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EFFECT ON MEMBRANE FOULING AND CAKE RESISTANCE IN A HYBRID MEMBRANE BIOREACTOR FOR PALM OIL MILL EFFLUENT TREATMENT

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ABSTRACT

There are currently 4.3 million hectares of oil palm plantation land in Malaysia and palm oil products export revenue was projected to exceed RM50 billions this year from last year's record of RM45.6 billions. With more than 500 palm oil mills, annually its produce some 13.9 million tonnes of crude palm oil and generate around 35 x 10^6 m^3 palm oil mill effluent (POME) with pollution-load of 50,000 mg COD/L. POME is difficult to biodegrade because it contains high concentration of tryacylglycerols and degradative products, such as di-and monoacylglycerols and fatty acids. The objective of this study was to observe the performance of a hybrid membrane bioreactor (MBR) for POME treatment and to study the fouling mechanisms of membrane modules. Raw POME with organic loading of 1.8 kgCOD/m^3.d was introduced into sequencing processes of anaerobic, anoxic and aerobic MBR in order to achieve biological nutrient removal. For the concentration of mixed liquor suspended solid (MLSS) was maintain at 8000 mg/L and the critical flux can be observed that transmembrane pressure (TMP) and fouling rate increased significantly. The critical flux was in the range of 14-16 LMH and fouling rate of 4-8 mbar/min. Membrane fouling due to cake resistance was 74% of total resistance in the zone of sub-critical, increased about 15% in the critical zone and rose to 96% in the supra-critical zone. The COD and SS removal were an average of 94% and 98% respectively.

Keywords: Hybrid MBR; POME; Flux; TMP; Cake Resistance.

INTRODUCTION

Over the last few decades, the Malaysian palm oil industry has grown to be an important agriculture-based industry, where the country is today the world’s leading producer and exporter of palm oil. Since the 1950s the palm oil has been considered as a promising agriculture industry. Therefore, Malaysia’s government was initiating the population of palm oil estate (Yusoff, 2006). Today, palm oil is the leading agriculture crop in Malaysia, about 4.3 million hectares of oil palm plantation land in Malaysia and palm oil products export revenue was projected to exceed RM50 billions this year from last year's record of RM45.6 billions. With more than 500 palm oil mills, annually its produce some 13.9 million tonnes of crude palm oil and generate around 35 x 10^6 m^3 of palm oil mill effluent (POME) with high pollution-load of 50,000 mg COD/L.

POME consists of high amount of oils; it is usually present in complex form that contains significant amount of triacylglycerides, di- and monoacyl glycerides and monoglycerides and some derivatives of fatty acids (Alias and Tan, 2005). These forms are difficult to degrade so as to obtain short chain derivatives. Therefore, a series of anaerobic, anoxic and aerobic treatment steps have been proposed to reduce their compound characterized and to achieve biological nutrient removal. The objective of this study was to observe the performance of a hybrid membrane bioreactor (MBR) to reuse POME for various purposes, primarily water recycling. This paper focuses on flux-step method to determine critical flux, to measure hydraulics resistance and to observe the membrane fouling mechanisms.

MATERIALS AND METHODS

Experimental set-up and operating conditions. The experimental set-up is shown in Figure 1. The hybrid MBR consists of anaerobic, anoxic, and aerobic reactors in series, where three modules of flat sheet membrane are immersed in the aerobic zone. The membrane modules are made from chlorinated polyethylene (Kubota, Japan) with nominal pore size of 0.4 μ m and effective area of $0.1m^2$/pc. The working volume and operating condition of hybrid MBR are mentioned in Table 1. The anoxic and aerobic conditions were controlled by the internal recycling of the mixed liquor directly from the aerobic zone to the anoxic zone. Returned sludge into the anaerobic zone was controlled by the internal recycling from the anoxic to anaerobic tank. An airlift was installed underneath the membrane modules in order to provide aeration to the membrane and oxygen to the biomass. The anaerobic and anoxic tanks were agitated with a mixer.

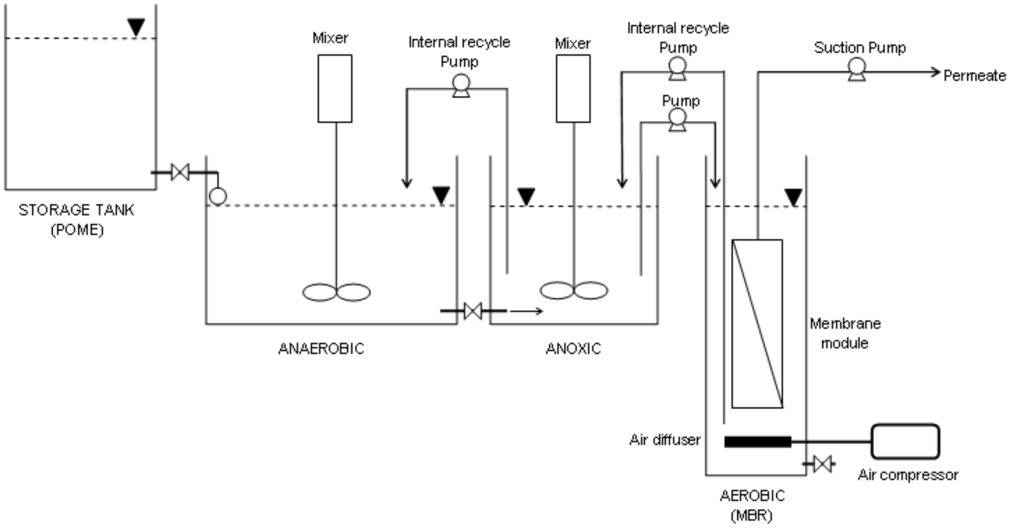

Figure 1: Schematic of Hybrid MBR

Table 1: Operating conditions of the Hybrid MBR

Parameter	*Anaerobic tank*	*Anoxic tank*	*Aerobic (MBR) tank*
Working volume, l	50	30	20
HRT, h	12	6	4
DO, mg/l	0 to 0.1	0.3 to 0.6	6 to 8
pH	5.5 to 6.5	7.2 to 8.5	7 to 7.5
Temp., ^{o}C	25 to 27	25 to 27	25 to 27
Airflow, l/min	-	-	10 to 15
Organic loading, kg COD/m^3.d	**1.77 to 1.87**		
Q_{in}, m^3/d	**0.108**		
Internal Recycle (IR)	**3Q_{in}**		
Suction time (on/off), min	**10/2**		
Constant flux, LMH	**15 (for long-term operation)**		
MLSS,mg/l	**4000 to 8000**		

The hybrid MBR was seeded with activated sludge obtained from the algae pond, POME treatment plant at Kilang Kelapa Sawit Bukit Besar, Kulai Johor, Malaysia. After 24 hours of acclimatisation, the membrane filtration was turned on progressively. The feeding was flowed into the sequencing processes of anaerobic, anoxic and aerobic zones in order to achieve biological nutrient removal. The feeding characteristics are showed in Table 2.

Table 2: Feeding Characteristics

Parameter	*Range*
COD, mg/l	**1680 ± 46**
SS, mg/l	**680 ± 30**
TN, mg/l	**28 ± 2**
TP, mg/l	**55 ± 3**

Analytical methods. Laboratory experiments were carried out in the UTM Environmental Engineering Laboratory. Experimental analysis was conducted according to standard methods (APHA, 1998). The activated sludge was regularly tested for MLSS and MLVSS concentrations. Chemical oxygen demand, total nitrogen, total phosphorus were analysed using a spectrophotometer (HACH/DR 5000). Dissolved oxygen concentration and temperature were monitored using portable HACH kits measurement and pH was also monitored using portable LaMotte kits measurement. The Brookfield Viscometer was used to measure the viscosity of permeate.

RESULTS AND DISCUSSION

Determination of Critical Flux. The critical flux concept has been defined in two distinct forms with no fouling and little fouling occurring at sub-critical operation for the strong and weak form (Le Clech *et al.*, 2003 and Jefferson *et al.*, 2004). The flux obtained during sub-critical flux (strong form) equate to the clean water flux obtained under the same conditions. In the alternative weak form, the sub-critical flux is the flux rapidly established and maintained during the start-up of the filtration, but does not necessarily equate to the clean water flux, as reviewed by Le Clech *et al.* (2006).

To determine the critical flux, the membrane bioreactor was fed with raw POME with the organic loading of 1.78 kg COD/m^3.d., MLSS of 4 to 8 g/l, to carry out the flux-step method experiments. Figure 1 shows the value of the step amplitude of 2 LMH and 15 min duration. TMP increases linearly until achieving the flux of 10 LMH and it ascends significantly beyond the flux of 16 LMH. The gradient of TMP can be observed to vary from 0.003 to 0.13 as shown in Table 3. The condition was due to the foul phenomena on the membrane surface. The trend of fouling has been extensively studied (Cho and Fane, 2002; Le Clech *et al.*, 2003; Lim and Ujang, 2004; Ognier *et al.*, 2004; and Guglielmi *et al.*, 2007). During this cycle test it was observed that the TMP values obtained during the descending phase were greater than the corresponding values recorded during the ascending phases. There the TMP values were observed for one hour before and after the peak point (Figure 1) and were found to be 0.25 bar of ascending and 0.65 bar of descending.

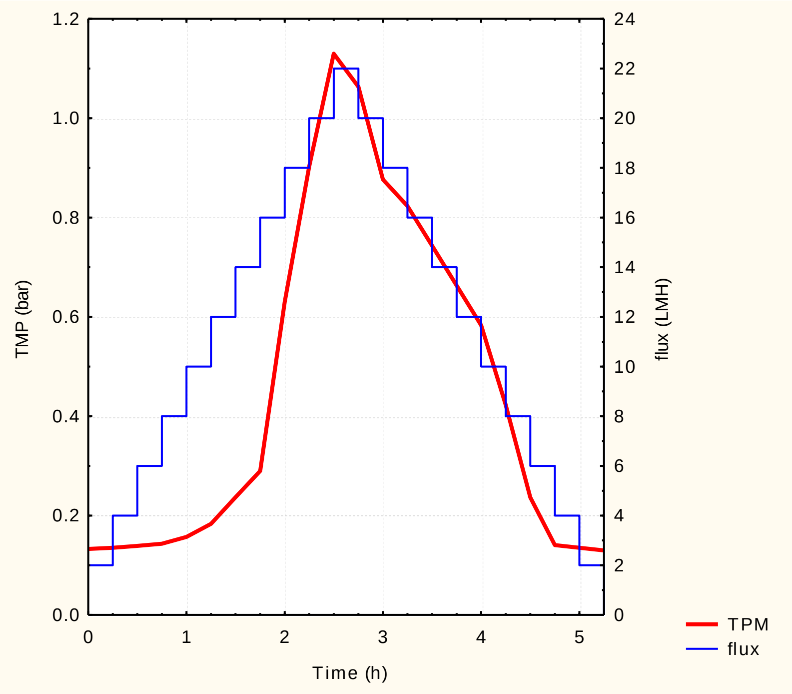

Figure 1: Critical flux determination

Figure 2 shows the experimental results obtained for different level of imposed permeate flow of POME and clean water. These results represent a linear variation between flux and TMP in which the slope is slightly above the one observed in flow of clean water through the membrane. There the gradient of POME (Φ_{TMP}) is in the range of 0.003 to 0.02 and the gradient of clean water ($\Phi_{TMP(CW)}$) is 0.0005 (Table 3). These are typical observations generally made for sub-critical flow rates. Then, above a flux value of 14 LMH, a clear break occurs in the curve with a substantial change in TMP where the Φ_{TMP} varied from 0.02 to 0.05. The TMP rose significantly after flux of 16 LMH with its gradient (Φ_{TMP}) of 0.13. This is characteristic of filtration where biological flocs are deposited on the membrane and thus of supra-critical condition. The results thus show a critical flux value ranging from 14 to 16 LMH, an interval corresponding to the values indicated by Defrance and Jafferin (1999), Ognier *et al.* (2004) and Yang *et al.* (2006).

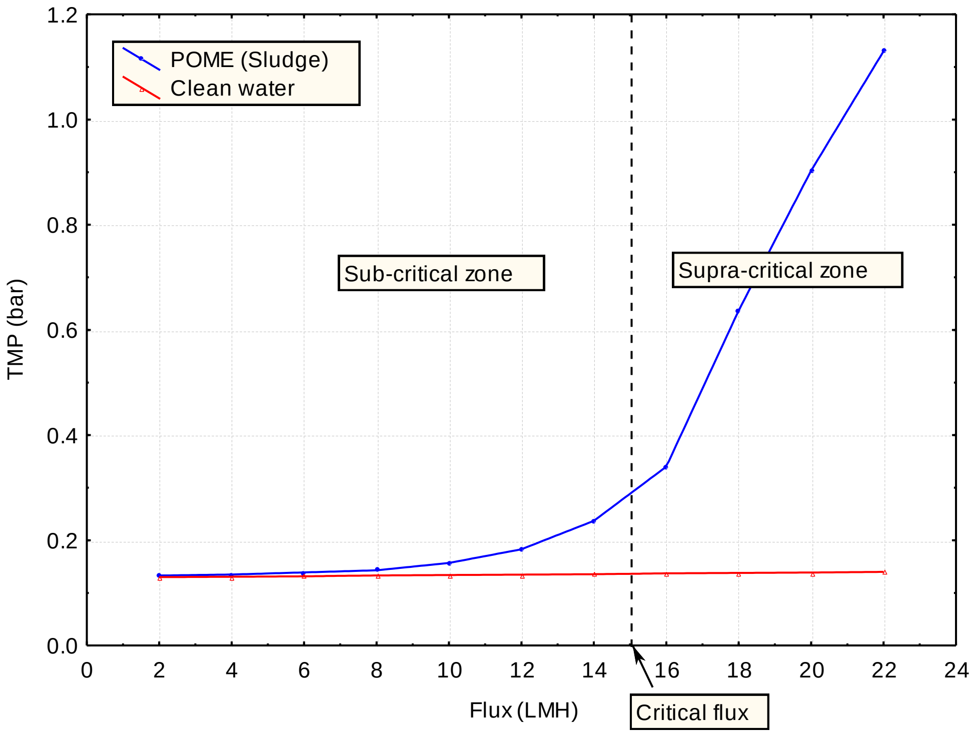

Figure 2: Relation between TMP and Flux

Effect of permeability and fouling rate is shown in Figure 3. For fluxes up to 10 LMH, permeability gradually increased up to 67 LMH/bar and fouling rate was nearly constant with its gradient (Φ_{FR}) of about 0.08 (Table 3). At this stage it could be observed that the membrane was in good condition and no fouling occurred. The permeability increased achieving of 70 LMH/bar at a flux of 12 LMH and started decreasing to 67 LMH/bar at a flux of 14 LMH and then it dropped to 61 LMH/bar (about 6 LMH/bar) for the flux 16 LMH. Thereafter, the permeability dropped significantly from 61 to 38 LMH/bar for the next flux level of 2 LMH. The fouling rate rose significantly after flux of 14 LMH where its gradient (Φ_{FR}) varied from 0.67 to 4.88 as mentioned in Table 3. Hence, the critical value fell in range of flux of 14 to 16 LMH while permeability and fouling rate were in range of 67 to 58 LMH/bar and 4 to 8 mbar/min respectively. Permeability and fouling rate related to flux in a short-term flux-step method to determine critical flux was studied by Le Clech *et al.* (2003).

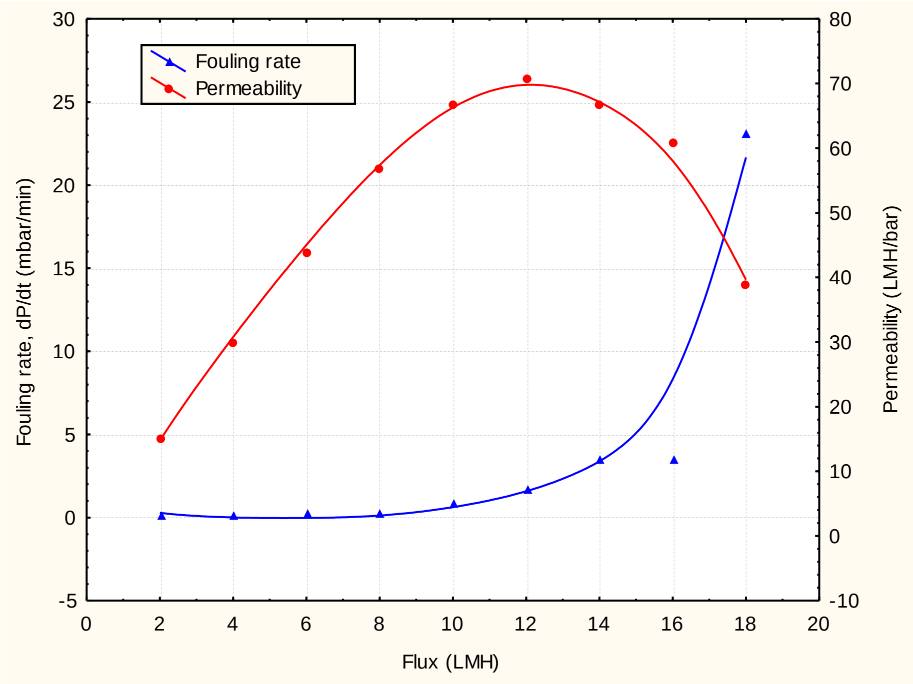

Figure 3: Permeability and fouling rate as function of flux

Table 3: Values of Φ_{TMP}, $\Phi_{TMP(CW)}$, Φ_{FR}, and Φ_K with Variable of Flux

Flux (LMH)	**Gradient**			
	POME (sludge) Φ_{TMP}	**clean water** $\Phi_{TMP(CW)}$	**fouling rate** Φ_{FR}	**Permeability** Φ_K
0-10	0.003	0.0005	0.08	6.49
10-14	0.02	0.0005	0.67	±1.96
14-16/14-18*	0.05	0.0005	4.88	-6.96
16-22	0.13	0.0005		

* Flux for Φ_{FR} and Φ_K

Hydraulic Resistance Analysis. According to the resistance-in-series model, the MBR permeate can be calculated by (Choo and Lee, 1996)

$$J = \frac{\Delta P}{\mu R_t} \quad \textbf{(1)}$$

$$R_t = R_m + R_c + R_b \quad \textbf{(2)}$$

Where J is the permeate flux, ΔP is TMP, μ is the viscosity of the permeate, R_t is the total resistance, R_m is the intrinsic membrane resistance, R_c is the cake resistance, and R_b is the fouling resistance due to irreversible adsorption and pore blocking. Flux and TMP data of the new membrane for the filtration of clean water were used for calculation according to Darcy's Law by Eq.1 to measure R_m. R_t was calculated from the filtration during the experiment, with flux and TPM were measured. For the calculation of R_m+R_b value (clean water resistance of fouled membrane), activated sludge was removed from the bioreactor, the membrane was washed with light spray and the bioreactor again filled with tap water to measure flux and TMP. Filtration data were used for calculation according to Eq.1. Rc was calculated using Eq.2.

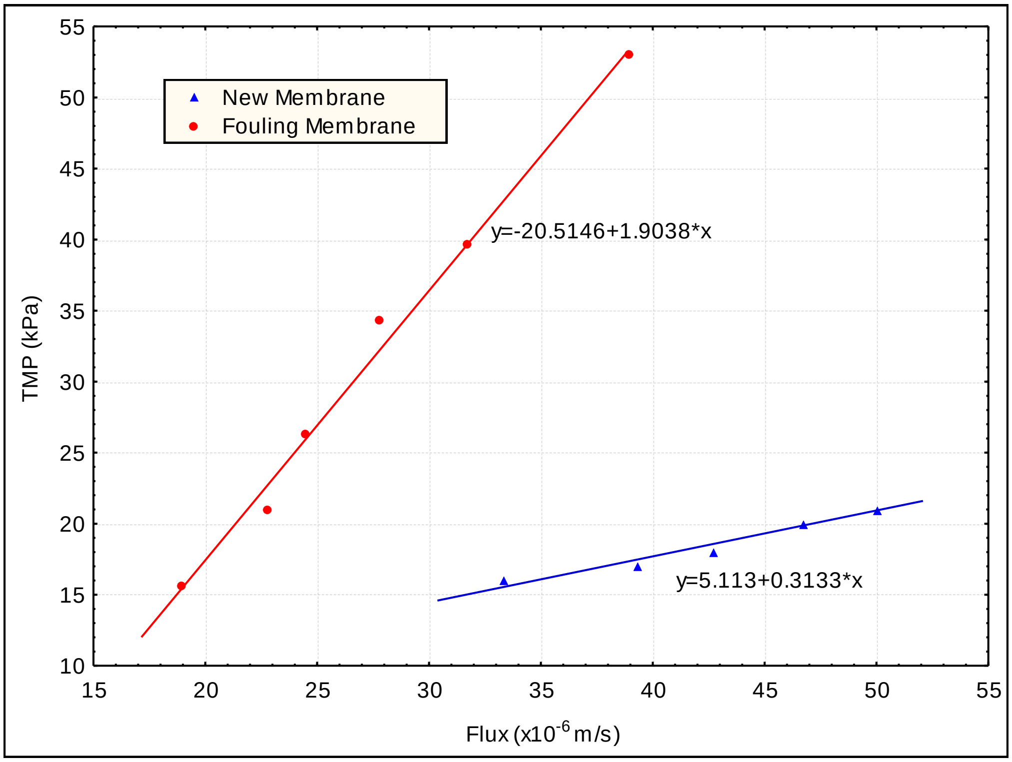

Figure 4: Determination of Rm, Rm+Rb using new and fouled membrane

The value of Rm and Rm+Rb was obtained from the gradient (Fig.4) and Eq.1. While the value of Rt and Rc was determined from the gradient (Fig.3) and Table 3. The value of membrane resistance for sub-critical, critical and supra-critical zones has been calculated as shown in Table 4. It was showed that the initial membrane resistance (Rm) for all the three zones remained small if comparing to the total resistance i.e. 4% for super critical, 2% for critical and 1% for supra-critical zones. The studies revealed that membrane fouling due to cake resistance was 74% in the zone of sub-critical and increased up to 15% in the critical zone. And cake resistance in the supra-critical zone was 96% of the total resistance. Fouling resistance due to irreversible and pore blocking in the zone sub-critical, critical and supra-critical were 22%, 9% and 3%respectively. Initial membrane resistance (Rm) was reported by *Jiang el al.* (2003) with flux of 41 LMH and initial resistance rate of 0.034×10^{10} $(m.min)^{-1}$. Cake Resistance under sub-critical condition has been reported by *Yang et al.* (2006) was about 67%. The cake resistance and pore blocking for 52days operation was 69% (*Matosic et al.*, 2008).

Table 4 : Resistance and Fraction of Membrane for Sub-critical, Critical and Supra-critical

Zone	*Resistance [x 10^{10} m^{-1}] (Fraction of Rt [%])*				
	Rm	*Rm+Rb*	*Rb*	*Rt*	*Rc*
Sub-critical	**0.03** **(4)**	**0.19** **(26)**	**0.16** **(22)**	**0.72** **(100)**	**0.53** **(74)**
Critical Flux	**0.03** **(2)**	**0.19** **(11)**	**0.16** **(9)**	**1.80** **(100)**	**1.60** **(89)**
Supra-critical	**0.03** **(1)**	**0.19** **(4)**	**0.16** **(3)**	**4.67** **(100)**	**4.48** **(96)**

Figure 5 shows the relationship between fouling rate and membrane resistance with constant flux of 12, 15, 18 and 20 LMH. For critical zone (Figure 3), fouling rate was in range of 4-8 mbar/min and membrane resistance (total) for sub-critical to critical zone was in range of 0.7 – 1.8 x $10^{10}m^{-1}$ (Table 4). In that range, fouling rate for the flux of 12, 15 and 18 LMH were in range of 3 to 9.5 mbar/min, 5 to 14.5 mbar/min and 8.5 to 22 mbar/min respectively. And for the flux of 20 LMH, the fouling rate of sub-critical zone was about 15mbar/min. Figure 5 also shows that the total membrane resistance of 0.7 x $10^{10}m^{-1}$, the fouling rate of flux 12, 15 and 18 were less than 8mbar/min and the flux of 20mbar/min was 14mbar/min. Under critical zone which the total resistance was 1.8 x $10^{10}m^{-1}$, the membrane were significant foul with the fouling rate exceeding 8mbar/min for the flux of 15, 18 and 20 LMH. For the total resistance of 11 x $10^{10}m^{-1}$, the flux of 12 and 15 LMH were in range of fouling rate of the critical zone. The result can be also revealed that the lower operation of flux the higher sustainable of membrane resistance for the fouling rate at the critical zone.

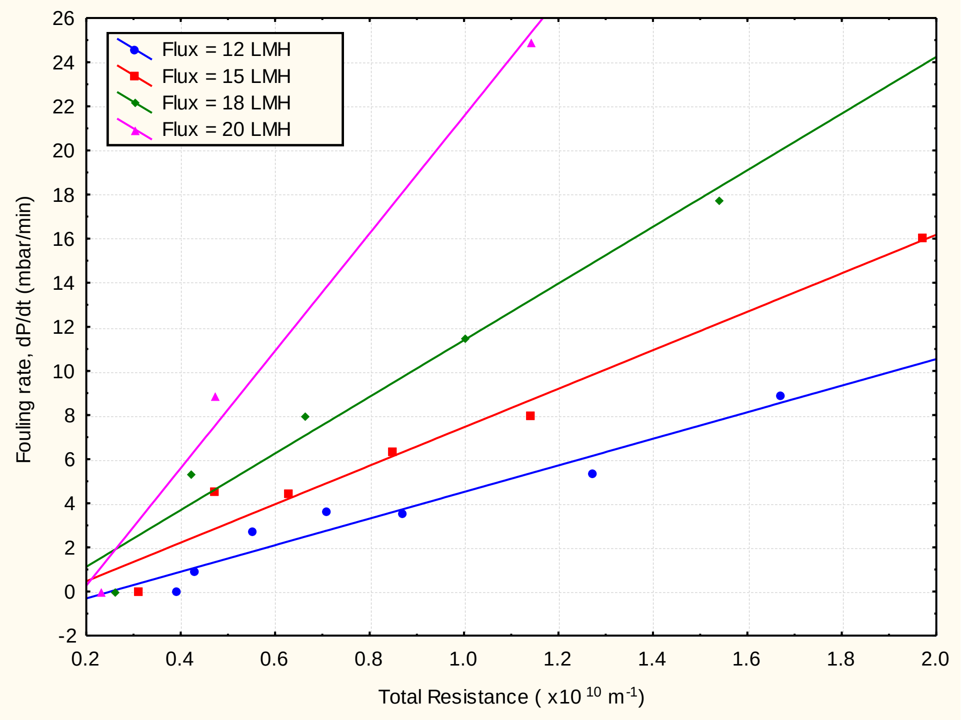

Figure 5: Fouling Rate and Total Resistance With Difference Constant Flux

Performance. Feeding and permeate were analyzed every week for a period of 5 weeks. The concentration of feeding and permeate are shown in Table 5. The average COD removal was about 94%. At an average the total removal was 98% for suspended solids, 83% for total nitrogen and only 64% for total phosphate. The COD removal is better compared to the value of 91-97% removal that reported by Xing *et al* (2000) and Chang *et al (*2001).

Table 5: Concentration of Feeding and Permeate

Feeding				**Permeate**				**Performance**			
COD (mg/l)	SS (mg/l)	TN (mg/l)	TP (mg/l)	COD (mg/l)	SS (mg/l)	TN (mg/l)	TP (mg/l)	COD (%)	SS (%)	TN (%)	TP (%)
1728	667	26	52.7	111	10	4.0	19.1	94	99	85	64
1682	681	28	57.7	92	16	4.7	20.6	95	98	83	64
1643	654	30	53.6	98	12	5.4	21.4	94	98	82	60
1637	691	27	55.7	102	13	5.1	19.6	94	98	81	65
1654	713	28	51.9	128	28	4.8	17.6	92	96	83	66
				Average (%)				94	98	83	64

CONCLUSIONS

The hybrid MBR was capable to operate under critical flux of 14 to 16 LMH which permeability descended from 67 to 61 LMH/bar and fouling rate increased from 4 to 8 mbar/min. The total membrane resistance at the fouling rate stage for sub-critical, critical and supra critical zone were 0.7 x 10^{10}, 1.8 x 10^{10} and 4.6 x 10^{10} m^{-1} respectively. Cake resistance was main membrane fouling which contributed more than 74% of total resistance. The system is efficient to remove COD and SS with an average removal of 94% and 98% respectively. The TN removal was 83% and the TP was 64%.

REFERENCES

[1] Ahmad A.L., S. Ismail and S. Bhatia, Membrane Treatment for Palm Oil Mill Effluent: Effect of Transmembrane Pressure and Crossflow Velocity, *Desalination* Vol. 179, 2005, pp. 245-255.

[2] Alias Z. and I. K. Tan, Isolation of Palm Oil-Utilising, Polyhydroxyalkanoate (PHA)-Producing Bacteria By an Enrichment Technique, *Bioresource Technology,* Vol. 96, No. 11, 2005, pp. 1229-1234.

[3] APHA, AWWA, WEF, Standard Methods, American Public Health Association, American Water Works Association and Water Environment Federation, Washington D.C, USA, 1998.

[4] Bella G.D., The Role of Fouling Mechanisms in a Submerged Membrane Bioreactor During the Start-up. *Desalination*, Vol. 200, 2006, pp. 722-724.

[5] Chang I.S., M. Gander, B. Jeffreson and S. Judd, Low-Cost Membranes For Use In a Submerged MBR. *Trans IChemE*, Vol. 79, pp. 183-188.

[6] Cho B.D. and A.G. Fane, Fouling Transients in Nominally Sub-Critical Flux Operation of a Membrane Bioreactor, *Journal of membrane science*, Vol. 209, 2002, pp. 391-403.

[7] Defrance L. and M.Y. Jaffrin, Comparison between Filtrations at Fixed Transmembrane Pressure and Fixed Flux: Application to Membrane Bioreactor Used For Wastewater Treatment, *Journal of Membrane Science*, Vol. 152, 1999, pp. 203-210.

[8] Jefferson B., A. Brookes, P. Le Clech and S.J. Judd, Methods for Understanding Organic Fouling in MBRs, *Water Science Technology*, Vol. 49, 2004, pp. 237-244.

[9] Gressel J. and R. Hoh, Malaysia oilseeds and products update (Oct) 2005. GAIN Report: USDA Foreign Agricultural Service. *Global Agriculture Information Network*. 2005, MY5045:1-8.

[10] Guglielmi G., D. Chiarani, S. J. Judd, and G. Andreattola, Flux Criticality and Sustainability in a Hollow Fibre Submerged Membrane Bioreactor for Municipal Wastewater Treatment. *Journal of Membrane Science*, Vol. 289, 2007, pp 241-248.

[11] Le Clech P., B. Jefferson, I. S. Chang and S. Judd, Critical Flux Determination by the Flux-Step Method in a Submerged Membrane Bioreactor, *Journal of Membrane Science*, Vol. 227, 2003, pp 81-93.

[12] Le Clech P., V. Chen, Tony and A.G. Fane, Review Fouling in Membrane Bioreactor Used in Wastewater Treatment. *Journal Membrane Science*, Vol. 284, 2006, pp 17-53.

[13] Lim L.P. and Z. Ujang, Critical Flux of Membrane Bioreactor (MBR) for Digested Palm Oil Mill Effluent (POME) Treatment. *Proceedings of the Water Environment - Membrane Technology (WEMT2004)*. June 7 – 10. Seoul, Korea, 2004, pp 793-799.

[14] Lim L.P. and Z. Ujang, The Operating Strategy for Treatment of Digested Palm Oil Mill Effluent (POME) in a Flat Sheet Aerobic Membrane Bioreactor Under Tropical Condition. *Conference Asia Water 2004*, Kuala Lumpur.

[15] Malaysia Palm Oil Board, Palm Oil Update – For the Latest Information on Palm Oil. 25(09/05). Ministry of Plantation Industries and Commodities Malaysia, 2005.

[16] Ognier S., C. Wisniewski, and A. Grasmick, Membrane Bioreactor Fouling in Sub-Critical Filtration Condition: A Local Critical Flux Concept. *Journal of Membrane Science*, Vol. 229, 2004, pp 171-177**.**

[17] Yacob S., M.A. Hassan, Y. Shirai, M. Wakisaka and S. Subash, Baseline Study of Methane Emission From Open Digesting Tanks of Palm Oil Mill Effluent Treatment, *Chemospher,*Vol. 59, 2005, pp 1575-1581.

[18] Yang Q., J. Chen and F. Zhang, Membrane Fouling Control in a Submerged Membrane Bioreactor With Porous, Flexible Suspended Carriers. *Desalination,* Vol. 189, 2006, pp 292-302.

[19] Yeoh B.G., A Technical and Economic Analysis of Heat and Power Generation from Biomethanation of Palm Oil Mill Effluent, *Electricity Supply Industry in Transition: Issues and Prospect for Asia, 2004, pp* 20-63.

[20] Yusoff S., Renewable Energy From Palm Oil-Innovation on Effective Utilization of Waste. *Journal of Cleaner Production*, Vol. 14, 2006, pp 87-93.

[21] Xing C.H., E. Tardieu, Y. Qian, and X. H. Wen, Ultrafiltration Membrane Bioreactor for Urban Wastewater Reclamation. *Journal of Membrane Science*, Vol. 177, 2000, pp 73-82.