Membrane-Coupled Methanogenic and Facultative Bioreactor in Wastewater Treatment

Huey-Song You, Shanshan Chou, Kuan-Foo Chang, C. H. Ni, J. R. Pan, and Chihpin Huang

***Abstract*—This paper evaluates the feasibility of a membrane-coupled methanogenic and facultative bioreactor (MCMFB) system in treating the wastewater from the liquid crystal display (LCD)-related industry. The treatment unit is comprised of an anaerobic (methanogenic) and an aerobic reactor. The hollow fiber membrane module (0.036 μm) was submerged in the aerobic reactor for solids/liquid separation. An average 80% COD removal was achieved in the anaerobic reactor when the volumetric loading reached 7.2 kg COD/m^3 per day. The effluent of the anaerobic treatment was fed into the aerobic-membrane tank to treat the residual COD. The mixed liquor suspended solids of the aerobic tank was 7000 mg/L with an average F/M of 0.14 g COD/g SS per day, and the removal efficiency of the aerobic tank was 90% in average. The transmembrane pressure and the flux of the membrane remained stable during the entire period of the 140-day operation without any backwash or chemical wash, indicating the applicability of the MCMFB system on treating the targeted wastewater.**

***Index Terms*—Anaerobic, facultative, liquid crystal display (LCD), membrane, methanogenic.**

I. INTRODUCTION

MEMBRANE technology has recently become a popular tool to reclaim wastewater. By combining it with a membrane separation, the traditional biological treatment process has been redefined. It transforms the biological operation parameters into physical operation parameters, which facilitates the operation of a wastewater treatment system dramatically. Biological treatment with membrane separation is called membrane bioreactor (MBR). To date, many successful applications of aerobic MBRs have been reported, mostly on municipal wastewater [1]. Despite its numerous advantages, MBRs have not yet been widely practiced because of the high capital cost, mainly due to the original cost of the membrane and the difficulty in controlling membrane fouling which shortens the life of membrane operation. The capital cost can be reduced tremendously by applying the membrane separation to anaerobic biological treatment systems which requires much less reaction volume, consumes less power, and produces less sludge.

Anaerobic biological treatment is superior to aerobic biological treatment in the lower sludge yield and higher volumetric loading [2]. However, the anaerobic process needs longer startup time due to the slow growth of the anaerobic bacteria. Biomass of the anaerobic bacteria can be accumulated much faster by retaining microbes in the MBR [3], [4]. The cost of an anaerobic reactor can be reduced substantially without the need for a solid/liquid/gas separator. In addition, the system can be operated at high flux due to the low COD of the bulk solution. Similar to aerobic MBRs, anaerobic MBRs can be designed in two ways: 1) the submerged anaerobic MBRs [5], [6] and 2) the side-stream anaerobic MBRs [7]–[9].

The most notorious problem with MBR operation is the fouling phenomenon on membrane surfaces. For aerobic MBRs, fouling on the membrane surfaces mainly results from the deposition of organic substances and microbes on the membrane surfaces [1]. Besides organic fouling, scaling is also a problem for anaerobic MBRs. Due to the CO_2 produced from the microbes metabolism, when the pH exceeds 8.3, the carbonate concentration in the anaerobic bioreactor will increase to a level that calcium and/or magnesium carbonates crystallize on the membrane. To solve this problem, the Industrial Technology Research Institute (ITRI) in Taiwan has developed a novel anaerobic/aerobic membrane bioreactor system, the membrane-coupled methanogenic and facultative bioreactor (MCMFB) [10]. In the system, a three-step anaerobic-aerobic-membrane reactor is designed when Ca/Mg ions are present in the wastewater. A two-step method containing an aerobic tank with a membrane separation tank is used when the concentration of Ca/Mg ions is not high enough to cause scaling [11].

Taiwan is projected to be the largest supplier for large-scale thin-film transistor liquid-crystal display (TFT-LCD) in 2006. Complying with the increasing production of TFT-LCD, the peripheral industry also is developing vigorously. The concentrated organic wastewater generated from this industry is mainly comprised of glue and dye wastewaters in which polyvinyl alcohol (PVA) is the primary constituent. PVA is biodegradable by aerobic microorganisms [12]. Other technologies for treating PVA wastewater include chemical coagulation [13], UF/RO filtration [14], and advanced oxidation such as photo-Fenton techniques [15]. Currently, one plant of this industry in Taiwan adopts the coagulation and flocculation to treat the wastewater, however, without effective COD removal. In this paper, the wastewater was treated with the MCMFB system and its feasibility in COD removal was evaluated.

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TABLE I
CHARACTERISTICS OF GLUE AND DYE WASTEWATERS

Parameters	Glue wastewater	Dye wastewater
pH	5.7-6.2	5.2-5.6
COD (mg/L)	10,000-31,000	2,000-4,000
BOD_5 (mg/L)	5,500-15,300	NA**
SS (mg/L)	20-50	20-40
TN (mg/L)	ND*	ND
Ca^{2+} (mg/L)	30-45	30-50
Mg^{2+} (mg/L)	10-17	10-20
Viscosity (m Pa s)	11.5-88.6	1
Flowrate (m^3/day)	55	45

* not detected; ** not available

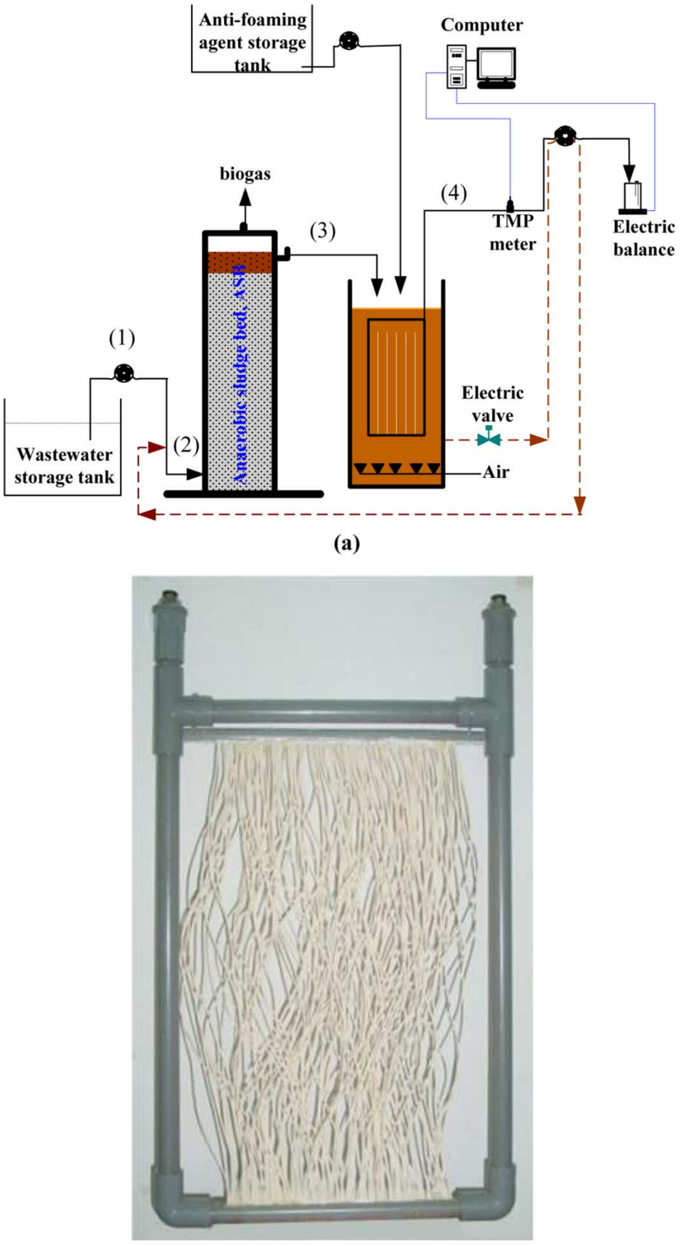
II. MATERIAL AND METHODS

A. *Characteristics of Wastewater*

The glue and dye wastewaters were sampled from the plant every other week as the raw wastewater sources for this study. The characteristics of these two wastewaters are shown in Table I. The glue water contains high concentrations of COD and BOD_5, in which the major pollutant is PVA. The dye wastewater contains less organic materials, with nondetectable BOD_5. It also contains an iodine complex such as I_3, IO_3^-, and IO_5^-, etc., being discharged from the dyeing process. The Ca $^{2+}$ and Mg $^{2+}$ compositions in the two wastewaters are about the same, of which the concentration is unlikely to cause scaling on the membrane surfaces. The viscosity of the glue wastewater is in the range of 11.5 to 88.6 mPas, which is proportional to the level of COD.

B. *Batch Biochemical Methane Potential (BMP) Tests*

The serum bottle technique (Owen *et al.*, 1979) was used to assess the biomethane potential (BMP) of the raw wastewater at 35 ± 1 °C and pH 7.2±0.2. The composite wastewater was prepared by mixing the dye wastewater with the glue wastewater in a ratio of 1.22 : 1 to simulate the wastewater. The wastewater mixture was diluted to the desired COD level with tap water. A 250-mL flask was used in the BMP test. The anaerobic sludge and wastewater mixture was 200 mL with SS concentration of 10 000 mg/L (VSS concentration was about 9000 mg/L). The anaerobic granulated sludge for seeding was taken from the upflow anaerobic sludge bed (UASB) of a food factory. Stock solutions S1 and S2 were added into the flask to make up the trace elements for the liquid medium of the BMP test. Each liter of S1 solution contains 12 g K_2 HPO_4, 7.2 g KH_2 PO_4, 20 g NH_4 Cl, 20 g $(NH)_2$ HPO_4, 3.6 g $MgSO_4\cdot$ $7H_2O$, 2.4 g $CaCl_2\cdot$ $2H_2O$, 0.72 g $CoCl_2\cdot$ $6H_2O$, 0.72 g $NiCl_2\cdot$ $6H_2O$, 0.6 g $MnSO_4\cdot$ $4H_2O$, 0.2 g $CuSO_4\cdot$ $5H_2O$, and 0.8 g $FeSO_4\cdot$ $7H_2O$, while the S2 solution contains 20 g Na_2 $S9H_2$ O. The biogas was collected in a bottle filled with 1 N NaOH solution. The quantity of the methane gas was recorded periodically. Two replicates of BMP tests assay were used.



(a)

(b)

Fig. 1. (a) Overall schematic diagram and (b) membrane module of MCMFB system. (1) Raw wastewater. (2) Anaerobic influent. (3) Anaerobic effluent. (4) Permeate.

C. *Membrane-Coupled Methanogenic and Facultative Bioreactor*

The schematic diagram of the MCMFB system and the configuration of the membrane are depicted in Fig. 1. The dimensions of the anaerobic and aerobic tank are 10 × 10 × 100 cm (effective volume of 10 L) and 40 × 6 × 85 cm (effective volume of 20 L), respectively. The ultrafiltration membrane module (Green Environmental Technology Company) was submerged in the aerobic tank. The pore size of the membrane was 0.036 μm, and the total surface area of the membrane was 0.2 m^2. Sampling ports were located at 22 (bottom layer), 52 (middle layer), and 88 (top layer) cm, respectively, from the bottom of the anaerobic tank. The UASB granulated sludge was

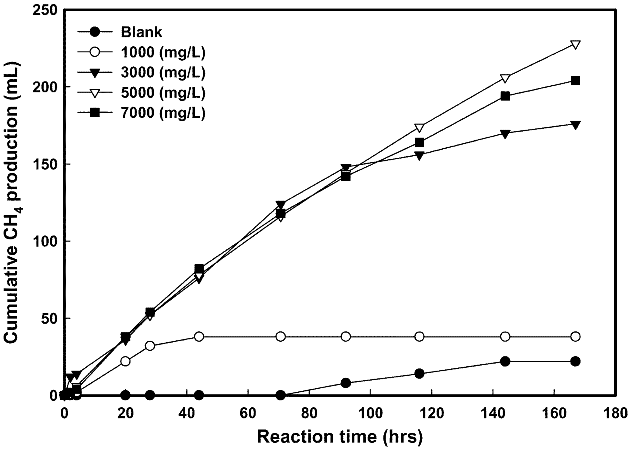


Fig. 2. Cumulative methane production of BMP test of composite wastewater.

seeded in the anaerobic tank. The breakups of the same anaerobic granulated sludge were used as the seeding of the aerobic tank. Urea and phosphoric acid were added as the N and P sources in the mass ratio of COD: N: P $= 500:5:1$. About 1000 mg/L of NaHCO$_3$ was added to the solution to buffer the pH and supply the alkalinity. Three pumps were used to maintain the flow rates of the raw wastewater, anti-foaming reagents, and recycled sludge from the aerobic tank. The sludge was recycled at the same rate as the flow rate of the influent. Raw wastewater (1), anaerobic effluent (3), and permeate (4) samples were sampled and analyzed. The COD concentration of the anaerobic influent (2) was calculated from the COD levels of the raw wastewater and the membrane permeate.

D. Data Analysis and Measurement

COD and SS were determined in accordance with the Standard Methods (APHA, 1995). The water samples were filtered through a 0.45-μm filter (Toya Roshi Kaisha, Ltd., Japan) before the COD analysis. Transmembrane pressure (TMP) was measured by a micro gauge. Flux was calculated from the permeate rate and the surface area of the membrane. The calcium and magnesium ions were determined by atomic adsorption (Varian, FS-220, USA).

III. RESULTS AND DISCUSSION

A. Batch BMP Tests

The composite wastewater was prepared in the range of 1000–7000 mg COD/L and the BMP tests were conducted for 170 hours. The results of the batch BMP tests are shown in Fig. 2. The cumulative methane production increased with the increasing initial COD of the wastewater from 1000 to 5000 mg/L. However, when the initial COD of the wastewater increased to 7000 mg/L, no further increase in methane production was observed, probably due to the inhibition of high organic content on methanogens. More evidence is when the methane production rate remained fairly constant (from 59.2% to 70.2%) with COD loading up to 5000 mg COD/L yet dropped to 36.7% at 7000 mg COD/L. Therefore, the influent COD of the composite wastewater was controlled under 5000 mg/L for the following continuous tests of the MCMFB system.

TABLE II
RESULTS OF BMP TESTS OF GLUE AND DYE WASTEWATERS

	Glue wastewater					Dye wastewater	
Initial COD (mg/l)	4000	6000	9000	13 000	20 000	1200	4000
COD at 191 hr (mg/l)	651	963	1,530	10 920	17 600	950	3037
COD removal (%) at 191 hr	84	84	83	16	12	21	24
Methane production at 191 hr (ml)	254	355	574	146	180	27	109
Methane production at 242 hr (ml)	256	360	624	715	696	28	111
Theoretical methane production (ml)	304	456	684	931	1432	91	304

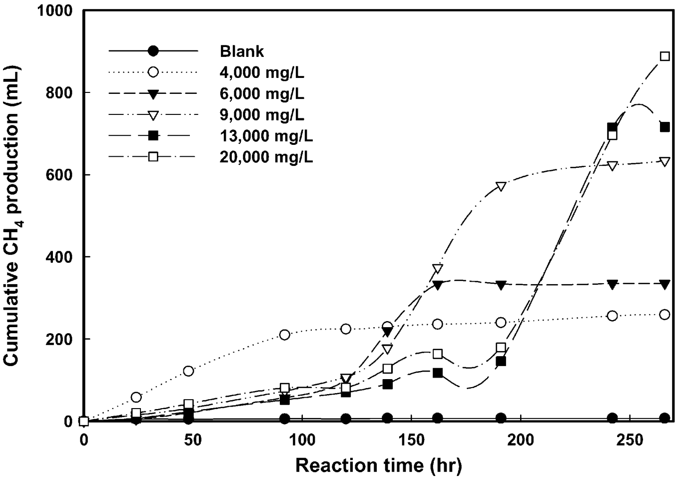


Fig. 3. Cumulative methane production of BMP test of glue wastewater under various strengths.

The BMP tests were also performed on separate glue and dye wastewaters (Table II). After operated for 191 hours, around 84% COD removed from the glue wastewater was observed in the initial COD range of 4000–9000 mg/L. It can be seen in Fig. 3 that the maximum BMP was achieved for COD concentration of 4000, 6000, and 9000 mg/L in which the maximum methane production rates of the glue wastewaters were 97.3%, 82.3%, and 89.2%, respectively, after 191 hours. It suggests that the glue wastewater can be biodegraded when the COD concentration less than 9000 mg/L. A much lower COD removal, less than 20%, was detected when the initial COD of the glue wastewater increased to 13 000 and 20 000 mg/L, which was accompanied by a significant decrease in methane production. After 242 hours of operation, the methane production returned to a more reasonable value. The variation of cumulative methane production with reaction time under different initial concentration of glue water was presented in Fig. 3. In the early stage of the BMP test, the granular sludge was covered by the highly viscous glue wastewater which interfered with the transfer of the organic substrate from bulk solution to the surface of the granular sludge. As a result, the methane production was lowered in

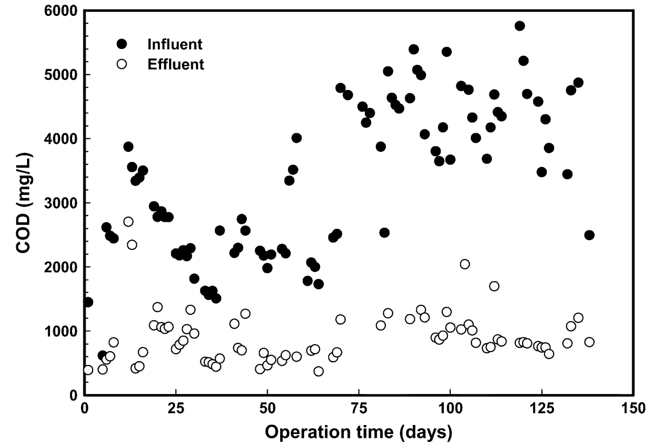


Fig. 4. COD variations in influent and effluent of anaerobic reactor of MCMFB.

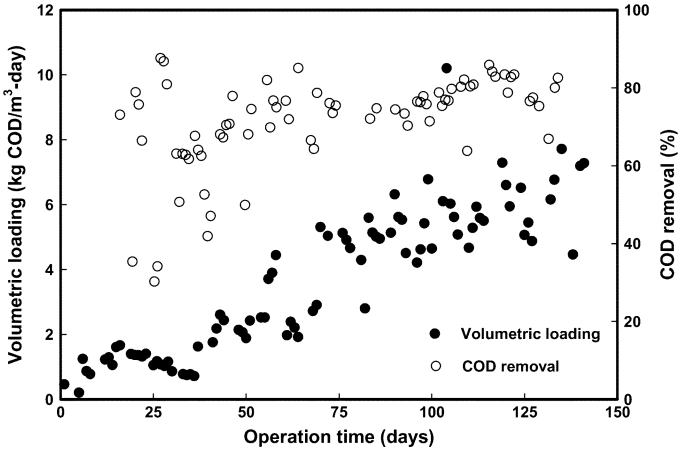


Fig. 5. Variations of COD removal and volumetric loading of the anaerobic reactor of MCMFB.

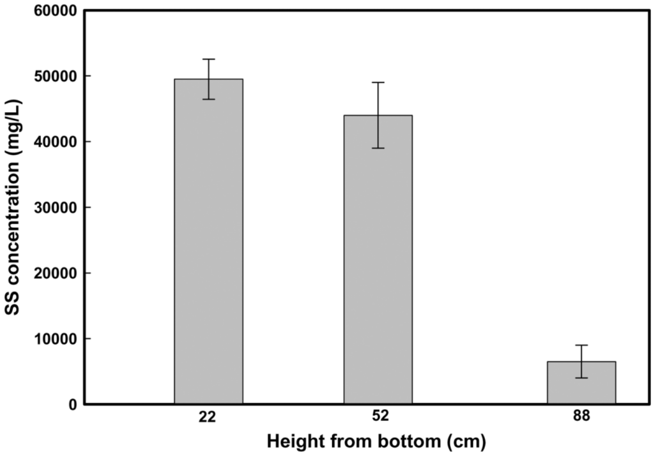


Fig. 6. Sludge concentration at different locations of anaerobic reactor in MCMFB.

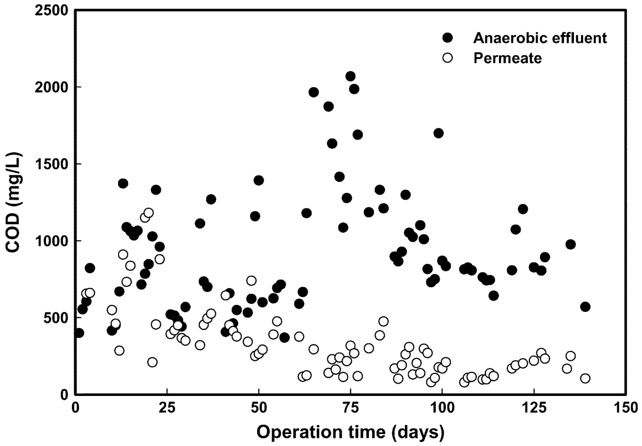


Fig. 7. Variations in CODs of anaerobic effluent and permeate of aerobic reactor of MCMFB.

this period of time. On the other hand, the COD removal of the dye wastewater was relatively low, only around 20%, accompanied by a low methane production, which may be due to the formation of complex iodide compounds. The biodegradability of the dye wastewater was determined with aeration at a 2000 mg/L sludge concentration taken from a sewage treatment plant. No COD removal was detected (data not shown here).

B. Continuous Anaerobic Treatment in MCMFB System

The influent COD of the anaerobic reactor of the MCMFB was maintained in the range of 1500–6000 mg/L by adding a small amount of PVA wastewater. During the startup operation, the influent COD was controlled below 3000 mg/L with low flow rate. The acclimation period for the anaerobic reactor lasted about 70 days. After that, both the COD and the flow rate were increased. The COD variations of the influent and the effluent of the anaerobic reactor are shown in Fig. 4. After the acclimation period, the effluent COD of the anaerobic reactor was between 500 and 2000 mg/L, mostly between 800 and 1200 mg/L. Fig. 5 compares the COD removal with the volumetric loading during the 150 days operation. During the acclimation period, although the influent COD was controlled below 3000 mg/L, the COD removal was not stable, fluctuating between 35% and 85%. After the acclimation, the COD removal remained between 75% and 85% at volumetric loading of 4 to 7 kg COD/m^3 per day. It suggests that the acclimation of the system to specific wastewater is very important for a full-scale plant.

Sludge samples were collected from the anaerobic reactor from the bottom, middle, and top ports. The suspended solid (SS) concentrations of the sludge varied slightly from bottom to the middle part of the reactor, as shown in Fig. 6. The SS concentration of the top layer of the anaerobic reactor dropped tremendously to 7000 mg/L.

C. Continuous Aerobic Treatment in MCMFB System

The COD values of the influent and effluent of the aerobic treatment were monitored, as shown in Fig. 7. The effluent of the anaerobic reactor was the same as the influent of the aerobic. After the acclimation period for the anaerobic microorganism, although the effluent COD varied significantly between 500 and 2000 mg/L, the effluent COD concentration of the MBR remained between 150 and 400 mg/L. The average mixed liquor suspended solids (MLSS) concentration of the aerobic reactor was 7000 mg/L with an average F/M of 0.14 g COD/g SS per day.

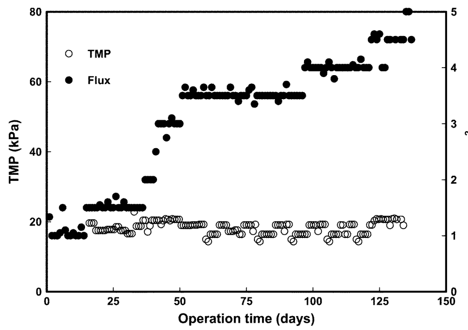


Fig. 8. Variations in membrane TMP and flux of aerobic reactor of MCMFB.

Because this wastewater contains a high concentration of surfactant, foaming might be a problem for the aerobic reactor. An anti-foaming agent was added to prevent the sludge from lifting out of the aerobic reactor. Unfortunately, the dosage of the anti-foaming agent could not be controlled properly in a small-scale experimental facility. As a result, the effluent of the aerobic reactor contained more COD due to the excessive anti-foaming agent. This would be less a problem for a full-scale operation.

After the treatment with the MCMFB system, the concentration of Mg remained almost unchanged, between 10 to 20 mg/L, while the Ca was reduced from 30–50 to 10 mg/L. The TMP and flux over the 150-day operation are shown in Fig. 8. The TMP remains around 20 kPa, and the flux were kept between 3 to 5 L/m^2 per hour during the 50–100 days of operation.

Because the anaerobic reactor did not contain a solid/liquid/gas separator, the anaerobic sludge overflowed into the aerobic reactor. The sludge concentration of the aerobic reactor was close to that of the overflow from the anaerobic reactor (i.e., 7000 mg/L), as shown in Fig. 6. Since part of the aerobic sludge was recycled back to the anaerobic reactor, the facultative microorganisms existed in both the anaerobic and the aerobic reactors. In a previous study, we have proven that the anaerobic microbes do not lose methane production ability and the aerobic microbes do not lose the aerobic biodegradability through continuous exchange between anaerobic and aerobic conditions [10].

D. Design of Full-Scale MCMFB Treatment Plant

Based on the result of this paper, a full-scale MCMFB has been built in Taiwan to treat 45 m^3 per day glue wastewater, 55 m^3 per day dye wastewater, and a low concentration stream. By adding the PVA wastewater of 400 mg/L COD at 100 m^3 per day, the influent wastewater of the full-scale MCMFB contains 5000 to 6000 mg/L total COD at the flow rate of 200 m^3 per day. The volumes of the anaerobic and aerobic tanks are 200 and 260 m^3, and the volumetric loadings are approximately 5 to 6 and 0.7 to 0.9 kg COD/m^3 per day, respectively. The MCMFB plant is designed to produce a permeate lower than 250 mg/L to meet the effluent standard regulated by the Industrial Science Park in Taiwan, namely, 500 mg/L COD with a total COD removal of 95%.

IV. CONCLUSION

1) The lab-scale MCMFB system maintained a steady TMP and flux without backwashing and chemical cleaning for over 140 days of operation.
2) The anaerobic treatment of this plant removed 75%–85% COD at volumetric loading of 7.2 kg COD/m^3 per day.
3) The MCMFB system is a feasible technology in treating the glue and dye wastewater from the LCD-manufacturing related industry.

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