Mohsen Abbasi[1], **Aboozar Taheri**[2]

SELECTING MODEL FOR TREATMENT OF OILY WASTEWATER BY MF-PAC HYBRID PROCESS USING MULLITE-ALUMINA CERAMIC MEMBRANES

[1]Department of Chemical Engineering,
School of Cemical and Petroleum Engineering,
Persian Gulf University, Bushehr, Iran,
[2]Department of Chemistry, Islamic Azad University, Lamerd, Iran
m.abbasi@pgu.ac.ir

Hermia's models for cross flow filtration were used to investigate the fouling mechanisms of mullite-alumina ceramic membranes in treatment of oily wastewaters in a hybrid microfiltration-powdered activated carbon process (MF-PAC). Results show that cake filtration model can be applied for prediction of permeation flux decline for MF and MF-PAC process up to 400 ppm PAC. The complete pore blocking model and the intermediate pore blocking model can predict permeation flux decline with time for MF-PAC with 800 and 1200 ppm PAC respectively. Average error for prediction of permeation flux with cake filtration model is 2.19% for MF process and 2.16; 2.06 and 1.31% for MF-PAC process with 100; 200 and 400 ppm PAC respectively. Also for MF-PAC process with 800 and 1200 ppm PAC, average error for prediction of permeation flux with complete pore blocking model and intermediate pore blocking model was 6.11 and 6% respectively.

Keywords: oily wastewater treatment, microfiltration, powdered activated carbon, mullite-alumina membranes, membrane Fouling.

1. Introduction

Oily wastewaters are one of the major pollutants of the aquatic environment and removing oil from these oil-in-water emulsions is an important aspect of pollution control. This is due to the emission of a variety of industrial oily wastewaters from sources such as refineries, petrochemical plants and transportation [1 – 3].

Low pressure driven membrane separation techniques such as microfiltration (MF) have been considered as indispensable treatment methods in water and wastewater treatment applications to remove specific pollutants which are not normally removed by conventional processes [4].

Adsorption using powdered activated carbon (PAC) in combination with membrane MF process can be used as a hybrid system for removing organic materials and improving permeate flux. PAC is generally used as a pretreatment step prior to the membrane operation or in combination with the membrane in feed tank. PAC was used as membrane pretreatment for both water and wastewater treatment [5 – 9].

Ceramic membranes have been known for years and used in many different applications and they have numerous advantages: stability at high temperature and pressure resistance, good chemical stability, high mechanical resistance, long life and good antifouling properties. Mullite-alumina ceramic membranes have very high chemical and thermal stability and are very cheap because they can be prepared by extruding and calcining kaolin clay [1].

One of the major inhibiting factors for successful commercialization of the membrane processes is membrane fouling. Membrane fouling is characterized in general as the reduction of permeate flux through the membrane, and hence leads to an irreversible loss of system productivity over time, caused by interactions between the membrane and the various components in the process stream [10 – 13].

In order to enhance economy and efficiency of MF membranes, understanding the membrane fouling mechanisms is necessary for the further development.

In the last two decades there have been a large number of studies focused on effects of operating parameters on flux decline and membrane fouling mechanisms. In these studies, membrane filtration testes under different experimental conditions were preformed to obtain data on permeate flux variation with time [10, 14]. Although some advances in fundamental MF membrane fouling mechanisms have been achieved, further researches are needed to better understand the fouling mechanisms. From the analyses of permeation loss and resistance coefficient of fouling, the filtration flux can then be predicted by using the blocking models [15 – 17].

The behavior of permeation flux decline with time of ceramic membranes for treatment of oily wastewater in MF-PAC process has not been demonstrated in literature. Therefore for knowledge of fouling mechanisms, Hermia's models for cross flow filtration [18] were used to investigate the fouling mechanisms involved in MF-PAC process of oily wastewater at different time intervals ((0 – 2.5 min), (0 – 5 min), (5 – 20 min), (20 – 60 min) and (0 – 60 min)) with mullite-alumina ceramic membranes. The fitted results of the models for cross flow filtration were presented and compared with the experimental data in this novel research. Also, more detailed study of the models was provided for cross flow filtration to explain the fouling mechanisms in MF-PAC of the oily wastewaters.

2. Experimental

2.1. Theory. Permeation flux, flux reduction and total organic carbon (TOC) rejection are important parameters in design and construction of MF separation units.

Permeation flux (J) is volume of permeate (V) collected per unit membrane area (A) per unit time (t):

$$J = \frac{V}{A_t}. \qquad (1)$$

Flux reduction (FR,%) is calculated as follows [1]:

$$FR = \frac{J_{wi} - J_{ww}}{J_{wi}} \cdot 100, \qquad (2)$$

where J_{wi} is water flux of clean membranes and J_{ww} is water flux of fouled membranes (at the end of filtration) were measure in operating condition with a pressure of 1 bar, temperature of 25°C and cross flow velocity (CFV) of 1 (m · s^{-1}).

TOC rejection (R,%) is calculated as follows [1]:

$$R = 1 - \frac{C_p}{C_f} \cdot 100, \qquad (3)$$

where C_p represents concentration of a particular component (i.e. TOC) in permeate, while C_f is its feed concentration.

2.2. Membranes. In this research, mullite-alumina (50% alumina content) MF membranes were synthesized from kaolin clay and α-alumina powder. Commercial grade of α-alumina with 99.6% purity was used to prepare the mullite-alumina membranes. The powder had an average particle size of 75 µm. Chemical analysis of the kaolin clay is listed in Table 1. Fig. 1 shows surface and cross section of a synthetic mullite-alumina ceramic membrane. Preparation and characterization of membranes has been illustrated in previous research [1].

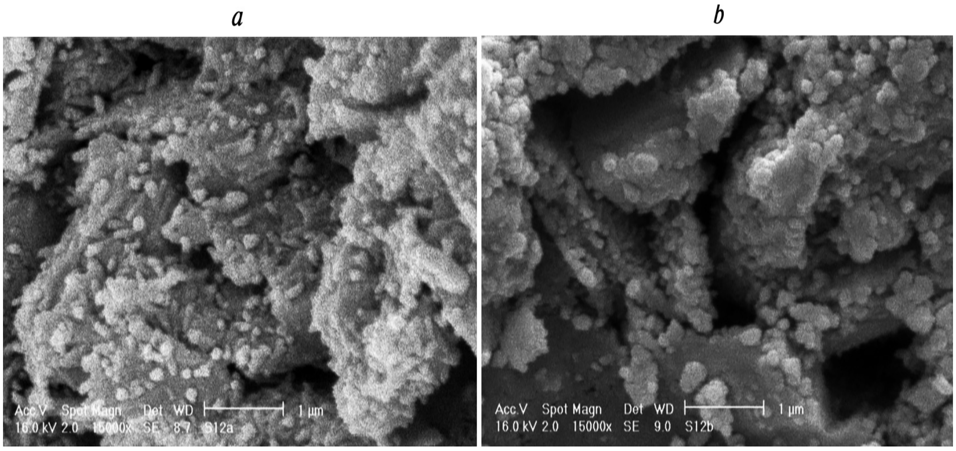

Fig. 1. SEM micrograhs of the mullite-alumina ceramic membrane: a – surface 15000 x, b – cross section 30000 x.

Table 1. Chemical analysis of the kaolin clay

Component	Percent	Phases	Percent
SiO_2	61.62	Kaolinite	64
TiO_2	0.4	–	–
Al_2O_3	24 –25	Illite	2.4
Fe_2O_3	0.45 – 0.65	–	–
K_2O	0.4	Quartz	27
Na_2O	0.5	–	–
L.O.I	9.5 – 10	Feldspar	6.6
Total	100	–	100

2.3. Process feed. Oil-in-water emulsions (synthetic oily wastewaters) with 1000 ppm oil were prepared by mixing condensate gas from Seraje, Ghom, Iran, (C_8 – C_{12}) and distilled water. Droplet size distribution of the emulsion (1000 ppm oil in water) is presented in Fig. 2. As observed, mean droplet size of oil droplets is 1.09 µm. Detail of information has been illustrated in previous paper [1].

2.4. Setup. Fig. 3, *a* shows the experimental setup used in all the experiments. The laboratory scale setup was operated in cross flow mode. Also Fig. 3, *b* gives structure of MF membranes module. More information has been presented in previous paper [1].

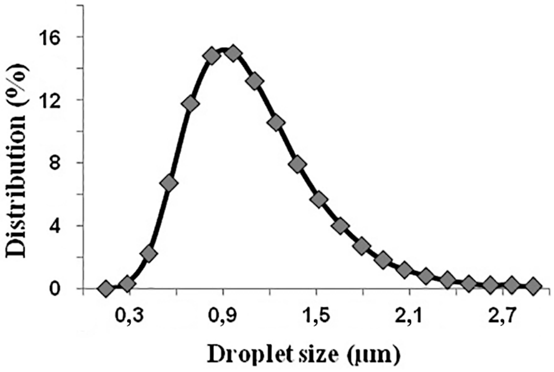

Fig. 2. Droplet size distribution of the synthetic oily wastewater with 1000 ppm oil in water.

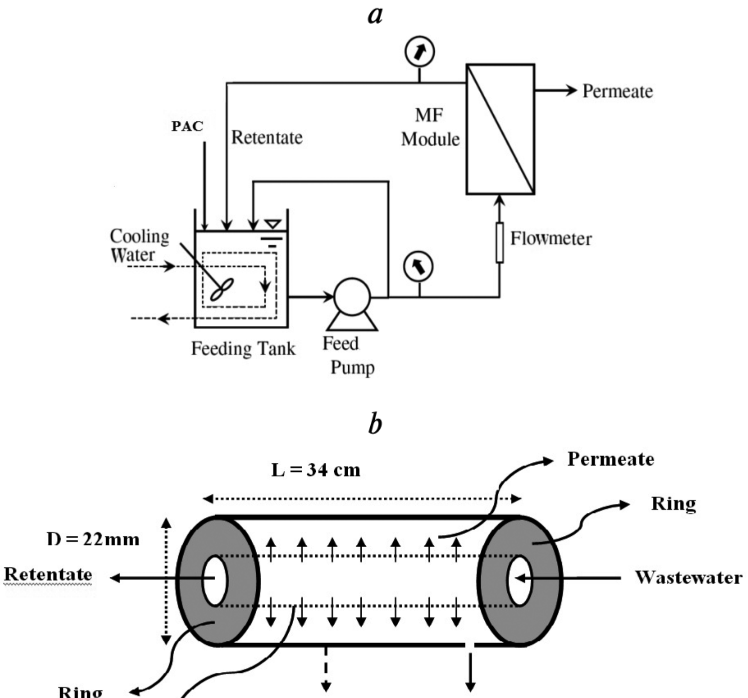

Fig. 3. Microfiltration setup (a) and structures of membranes module (b).

2.5. Experimental procedure. In order to determine the best operating conditions, 1000 ppm condensate gas in water emulsions were employed as synthetic oily wastewaters using mullite-alumina membrane. The effects of different operating parameters such as pressure (0.5 – 4 bar), cross flow velocity (0 – 2 $m \cdot s^{-1}$), temperature

(15 – 55°C), on permeation flux, FR, and TOC R of mullite-alumina membranes for treatment of synthetic wastewaters were investigated [1].

Table 2 shows performance of MF and MF-PAC process for treatment of synthetic wastewaters using mullite-alumina membranes at the best operating conditions (pressure 3 bar, cross flow velocity 1.5 ($m \cdot s^{-1}$) and temperature 35°C). Results indicate that addition of PAC in best concentration (400 ppm) is effective to increase permeation flux and TOC rejection and decreasing membranes fouling [5].

Table 2. Summary results of MF and MF-PAC system using mullite-alumina ceramic membranes

PAC concentration, ppm	Permeation flux, $Lm^{-2}h^{-1}$	*FR*, %	TOC rejection, %
0	118.32	58.5	89.6
100	157.53	42.13	89.8
200	178.1	35.32	89.9
400	190.47	31.22	90.2
800	95.82	64.39	91.9
1200	88.23	65.61	92.4

3. Modeling

Hermia's models for cross flow filtration are the most useful and applicable models for microfiltration flux decline prediction. The general equation is as follows [17, 18]:

$$\frac{dJ}{dt} = \mathrm{K}(J - J_{ss})J^{2-n}., \qquad (4)$$

where $n = 2$ for complete blocking; $n = 1.5$ for standard blocking; $n = 1$ for in complete pore blocking (intermediate fouling) and $n = 0$ for cake filtration. K is a constant and depends on the pressure, the dynamic viscosity of permeate, the blocked area and the membrane resistance, also J_{ss} is steady state permeation flux. If the models can predict permeation flux decline of membranes, by linearization of this models and with selection of largest the best coefficient of determination (R^2), slope shows constant of models (K). Therefore with theses fitting parameters, permeation flux at each time during filtration and fouling mechanism can be predicted.

3.1. Cake formation model. Cake/gel formation usually occurs when particles/oil droplets larger than the average pore size accumulate on the membrane surface, forming a "cake/gel". Permeation flux can be predicted as follows [17, 18]:

$$J = \left[\left(1-Y\right)J_{ss}\right]\frac{\sqrt{[(Y-1)(J_{ss})]^2-4(X-Y)(J_{ss}{}^2)}}{2(X-Y)}\,;\qquad(5)$$
$$Y = [\exp(KJ_{ss}{}^2t)]-\frac{J_{ss}}{J_0}\,;\;\; X=\frac{J_0-J_{ss}}{J_0}\,.$$

J_0 in the initial permeation flux ($J = J_0$ at $t = 0$).

3.2. Standard pore blocking model. Standard pore block is the most dominant phenomenon when retained particles/oil droplets are dimensionally smaller than the average pore size of the membrane. Permeate flux can be obtained by the following equation [17, 18]:

$$\frac{1}{J^{0.5}}=\frac{1}{J_{\circ}^{0.5}}+(K)(t).\qquad(6)$$

3.3. Complete pore blocking model. This process typically occurs when the particles/oil droplets are dimensionally similar to the mean pore size of the membrane. In this model, particles/oil droplets plug individual pores.

Permeate flux can be simply represented by the following equation [17, 18]:

$$J = J_{ss} + (J_0 - J_{ss})\exp[(-\mathrm{K}J_0)t].\qquad(7)$$

3.4. Intermediate pore blocking model. This model assumes each particle/oil droplet can block some membrane pores or settle on other particles/oil droplets previously blocked some other pores with superposition of particles/oil droplets. Permeate flux can be obtained by the following equation [17, 18]:

$$J=\frac{J_0J_{ss}B}{J_{ss}+J_0[P-1]};\; B=\exp[(KJ_{ss})t].\qquad(8)$$

For modeling, firstly, the relationship between time (t) and permeate flux (J) was drawn for all mullite-alumina membranes in MF and MF-PAC process.

In all cases, the permeate volume decreased with time. A linear relationship of M versus *t*, $1/J^{0.5}$ versus *t*, $\ln[(J - J_{ss})/(J_0 - J_{ss})]$ versus *t* and $\ln[J(J_0 - J_{ss})/J_0(J - J_{ss})]$ versus *t* was determined experimentally for cake filtration model, standard pore blocking model, complete pore blocking model and intermediate pore blocking model to calculate constants (K) in models respectively:

$$\mathrm{M} = \ln[(\frac{J(J_0 - J_{ss})}{J_0(J - J_{ss})}) - J_{ss}(\frac{1}{J} - \frac{1}{J_0})]. \qquad (9)$$

To determine whether the data agree with any of the considered models, the coefficient of determination (R^2) of each plot for one model was compared with the others. For better comparison of the models, average prediction errors of models are calculated. For determination of average prediction errors of models, by using the experimental data, average value of models constant (K) are calculated and replaced in equations (2) – (5) to calculate predicted permeation flux. Therefore average error at different times for predicted flux and actual flux are determined:

$$Error = \frac{1}{n}\left|\frac{J_{\mathrm{mod}} - J_{\mathrm{exp}}}{J_{\mathrm{exp}}}\right|. \qquad (10)$$

It is possible that fouling mechanisms has been changed during filtration and transitions of fouling mechanisms were occurred [16, 17]. Therefore models were used to investigate the fouling mechanisms of membranes at different time intervals ((0 – 2.5 min), (0 – 5 min), (5 – 20 min), (20 – 60 min) and (0 – 60 min)) for MF and MF-PAC process.

4. Results and discussions

4.1. Prediction of permeation flux decline by pore blocking models for MF process. Tables 3, 4 for all models, indicate that the cake filtration model with average error of 2.19% coincidence better relative to the intermediate pore blocking and complete pore blocking models (average error of 3.56 and 7.43% respectively). Large deviations between experimental and predicted flux decline are observed for the standard pore blocking model with average error of 14.16%.

Results of Table 3 show that cake filtration model can predict flux of permeate better than other model at first times of filtration ((0 – 2.5 min) and

(0 – 5 min)). By increasing time to 60 min, results indicate that prediction of permeation flux with cake filtration model can be applied for prediction of permeation flux for other intervals. Therefore it can be conclude that pores of mullite-alumina membranes becomes fill and cake layer formed and it become thicker by increasing time at the begin of filtration [6, 16]. It must be noted that by comparing particle size distribution of oil droplet (see Fig. 2) and mean average pore diameter of mullite-alumina membranes (0.728 μm), it can be found that mean diameter of oil droplets is larger than average pore diameter of mullite-alumina membranes and a large percent of oil droplets cannot inter into mullite-alumina pores. After cake filtration model, intermediate pore blocking model, can predict filtration flux well.

Table 3. (R^2) of models for prediction of permeation flux with time at different time intervals without PAC and with different PAC concentrations

Models	0 – 2.5	0 – 5	5 – 20	20 – 120	Total time (0 – 120 min)
	min				
	Without PAC				
Cake filtration model	0.999	0.999	0.999	0.999	0.999
Intermediate pore blocking model	0.997	0.997	0.998	0.999	0.992
Standard pore blocking model	0.995	0.993	0.99	0.983	0.917
Complete pore blocking model	0.995	0.994	0.994	0.994	0.996
	100 ppm				
Cake filtration model	0.997	0.998	0.991	0.998	0.998
Intermediate pore blocking model	0.995	0.996	0.977	0.995	0.988
Standard pore blocking model	0.993	0.994	0.958	0.974	0.924
Complete pore blocking model	0.994	0.994	0.965	0.989	0.958
	200 ppm				
Cake filtration model	0.995	0.998	0.996	0.984	0.994
Intermediate pore blocking model	0.991	0.996	0.979	0.977	0.988
Standard pore blocking model	0.993	0.994	0.958	0.974	0.924
Complete pore blocking model	0.996	0.979	0.999	0.973	0.977

Table 3. (Cont.)

Complete pore blocking model	0.994	0.994	0.965	0.989	0.958
	400 ppm				
Cake filtration model	0.999	0.988	0.987	0.98	0.991
Intermediate pore blocking model	0.999	0.977	0.995	0.973	0.98
Standard pore blocking model	0.998	0.968	0.998	0.934	0.912
Complete pore blocking model	0.998	0.97	0.997	0.962	0.956
	800 ppm				
Cake filtration model	0.997	0.995	0.993	0.934	0.904
Intermediate pore blocking model	0.999	0.999	0.998	0.964	0.979
Standard pore blocking model	0.999	0.998	0.99	0.998	0.982
Complete pore blocking model	0.999	0.998	0.989	0.99	0.988
	1200 ppm				
Cake filtration model	0.906	0.962	0.983	0.97	0.977
Intermediate pore blocking model	0.997	0.983	0.998	0.981	0.99
Standard pore blocking model	0.996	0.977	0.998	0.941	0.936
Complete pore blocking model	0.996	0.979	0.999	0.973	0.977

Table 4. Average error of models for prediction of permeation flux and constant of models (K) at total time (0 – 60 min) for MF process without PAC and with different PAC concentrations

Models	K	Average error for prediction of permeation flux, %
	Without PAC	
Cake filtration model	$1.84 \cdot 10^{-6}$	2.19
Intermediate pore blocking model	$1.98 \cdot 10^{-4}$	3.56
Standard pore blocking model	$5.17 \cdot 10^{-4}$	14.16
Complete pore blocking model	$1.78 \cdot 10^{-4}$	7.43
	100 ppm	
Cake filtration model	$9.31 \cdot 10^{-7}$	2.16
Intermediate pore blocking model	$1.34 \cdot 10^{-4}$	2.72

Table 4. (Cont.)

Standard pore blocking model	$4.14 \cdot 10^{-4}$	10.08
Complete pore blocking model	$8.67 \cdot 10^{-5}$	6.97
	200 ppm	
Cake filtration model	$8.10 \cdot 10^{-7}$	2.06
Intermediate pore blocking model	$1.32 \cdot 10^{-4}$	2. 03
Standard pore blocking model	$3.65 \cdot 10^{-4}$	8.81
Complete pore blocking model	$8.98 \cdot 10^{-5}$	5.18
	400 ppm	
Cake filtration model	$7.19 \cdot 10^{-7}$	1.31
Intermediate pore blocking model	$1.23 \cdot 10^{-4}$	4.35
Standard pore blocking model	$3.47 \cdot 10^{-4}$	12.95
Complete pore blocking model	$8.13 \cdot 10^{-5}$	8.35
	800 ppm	
Cake filtration model	$2.57 \cdot 10^{-6}$	15.87
Intermediate pore blocking model	$2.40 \cdot 10^{-4}$	28.37
Standard pore blocking model	$8.49 \cdot 10^{-4}$	8.00
Complete pore blocking model	$1.06 \cdot 10^{-4}$	6.11
	1200 ppm	
Cake filtration model	$3.02 \cdot 10^{-6}$	15.78
Intermediate pore blocking model	$2.58 \cdot 10^{-4}$	6.00
Standard pore blocking model	$9.28 \cdot 10^{-4}$	12.35
Complete pore blocking model	$1.04 \cdot 10^{-4}$	11.32

4.2. Prediction of permeation flux decline by pore blocking models for MF-PAC process. Tables 3, 4 shows (R^2) of models, average of predicted permeation flux and constant of models (K) at different time intervals. The results show that the fitting of models with experimental data for MF-PAC hybrid process is as good as MF process. Largest deviations between experimental and predicted flux decline were observed for the standard pore blocking model up to 400 ppm PAC concentration and intermediate pore blocking model and cake filtration models for 800 and 1200 ppm PAC concentration respectively. As shown in Table 3 for MF-PAC process with 100 ppm PAC, cake filtration model with average error of 2.16% is best model for prediction of flux decline. By employing models for different time intervals, permeation flux can predicted with cake filtration model for all time intervals similar to MF process (see Table 3). Also for concentration of 200 and 400 ppm PAC, cake filtration model is the best model at total time interval with average error of 2.06 and 1.31% respectively. After this model, intermediate pore blocking model, can predict flux decline well. For high dosage of PAC (800 and 1200 ppm), complete pore blocking model and intermediate pore blocking model with average error of 6.11 and 6% is best model respectively. The reason for this phenomenon is that PAC particles adsorb some of the oil droplets and also detach the layer formed by the oil droplets at begins of filtration [6]. Of course at the beginning of filtration, membrane surface is clean and pores of membrane are empty, therefore small oil droplets enters into membranes pore and complete the pores [17]. With 800 and 1200 ppm PAC in experiments, wastewater and fouled membranes were become dark. This is due to filling of membranes pore with PAC particles. Also high dosage of PAC can well reduce fouling layer of oil and adsorb oil droplets but PAC particles cover membranes surface and fill membrane pores. Results of Table 3 indicate that for all time intervals with 200 ppm PAC, cake filtration models is best model for all time intervals because R^2 of it is larger than other models. But by increasing PAC concentration to 400 ppm, for first time intervals (0 – 2.5 min) and (0 – 5 min), cake filtration models has largest (R^2) (see Table 3) but for (5 – 20 min) complete pore blocking model is best model. Results in Table 3 indicate that in for different time intervals (0 – 2.5 min), (0 – 5 min), (5 – 20 min) intermediate pore blocking models can predict permeation flux decline with 800 ppm PAC. In addition, for (20 – 60 min), standard pore blocking models has largest (R^2). According to results of Table 3, for first time intervals (0 – 2.5 min) and (0 – 5 min), complete pore blocking model has largest (R^2) but for (5 – 20 min), standard pore blocking model is best model.

5. Conclusions

In this novel research, mechanisms of flux decline for treatment of oily wastewaters in MF-PAC hybrid process using homemade mullite-alumina ceramic membranes have been investigated. For this purpose Hermia's models for cross flow filtration were used in different time intervals with different PAC concentration. The coefficient of determination (R^2) of each case and average error of models for prediction of permeation flux, were compared between the fouling models. According to the obtained results, it can be concluded that the best fit to experimental data is for the cake layer formation model for MF and MF-PAC process with PAC concentration up to 400 ppm with maximum and minimum average error of 2.19 and 1.31%. But for MF-PAC hybrid process with 800 and 1200 ppm PAC concentration, complete pore blocking model intermediate pore blocking model with average error equal to 6.11 and 6% are best models for prediction of flux decline. Average error for prediction of permeation flux with cake filtration model is 2.19% for MF process and 2.16; 2.06 and 1.31% for MF-PAC process with 100; 200 and 400 ppm PAC concentration respectively. Results of modeling show that pore blocking behavior of membrane during filtration is changed. Finally it can be concluded that modeling results for total time is practical and result of short time intervals is useful for knowledge of fouling mechanisms.

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