Fouling and Rejection Behaviour of Ultrafiltration for Oil in Water Emulsion Separation

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Abstract :

Oily waste water has been generated from food, automotive, metal processing industries as well as petroleum exploration and refinery. Polyethersulfone ultrafiltration membrane was investigated for treatment of oil in water emulsion. The emulsion models were made based on industrial oily wastewater characteristic in the oil refinery. Flux and rejection were evaluated in order study the fouling and rejection behaviour. Results showed that more than 90% of COD and 85% surfactant were rejected. The permeate flux decline was analyzed in order to study the membrane fouling. In addition, the Hermia model is adopted to investigate the fouling mechanism during ultrafiltration of oil in water emulsion. Analyze of blocking mechanism using Hermia's model reveal that ultrafiltration of both diesel and mineral oil have good agreement with complete blocking mechanism.

Keywords: emulsion, fouling, Hermia's model, oily wastewater, ultrafiltration

1. Introduction

Oily wastewater is one of industrial wastewater source in food, automotive, metal processing as well as petroleum exploration and refineries. Exploration of crude oil consumes water injection and results on produced water. Exploration of 1 barrel crude oil requires 3 barrel produced water **[1]**. In addition, petroleum refineries result on oily wastewater 0,4 to 1,6 times of oil production **[2]**. Typical composition ranges of produced water generated from onshore oil and gas operation include 50-1000 mg/L of total oil and grease. Indonesian environmental regulations stated that maximum total oil and grease concentrations in discharge waters be 25–50 mg/L .

The oily wastewaters were found in the form of free-floating oil or oil in water emulsion. Free-floating oil or unstable oil/water emulsions can be readily removed by using conventional separation processes **[3, 4]**. However, for removing stable oil/water emulsion wastewater requires complex process comprising demulsification (breaking) of emulsion using coagulants, acids or heat treatment followed by separation of oil from water. The methods of oily wastewater treatment are frequently not efficient enough especially when the oil droplets are finely dispersed and the concentration is very low.

The membrane techniques such as ultrafiltration (UF) is a promising methods for emulsion separation. Ultrafiltration is a low-pressure membrane filtration process which operates between a pressure of 5 to 150 psi, an order of magnitude lower than that of reverse osmosis **[5]**. The pore sizes in UF membranes range from 0.001 μm to 0.1 μm, which result in rejections of compounds in the molecular weight range from 1000 to 100 000 Daltons. Generally the compounds that make up the petroleum hydrocarbon (PHC) contamination commonly detected in surface waters are semivolatile compounds such as benzene, ethylbenzene, toluene, xylene (BETX) which have molecular weights lower than the molecular-weight cut off (MWCO) range of the ultrafiltration membranes **[6]**. However, limitation in ultrafiltration of oily wastewater is membrane fouling. The main mechanisms of fouling involved surface area, pore clogging and pore restriction due to adsorption onto the pore walls **[7]**.

The Hermia's model describes mechanism of membrane fouling based on blocking filtration law, consisting of complete pore blocking, standard pore blocking, intermediate pore blocking and cake filtration **[8]**. The fouling mechanisms were illustrated in Figure 1.

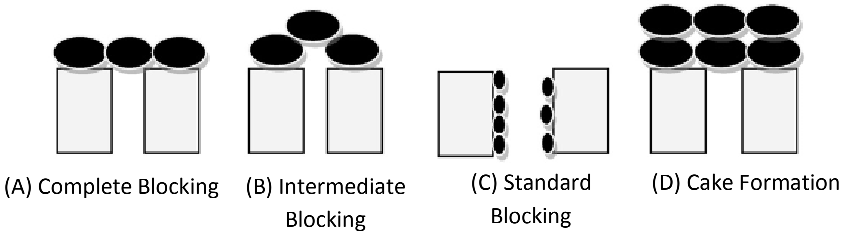


Figure 1. Blocking Mechanism by Hermia Model **[7]**

In the complete blocking model, it is assumed that every solute participate in blocking the entrance of the membrane pores completely. For intermediate blocking, it is assumed that each solute is settled on previously deposited solute. Standard blocking considers the deposition of each solute to the internal pore wall. The cake layer formation applied based on the accumulation of the sollute on the membrane surface in the cake form.

This paper reports data for the ultrafiltration of oil in water emulsion using diesel oil and mineral oil as dispersed (oil) phase. The performance in the term of COD and surfactant rejection as well as fouling mechanism based on Hermia's model were determined.

2. Materials and Methods

Feed of oil in water emulsion models were prepared by dispersing oil phase (diesel oil and mineral oil) into continuous phase using Manual Ultra Turax Homogenizer, 2500 rpm for 5 minutes. The diesel oil were provided by Pertamina and the mineral oil was a commercial cutting oil, Eontrim E 9010, having specifiication of 70% v mineral oil, 30% v surfactant, co surfactant and corrosion inhibitor. All oils were used without further treatment. The concentration of oil was 50 mg/L continuous phase. The continuous phase was a mixture of 2% v/v Tween 80 (Polysorbate 80) and distilled water.

The ol in water emulsion models were characterized based on their viscosity, density and Chemical Oxigen Demand (COD) and the characteristic is listed in Table 1.

Table 1 Characteristic of Oil in Water Emulsion (50 mg/L oil, 2% Tween 80)

Oil Types	Viscosity (Cp)	Density (g/ml)	COD (mg/L)
Diesel Oil	11,2	0,984	108.757,82
Mineral Oil	10,4	1,021	137.950,71

The membrane used in the experiments was a round flat membrane Polyethersulphone (PES) membrane with a nominal pore size of 20kDa , a surface area of 0,00138 m^2, provided by NADIR Filtration, Germany. An ultrafiltration cell of 500 ml capacity. Schematic diagram of the experimental apparatus is shown in Figure 1.

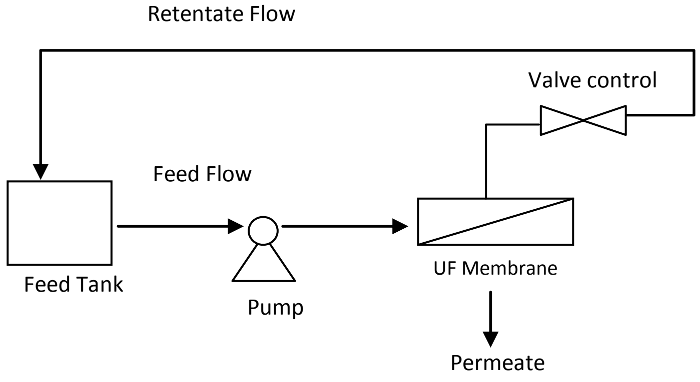


Figure 1. Schematic Diagram of Experimental Set-up

Membrane permeability was determined by operating the ultrafiltration cell using aquadest at Trans Membrane Pressure 1-3 bar. The water permeability of ultrafiltration membrane was 17,32 L/m^2.hr.bar. Membrane performance was evaluated based on its flux and rejection. The permeate was collected and the volume was measured at specific time in order to determine the membrane flux. The surfactant concentration in the permeate was analyzed by measuring the turbidity using Portable Turbidimetre Orbeco-Hellige Infrared. The concentration of surfactant was determined based on standard curve of surfactant concentration vs turbidity.

In order to evaluate the fouling mechanism, data of membrane flux was fitted with linearization of blocking mechanism by Hermia model as listed in Table 2.

Table 2 Linearized form of blocking mechanism by Hermia model

Blocking Mechanism	n	Linearized Equation Form	Physical Concept	Equation
Complete Blocking	2	$\ln J = \ln J_0 + k_c t$	Pore blocking	(1)
Intermediate Blocking	1	$1/J = 1/J_0 + k_i t$	Pore blocking + surface deposit	(2)
Standard Blocking	3/2	$1/\sqrt{J} = 1/\sqrt{J_0} + k_s t$	Pore constriction	(3)
Cake formation	0	$1/J^2 = 1/J_0^2 + k_{cf} t$	Formation of surface deposit	(4)

3. Results and Discussions

3.1. Flux and Rejection

Figure 2 shows the variation of normalized flux (J/J_0) as function of oil types.

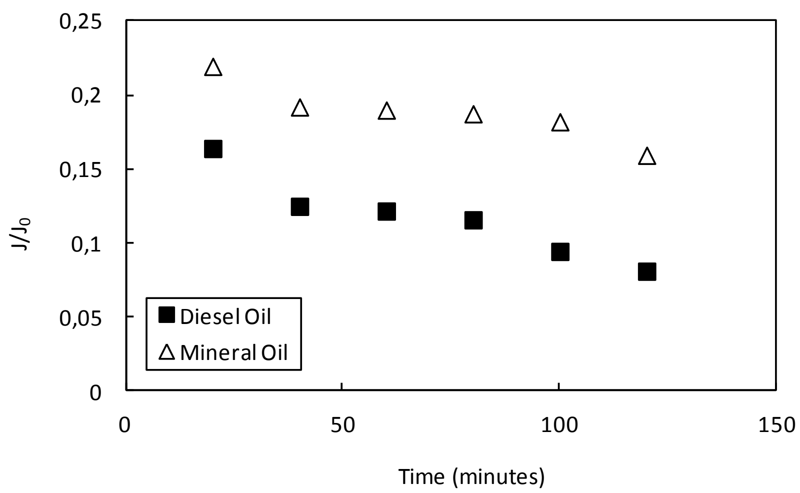


Figure 2. NormalilzedFlux Decline of Ultrafiltration of Oil in Water Emulsion at Different Oil Types

The figure illustrated that the use of mineral oil result on higher flux than the diesel oil. This is due to the high molecular weight of mineral oil which is higher compared to the diesel oil. Diesel oil has a chemical structure of

$C_{13}H_{28}$ and $C_{14}H_{30}$ while the mineral oil having chemical structure of $(CH_2)n$ when n is in the range number of 20-40. As the molecular weight of diesel oil was smaller, the diesel oil molecule flow inside the membrane pore faster than the mineral oil molecule. Inside the membrane pores, there is an adsorption of diesel oil which is one of the cause of membrane fouling.

Adsorption of hidrophobic material such as oil at the solid membrane surface can take place due to **[9]**:

1. Monolayer adsorption (amphiphilic material at hidrophobic surface)
2. Multilayer adsorption (solute hidrophobic at solid surface)
3. Capilary condensation (hidrophobic solute at membrane matrix)

The oil attcahted into membrane pore wall can reduce pore diameter and cause pore blocking. In additian, the oil can be deposited at the membrane surface, generating a layer that being a dominant resistance of water or permeate transfer **[6]**. In addition, the presence of surfactant on feed has effect on reduction of permeate flux. The surfactant on feed can be in the form of oil droplet attachment, free surfactant or micelle surfactant.

Concentration of COD on feed and permeate as well as its rejection are shown in Table 3.

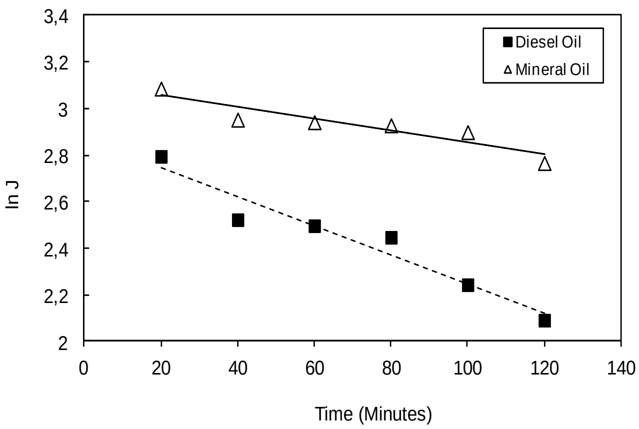
Table 3 COD Concentration on the feed, permeate and the rejection

Oil Types	COD of Feed (mg/l)	COD of Permeate (mg/l)	Rejection %
Diesel Oil	108.757,82	1,490.51	98,66
Mineral Oil	137.950,71	7,046.07	94,89

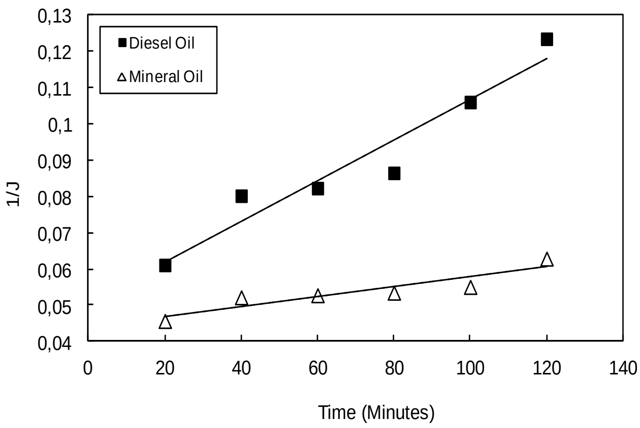
The results of COD rejection represents that the rejection rate is high, but the COD concentration is considerably higher that the regulation of COD limit due to very high COD concentration on the feed. However, since the rejection rate is more than 90%, it is certain that the membrane is appropriate for treatment of oily waste water to remove the oil or grease component.

3.2. Hermia's Model and Fouling Mechanisms

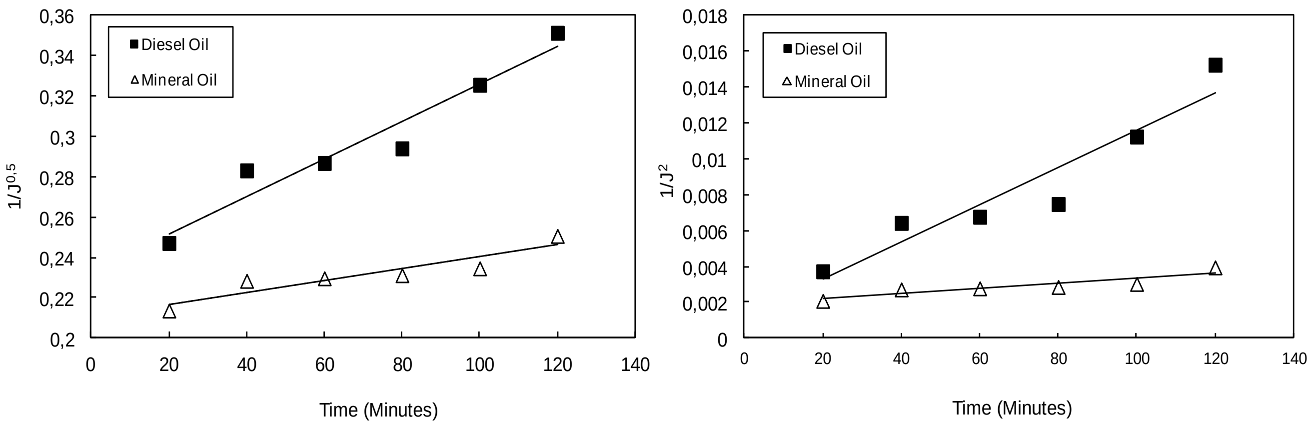
In thid study, Hermia's model was used in order to analyze the fouling mechanism during ultrafiltration of oil in water emulsion. The model fit was use to determine the cause of flux decline whether by cake formation or pore blocking. Figure 3 shows the fitting of blocking mechanism during ultrafiltration of oil in water emulsion based on Hermia's model.



(A)



(B)



(C) (D)

Figure 3. Effect of Oil Types to permeate Flux predicted by Blocking Mechanism: (A) Complete Blocking (B) Intermediate Blocking (C) Standard Blocking (D) Cake Layer

Figure 3 shows that the mineral oil seem to have good agreement with all blocking mechanism. On the other hand, the diesel oil only has good agreement with the Complete Blocking and Intermediate Blocking Mechanisms. In order to confirm the exact blocking mechanisms for both oil, value of R^2 of the fitting model as well as value of fitted parameter were calculated. The value of R2 and Fitted Hermia's model parameter are presented in Table 4 and Table 5, respectively.

Table 4 Values of R^2 to the experimental data by effect of oil types

Oil Types	n=2 Complete Blocking	n=1 Intermediate Blocking	n=3/2 Standard Blocking	n=0 Cake Layer
Diesel Oil	0,9368	0,9296	0,9367	0,8985
Mineral Oil	0,851	0,8448	0,8489	0,8315

Table 5. Fitted Hermia's Model Parameters for Different Oil Types

Oil Types	k_c	k_i	k_s	k_{cf}
Diesel Oil	0,0063	0,0006	0,0009	0,00001
Mineral Oil	0,0025	0,0001	0,0003	0,00001

Table 4 shows that both diesel oil and mineral oil having the greatest R^2 value for Complete Blocking Mechanisms. Moreover, the value of fitted parameter as shown in Table 5 supports this statement. The greatest value parameter for diesel oil and mineral oil are both found for complete blocking mechanisms. The values of this parameter should be higher for the conditions that exhibit to more severe flux decline of the membrane. Since the mineral oil exhibits less fouling to the membrane, the value of k_c, k_i, k_s, and k_{cf} are lower compared to the diesel oil. Based on the Hermia's model, both diesel and mineral oil have complete blocking mechnasim of fouling. The complete blocking mechanism assumes that all the solutes participate in blocking the membrane pore but do not overlapped upon one another.

4. Conclusions

Ultrafiltration of oil in water emulsion for diesel and mineral oil waste water model have been carried out using PES membrane. Experimental results show that flux of mineral oil was higher than the flux of diesel oil. This is due to the small molecular size of diesel oil. The small molecule of diesel oil make it possible to go inside membrane pore and adsorp into pore membrane. The adsorption of oil droplet into membrane pore can generate the membrane pore blocking. This cause the membrane fouling and hence reducing the membrane flux. The use of ultrafiltration membrane for oily waste water treatment model achieve rejection of more than 94%. Analyze of blocking mechanism using Hermia's model reveal that ultrafiltration of both diesel and mineral oil have good agreement with complete blocking mechanism.

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References

[1] Ahmadun F, Pendasteha A, Abdullah LC, Biaka R A, Madaaeni SS., Abidin ZZ. 2009. Review Technologies for Oil and Gas Produced Water Treatment. *J. of Hazardous Materials*, 170 : 530-551

[2] Coelho A, Castro A V, Dezotti M, 2006. Treatment of Petroleum Refinery Sourwater by Advanced Oxidation Process. *J. Hazard.Matter*, 137 : 174-184

[3] Chakrabarty B., Ghoshal A K, Purkait M K. 2008. Ultrafiltration of stable oil-in-water emulsion by polysulfone membrane. *J. of Membrane Science*, 325 : 427-437

[4] Benito J M, Rios G, Ortea E, Fernhdez E, Cambiella A, Pazos C, Coca J.2002 Design and construction of a modular pilot plant for the treatment of oil-containing waste waters. *Desalination*, 147 : 5-10

[5] Cheryan M. 1986. *Ultrafiltration Handbook*. Marcel Dekker, Technomic Publishers, Lancaster, Pennsylvania

[6] Benito, J. M, Ebel S., Gutierrez B, Pazos C, Coca J. 2001. Ultrafiltration of waste emulsified cutting oil using organic membrane, *Water, air and solid pollution*, 128: 181-195

[7] Amin I N H M, Mohammad A W, Markom M, Peng L C, Hilal N. 2010. Analysis of deposition mechanism during ultrafiltration of glycerin-rich solutions. *Desalination*, 261: 313-320

[8] Wang F., Tarabara V V. 2008. Pore Blocking Mechanisms during Early Stages of membrane fouling by colloids. *J. Colloid Interface Sci.*, 328: 464-469

[9] Jonsson, A. S., Lindau, J., Wimmerstedt, R., Brick, Jonsson, B. 1997. Influence of the consentration of a low-molecular organic solute on the flux reduction at a PES ultrafiltration membrane. *J. of Membr. Sci*., 135: 117-128