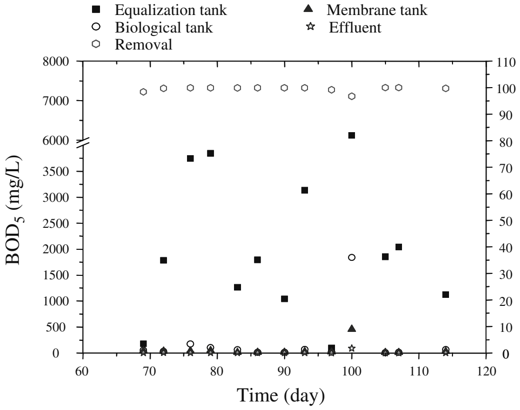


Fig. 3. Variations and removal of BOD.

3.2. Variation of MLSS and flux

Fig. 4 shows that the plant can be operated with a high biomass concentration by using membranes for sludge separation. MLSS concentration in MBR tank was maintained in the range of 6000–17,000 mg/L and excess sludge was wasted in accordance with the sludge growth rate (average SRT > 40 days). As shown as Fig. 4, the variation of MLSS could be classified into two stages. The trend in the MLSS growth rate during the first stage (day 1 to 60) was slowly raising followed by a sharp increase during the second stage. This is partly attributed to the influent COD concentration during stage 2 being on average higher than during stage 1. Further stages 1 and 2 could have corresponded respectively (i) to a stage of adaptation and acclimation of the biomass to the operating conditions and (ii) to a stabilized stage where the biomass can be considered as acclimated to the operating conditions.

The average sludge production during stages 1 and 2 were 0.035 kg SS/kg COD and 0.072 kg SS/kg COD respectively, which is much less than the conventional activated sludge process (0.2–0.3 kg SS/kg COD). Although the MLSS concentration was higher than 6000 mg/L, the treated water was free of suspended solids due to the complete rejection by the membrane.

Besides, the effluent SDI value is between 4 to 6 over the period of operation and approximately 40% of conductivity was reduced in this system. It revealed that further treatment should be adopted if the effluent is to be used as the feed water to a RO system for recycling purposes. Otherwise, a membrane with a smaller pore size such as NF could be employed to improve the SDI index.

Fig. 5 illustrates the variations of TMP and flux during the monitoring period. The membrane module was withdrawn for cleaning on days 43 and 92 to remove clogging. Chemical cleaning was carried out on day 102 by inside-out type washing (as shown in Fig. 5). It was found that the clogging occured periodically within about 40 days. It can be seen that there was an abrupt raise of TMP from 10 to 38 kPa prior to the second manual cleaning and the same phenomena was observed before the first manual cleaning. The TMP varied from 9 to 55 kPa with the flux change from 16–64 L m^{-2} h^{-1}. However, the TMP kept within a range of 10–25 kPa over most of the period of operation. It demonstrated that less power consumption is needed for the immersed membrane system than for the pressure driven type of membrane.

Some studies reported that fouling was independent of MLSS concentration until a very high

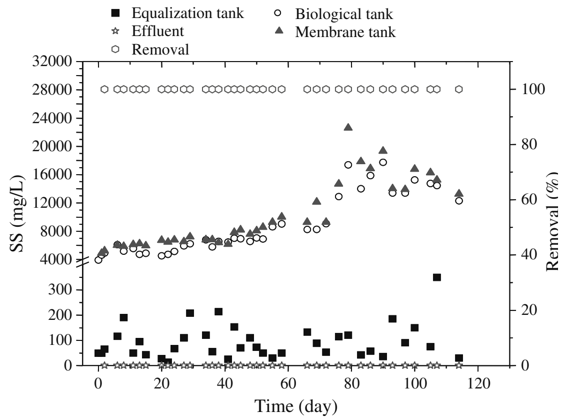


Fig. 4. Variations of MLSS and SS.

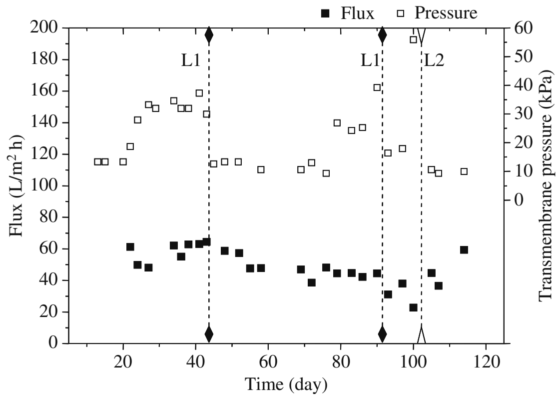


Fig. 5. Variations of flux, TMP and the cleaning of membrane (L1: manual cleaning; L2: chemical cleaning).

value was reached. Yamamoto et al. [6] reported that the critical MLSS concentration was about 30–40 g/L, but it varied with operating conditions. Ross et al. [7] also found that a dramatic increase in membrane fouling, i.e., a sharp decrease in permeate flux, occurred after a stable performance of up to 40 g/L of MLSS concentration. Based on the field observations in this study, a cake layer formed around the membrane fibres and seemed to contribute to the main part of membrane fouling even where the range of MLSS concentration investigated here was lower than the critical values reported in literature [6,7].

Fig. 6 shows the variation in viscosity during the period of operation. Similar to the trend observed with MLSS, three stages of variation in viscosity was observed. In the initial stage (upto day 50), the viscosity was low in a range between 8–13 mPa s, followed by a sharp increase from day 50 to 69, and finally achieving the higher viscosity in the range of 64–79 mPa s.

The relationship between viscosity and MLSS is shown in Fig. 7. The result showed that the mixed liquor viscosity increased logarithmically as the MLSS concentration increased. It indicates a decreasing influence of higher solid concentrations on viscosity.

Previous results often demonstrated the plot of viscosity versus suspended solids with power or exponential laws, resulting in curves having upward concavity [8,9]. According to Sanin [10], exponential pattern can explain the stronger non-Newtonian behavior of the sludge with increasing solid concentration.

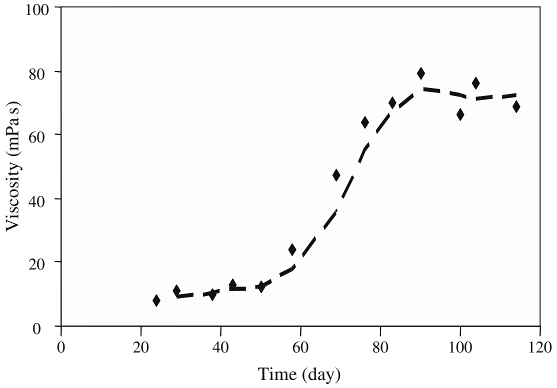


Fig. 6. Viscosity variation.

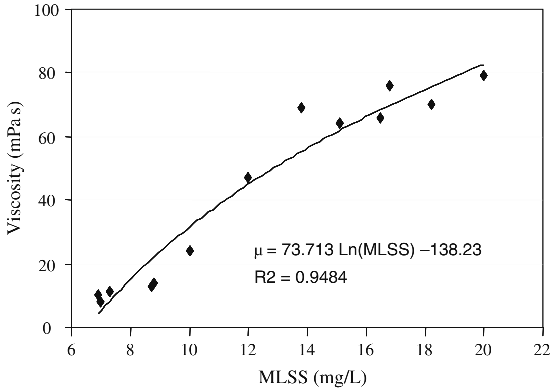


Fig. 7. Relationship between viscosity and MLSS.

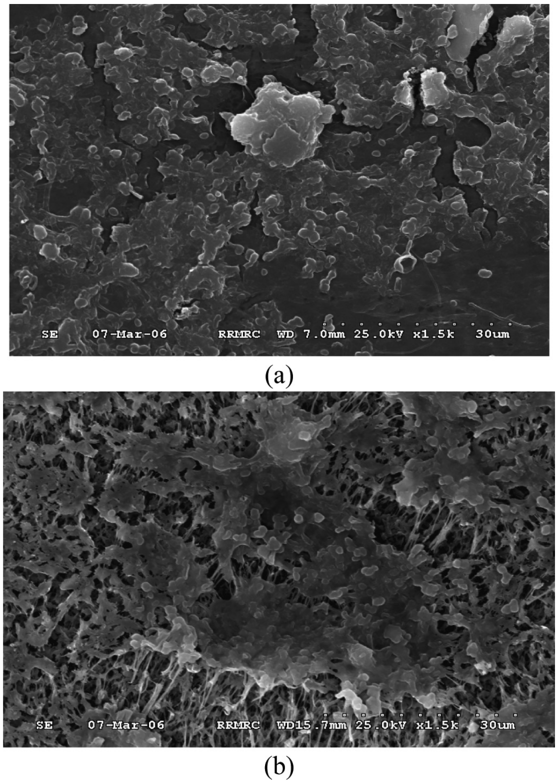
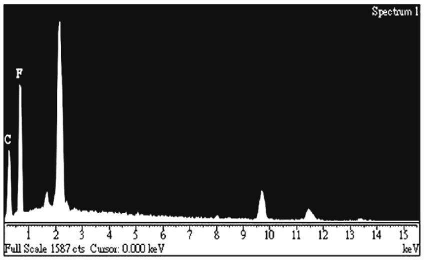
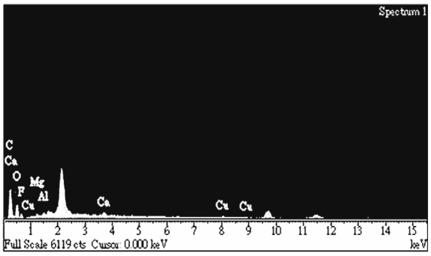


Fig. 8. The SEM of fouled membrane (a) outer surface and (b) inner surface.



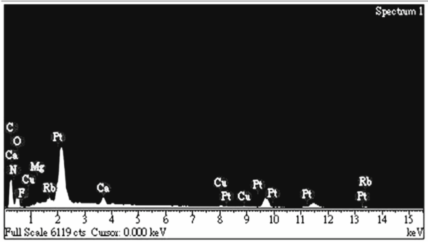
Element	*Wt.%*	*At%*
C	43.84	55.25
F	56.16	44.75

(a)



Element	*Wt.%*	*At%*
C	47.24	57.59
O	31.33	28.68
F	14.85	11.45
Mg	0.72	0.43
Al	0.88	0.48
Ca	1.66	0.61
Cu	3.32	0.76

(b)



Element	*Wt.%*	*At%*
C	35.49	45.57
N	15.92	17.53
O	31.51	30.38
F	4.09	3.32
Mg	0.85	0.54
Ca	3.60	1.39
Cu	2.79	0.68
Rb	1.36	0.24
Pt	4.40	0.35

(c)

Fig. 9. EDX spectra and elemental composition of nascent and fouled membranes (a) nascent membrane, (b) inner surface of fouled membrane and (c) outer surface of fouled membrane.

The exponential evolution of the viscosity with MLSS concentration for MBR systems was also observed others [11,12]. Trussell et al. [11] reported the relationship followed an exponential law at different MCRT (mean cell retention time) conditions. Pollice et al. [12] interpreted the plot of viscosity versus suspended solids with exponential laws but had a downward concavity similar to our work.

In fact, the dependence of viscosity with MLSS could be related to the sludge composition, the floc size and shape, the nature of the interactions between particles and to the quantity of bound water. The other parameters such as extracellular polymeric substances (EPS) and soluble microbial products (SMP) could also affect the variation of viscosity [8–10].

In this study, the evolution of the viscosity with MLSS concentration based on field data followed a natural logarithmic variation and is different from the results of other studies. It implies that further study could be carried out to clarify this finding.

3.3. SEM and EDX

SEM was used to examine the morphology of foulants on outer and inner surface of fouled membrane. As can be seen in Fig. 8(a), the outer surface has a huge deposit of foulants. On the other hand, the inner surface has less accumulation and the foulants have an irregular shape.

Fig. 9 demonstrates the results of EDX spectra and elemental composition of nascent and fouled membranes. As shown in Fig. 9, nitrogen was not detected on inner surface and two kinds of cations, Rb and Pr, were deposited on the outer surface. However, Al can pass through the membrane and accumulate on the inner surface.

The results of SEM and EDX demonstrated that the fouling on the membrane outer surface was mainly due to microorganisms and/or the sludge physiological properties, such as EPS. Steritt et al. [13] have shown that activated sludge could remove more than 50% of the heavy metal content in wastewater and it has been reported that EPS play a significant role in the complexation of heavy metal [14,15].

The EDS results showed that cations on the outer surface of membrane were with higher diversity and quantity compared with the results of inner surface. It indicated that most of the cations were rejected by the biotic absorption and/or adsorption.

4. Conclusion

This study demonstrates the field operation of pharmaceutical wastewater treatment by MBR. It was demonstrated that the MBR system is capable of removing 95% and 99% of COD and BOD_5 respectively. The results indicate that the MBR system has a great potential in treating this type of wastewater with stable operation and satisfactory removal performance.

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