Foulant interaction and RO productivity in textile wastewater reclamation plant ☆

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ABSTRACT

Foulant interaction and productivity of reverse osmosis (RO) membrane during textile wastewater reclamation were studied. Synthetic textile wastewater composed of salt, surfactant and reactive dye was used in the experiment. RO productivity was assessed using cross-flow membrane filtration unit. The result revealed that surfactant was the major cause of membrane fouling. When the surfactant concentration maintains lower than the critical micelle concentration (CMC), RO productivity was influenced by the concentration of surfactant. Therefore, lowest productivity was observed when the surfactant concentration approached CMC. When the concentration level rose above CMC, the surfactant micelle was formed within the bulk solution and this subsequently yielded an increase in RO productivity. The formed micelle decreased the adsorption capacity of surfactant monomer. Moreover, the appearance of aggregation between surfactant and reactive dye lowered the fouling potential of the mixtures especially when compared to the wastewater containing only surfactant at a higher concentration than CMC.

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1. Introduction

Fouling has adversely affected RO plant performance both in terms of production rate and quality of treated water. It increases the operating cost due to an increase in overall resistance reflected by increased trans-membrane pressure (TMP), routine-cleaning cycles, corrosive by-product from microorganism, and increased salt passage [1–3]. In a textile reclamation plant, surfactants and dyes are the primary constituents [4] and they become the general cause of RO fouling.

Surfactants fouling behavior rely on their properties that are altered at the critical micelle concentration (CMC). At lower concentration than CMC, surfactant monomers always adsorb on the hydrophobic membrane by their hydrophobic tail and present the hydrophilic head against the water stream [5–7]. The adsorbed surfactant monomers on membrane decrease the productivity even if they increase the hydrophilic condition because they reduced the surface roughness and surface area of membranes significantly [8]. Moreover, the hydrophobic/hydrophilic condition between membranes and foulants is distorted when the membrane surfaces are occupied by the foulants

[5,8]. In contrary, higher concentrations of surfactant more than CMC cause fouling by a concentration polarization and lead to colloidal formation in water [6].

Dyes fouling are affected by their charge properties, salt concentration, and cross-flow velocity (CFV) above the membrane surface [9,10]. At low salt concentration, dye removal efficiency and the productivity hinge upon CFV. In contrary, at high salt concentration, a dye forms colloids and the influence of CFV decreases [11]. Moreover, the negatively charged membrane gives higher salt and dye removal efficiency than the neutrally charged membrane but it gives more rapid fouling due to the concentration polarization [9].

An interaction between surfactants and dyes in the mixtures always takes place and affects not only the physical properties of wastewater but also the fouling mechanism. This interaction is influenced by the adhesion from hydrophobic interaction and ionic bond. Ionic dye and non-ionic surfactant aggregate themselves by the hydrophobic interaction between hydrophobic chains of surfactants within micelles with the hydrophobic part of dye [12,13]. Moreover, the stability of aggregation between dye and surfactant increases when their hydrophobic property increases [14]. Cationic dye prefers to aggregate with anionic surfactant more than non-ionic surfactant. The ionic bond plays an important role in their aggregate [15]. Moreover, non-ionic surfactant aggregates anionic dye with hydrophobic interaction better than anionic surfactant in the mixture containing anionic dye, non-ionic surfactant and anionic surfactant [16].

This research determines the effect of the foulant interaction containing in textile wastewater on RO productivity or flux decline.

The synthetic wastewater composing of salt, surfactant, and reactive dye was used in this study and the relationship between foulants interactions, depositions of foulants and RO productivity were quantified and modeled.

2. Flux decline due to deposition of foulants

Generally, when the foulants adsorb on the membrane surface they reduce available surface of membrane resulting in flux decline. Braeken et al. (2006) proposed that the occupied site (θ_T) is the function of logarithmically filtrated time ($t + t_o$) and a ratio of filtrated permeability to initial permeability (L/L_o) relates to an area of non-occupied site ($1 - \theta_T$). The relationship between total occupied sites and filtration time is shown in Eqs. (1) and (2) [17].

$$\theta_T = b \ln(t + t_o) - b \ln t_o \qquad 1$$

$$L = L_o(1 - b \ln(t + t_o) + b \ln t_o) \qquad 2$$

where t_o is the initial time on which available site is reduced due to deposition (min) and b is the reduction of available site due to fouling (min^{-1}). The relationship between total occupied sites and filtration time is expressed in Spiegler–Kedem equations ($J = L(\Delta P - \sigma \Delta \pi)$), RO flux can be estimated as shown in Eq. (3) [17].

$$J = L_o(1 - b \ln(t + t_o) + b \ln(t_o))(\Delta P - \sigma \Delta \pi) \qquad 3$$

where σ is the reflection coefficient and ($\Delta P - \sigma \Delta \pi$) is the represented actual TMP. To determine the model parameters, Eq. (3) was rewritten in term of normalized flux decline ($1 - \frac{J}{L_o xTMP}$) as shown in Eq. (4).

$$1 - \frac{J}{L_o xTMP} = b \ln(t + t_o) - b \ln(t_o) \qquad 4$$

The parameter b is the specific characteristic between each foulant and membrane surface relating to the concentration of foulant in the mixture. Larger b value means high fouling potential or low productivity in long-term operation. Moreover, b is proposed as a function of concentration (C_i) and fouling coefficient (α_i) as shown in Eq. (5). Therefore, the relationship between occupied site by foulant (θ_i) and filtration time can be rewritten in Eq. (6).

$$b = C_i \alpha_i \qquad 5$$

$$\theta_i = C_i \alpha_i \ln(t + t_o) - C_i \alpha_i \ln t_o \qquad 6$$

Actual TMP can be calculated from the difference between applied pressure and osmotic pressure at the membrane surface. In order to estimate the osmotic pressure at membrane surface, the resistance in series model and the osmotic pressure model are modified and assembled together as shown in Eqs. (7)–(9). To eliminate experimental errors, an average value of the osmotic pressure calculated from permeate flux at 1 h ($\Delta \pi_1$) and 24 h ($\Delta \pi_{24}$) is used.

$$\Delta \pi_{av} = \frac{\Delta \pi_1 + \Delta \pi_{24}}{2} \qquad 7$$

$$\Delta \pi_1 = \Delta P - (J_1 \eta R_{M,0}) \qquad 8$$

$$\Delta \pi_{24} = \Delta P - (J_{24} \eta R_{M,24}) \qquad 9$$

3. Foulant interaction

The concentrations of aggregates and monomers in the mixtures after the foulant interaction are derived from aggregate equilibrium. In this study, the maximum concentration of surfactant monomer in the solution is constant at CMC when the solution contains pure surfactant. In addition, the micelles appear when the surfactant concentration is higher than CMC.

The interaction between surfactant ([surfactant], mM as C) and reactive dye ([dye], mM as C) is the aggregation without production of new product. They aggregate themselves with the ratio of x and y respectively. The mass balance of the aggregation is shown in Eq. (10).

$$x[dye] + y[surfactant] = [dye_x surfactant_y] \qquad 10$$

According to the mass balance, the aggregation is represented by [A_{dye-SA}]. The concentration of surfactant and reactive dye at equilibrium are [C_{SA}] and [C_{dye}], respectively. The aggregate equilibrium constant (K_{eq}) becomes;

$$K_{eq} = \frac{[A_{dye-SA}]}{[C_{dye}]^x [C_{SA}]^y} \qquad 11$$

At equilibrium of the mixtures containing SA of concentration lower than CMC, C_{dye} and C_{SA} in the mixture are separated into two forms, the aggregated forms (A_{dye} and A_{SA}) and monomer forms (S_{dye} and S_{SA}). Total concentration of aggregation (A_{total}) equals the aggregation between reactive dye and surfactant (A_{dye-SA}). In case of SA concentration higher than CMC, A_{total} can be determined by summation of A_{dye-SA} and the aggregation due to SA itself (surfactant micelle, M_{SA}).

4. Material and methods

4.1. Synthetic wastewater and RO properties

Synthetic wastewater composing of NaCl (2000 mg/L), reactive dye (Marine E-EL, Nippon Kayaku Corp.), and surfactant (soaping agent, SA, Sunmoor RC 700E, Nikka-Kagaku Corp.) was prepared. CMC of SA was measured by the ring method using a surface tension meter (Fisher Surface Tensionmat model 21) as 1.62 mM as C at 30 °C. The concentrations of SA and reactive dye were measured in unit of mM as C using total organic carbon analyzer (Shimadzu model TOC-5000 A). The constituents of wastewater are shown in Table 1.

4.2. The experimental set up

RO flux was monitored using the cross-flow membrane filtration unit (C10-T, Nitto Denko) and RO membrane model ES20 (Nitto Denko). The feed flow rate and the applied pressure were controlled at 0.2 L/min and 0.5 MPa, respectively. The water temperature was controlled at 30 °C using a temperature controller. The permeate flux was monitored for 24 h. Triplicate experiments were repeated to confirm the experimental results. The schematic diagram is shown in Fig. 1.

Table 1
Synthetic wastewater.

Run	Wastewater
1	SA 0.78 mM as C
2	SA 1.43 mM as C
3	SA 4.08 mM as C
4	SA 6.72 mM as C
5	Dye 7.23 mM
6	SA 1.43 mM as C + dye 1.53 mM as C
7	SA 1.43 mM as C + dye 7.23 mM as C
8	SA 6.72 mM as C + dye 1.53 mM as C
9	SA 6.72 mM as C + dye 7.23 mM as C

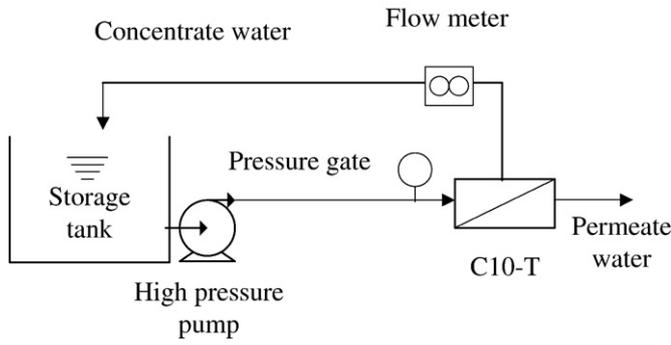Note: NaCl 2000 mg/L was added in all runs.

Fig. 1. The schematic diagram of cross-flow membrane filtration unit (C10-T).

4.3. Determination of K_{eq} and concentrations of aggregates and monomers

In order to estimate K_{eq}, an experiment for determination of the concentrations of aggregates and monomers in the mixtures were performed. The aggregate equilibrium constant (K_{eq}) was determined by filtration of synthetic wastewater containing surfactant, reactive dye, and their mixtures through ultrafiltration (UF) membrane (PLBC07610, MWCO of 3000, Millipore Corp). A dead-end membrane filtration unit (C40-B, Nitto Denko Corp.), a stirring batch-type cell, was used. Nitrogen gas with purification of 99.995% was applied to control pressure in the pressure vessel. The stirrer bar was used to simulate CFV above the membrane surface and to prevent the formation of concentration polarization. The stirrer bar was rotated at a speed of 200 rpm using magnetic stirrer. The aggregates were retained in C40-B cell above UF where the monomers passed through the membrane within permeate. The concentrations of surfactant and reactive dye within permeate and within wastewater were analyzed using high performance liquid chromatography (HPLC), Agilent Technologies model HP 1100, Column: ZORBAX Eclipse XDB-C18 (5 μm, 4.6 mm × 150 mm, Altech Associates, Ins.).

5. Result and discussions

5.1. Flux decline during RO filtration

Flux declines during RO filtration are shown in Fig. 2. It was found that dye produced higher flux comparing with SA (Fig. 2a). In case of SA concentration lower than CMC (1.62 mM as C), low concentration of 0.78 mM as C gave higher flux than high concentration of 1.43 mM as C. In contrary, when concentration increased higher than CMC, flux increased in the presence of elevated concentrations. In addition, the addition of higher dye increased RO flux in the mixtures comparing with the solution containing only SA especially when SA increased higher than CMC.

5.2. Determine of aggregates and monomers concentration

Qualification of the aggregation between reactive dye and surfactant was conducted by filtration with UF using C40-B cell. SA ranged from 0.77 to 4.07 mM as C was added with reactive dye of 0, 1.57, and 4.53 mM as C. The aggregated concentration between SA and dye (A_{dye-SA}) are shown in Fig. 3.

In case of SA concentration lower than CMC (<1.62 mM as C), the aggregate equilibrium constant (K_{eq}) was 0.304 as shown in Eq. (12). In addition, when concentration higher than CMC (>1.62 mM as C), K_{eq} was 0.5 as shown in Eq. (13).

$$[A_{dye-SA}] = 0.304[C_{Dye}]^{0.33}[C_{SA}]^{0.67} \qquad 12$$

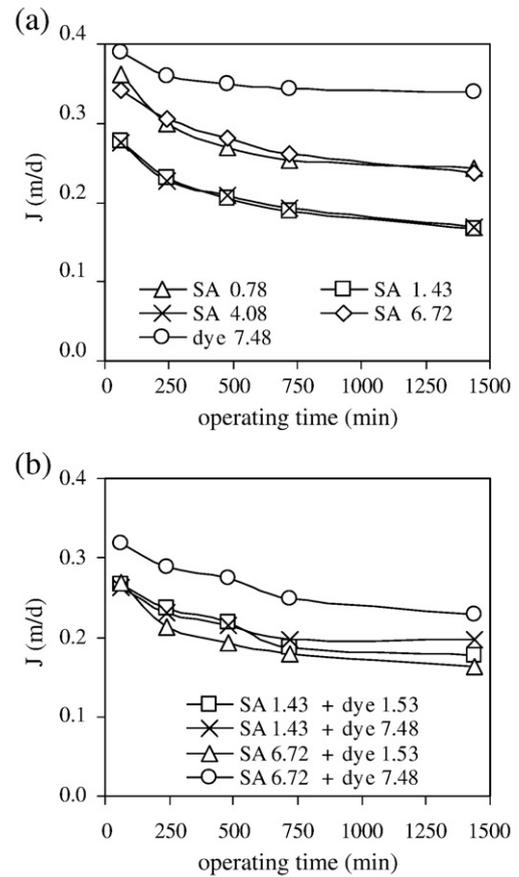$$[A_{dye-SA}] = 0.50[C_{Dye}]^{0.465}[C_{SA}]^{0.535} \qquad 13$$

Fig. 2. Flux decline during filtration.

The concentrations of aggregates and monomers calculating from Eqs. (12), (13) are shown in Table 2 and Fig. 3.

5.3. Reduction of available site due to deposition of organic foulant

The experimental data of flux were plot against the logarithmic values of operating time. The parameters b and t_o calculated from Fig. 4 are shown in Table 3.

It was found that the reduction of available site (b) of SA ranged between 0.084 and 0.095 min^{-1}. In case of SA concentration being lower than CMC (1.62 mM as C), b increased when the concentration increased. In addition, the flux decline tended to decrease when its concentration increased above CMC. Moreover, the addition of reactive
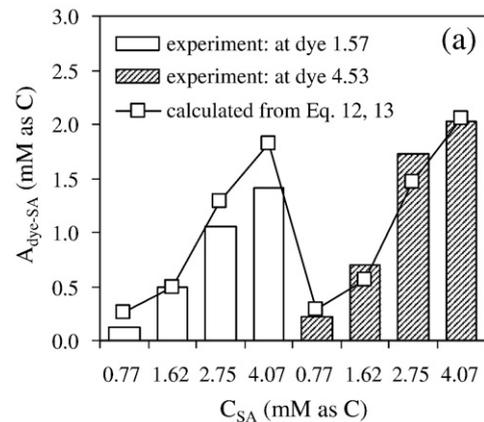

Fig. 3. Aggregated concentration.

Table 2
Concentration of aggregates and monomers within wastewater.

Wastewater composition	Concentration (mM as C)				
	S_{SA}	S_{Dye}	A_{Dye-SA}	M_{SA}	A_{Total}
SA 0.78	0.78	–	–	–	–
SA 1.43	1.43	–	–	–	–
SA 4.08	1.62	–	–	2.65	2.65
SA 6.72	1.62	–	–	5.10	5.10
Dye 7.48	–	7.48	–	–	–
SA 1.43 + Dye 1.53	1.29	1.24	0.44	–	0.44
SA 1.43 + Dye 7.48	1.19	1.04	0.73	–	0.73
SA 6.72 + Dye 1.53	1.62	0.02	2.81	3.79	6.61
SA 6.72 + Dye 7.48	1.62	5.66	3.40	3.52	6.92

Table 3
Model parameters of b and t_o.

Composition (mM as C)	Model parameters	
	b (min^{-1})	t_o (min)
SA 0.78	0.087	6.07
SA 1.43	0.095	4.62
SA 4.08	0.088	2.89
SA 6.72	0.084	13.15
Dye 7.48	0.042	25.71
SA 1.43 + Dye 1.53	0.085	7.60
SA 1.43 + Dye 7.48	0.069	6.93
SA 6.72 + Dye 1.53	0.089	3.63
SA 6.72 + Dye 7.48	0.066	3.38

dye into the mixtures, b decreased in range between 0.066 and 0.089 min^{-1}. Subsequent to comparison between the concentrations of aggregates, from the concentrations of monomers (Table 2), and the change in b (Table 3) it can be suggested that the presence of M_{SA} and A_{dye-SA} between reactive dye and SA showed a positive effect in reduction of flux decline.

5.4. Relationship between foulant deposition and RO flux

According to the experimental data of flux decline, concentrations of aggregates and monomers, and reduction of available site, it can be suggested that the monomers play an important role in flux decline. In contrary, the aggregates increase RO productivity even if they deposit on the membrane surface as well as the monomers because they increase the hydrophilic condition of membrane. Moreover, the deposition of aggregates competes against the monomers and confiscates the membrane surface therefore, it decreases fouling potential of monomers. The occupied site due to fouling can be determined as

shown in Eq. (14). The fouling coefficient (α) of reactive dye, SA and aggregate were determined using the concentrations of aggregates and monomers from Table 2 and parameters of b and t_o from Table 3. The occupied sites due to fouling of reactive dye, SA, and aggregate are shown in Eqs. (15)–(17).

$$\theta_T = \theta_{dye} + \theta_{SA} - \theta_{Aggregate} \tag{14}$$

$$\theta_{dye} = \frac{0.001 S_{Dye} \ln(t + 25.7) -}{0.001 S_{Dye} \ln 25.7} \tag{15}$$

$$\theta_{SA} = \frac{0.089 S_{SA} \ln(t + 6.7) -}{0.089 S_{SA} \ln 6.7} \tag{16}$$

$$\theta_{Agrregate} = \frac{0.01 A_{total} \ln(t + 6.7) -}{0.01 A_{total} \ln 6.7} \tag{17}$$

The RO productivities calculating from model were compare with the experimental data as shown in Fig. 5.

6. Conclusions

This research is carried out to determine the relationship between foulant interactions during textile wastewater reclamation using RO membrane. The following conclusions can be drawn from our study.

1. The surfactant yielded higher flux decline than reactive dye and was the major cause of RO fouling during textile wastewater reclamation especially when its concentration approached CMC. In contrary, when its concentration rose above CMC, RO flux increased due to the formation of micelles.
2. Depositions of monomers and aggregates decreased available site of membrane however only monomers caused flux decline. Appearances
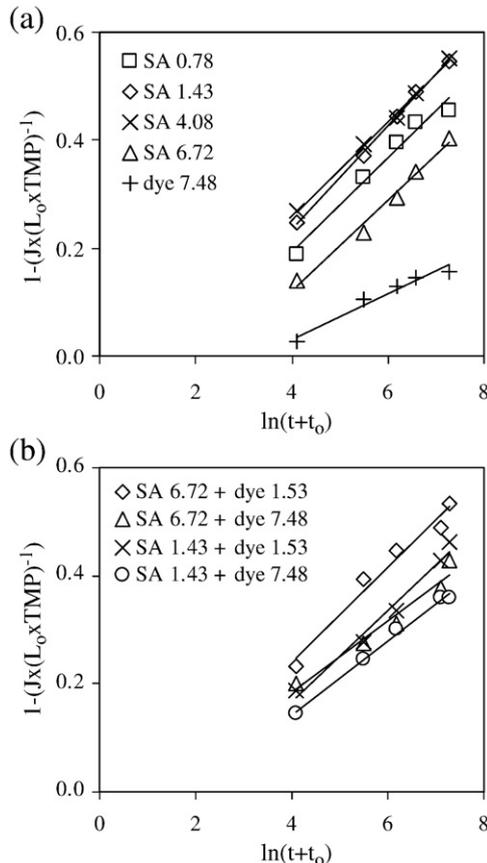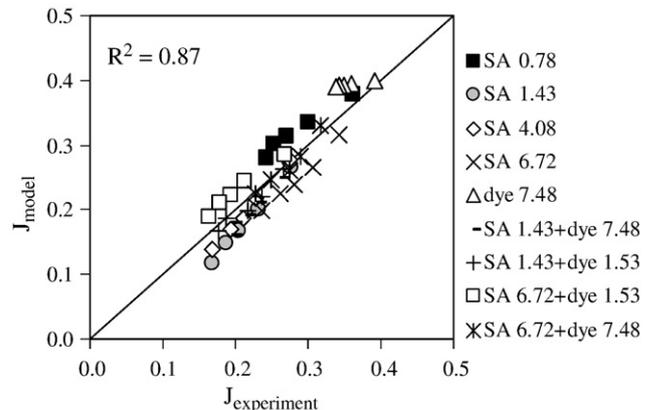

Fig. 4. Normalized flux decline VS time.

Fig. 5. Correlation between permeate flux from experiment and predicted model.

of aggregates reduced the deposition of monomers resulting in enhancement of RO flux.

3 Mathematical model derived from the deposition of aggregates and monomers successfully predicted RO flux during the filtration of textile wastewater with different foulant compositions.

Acknowledgements

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