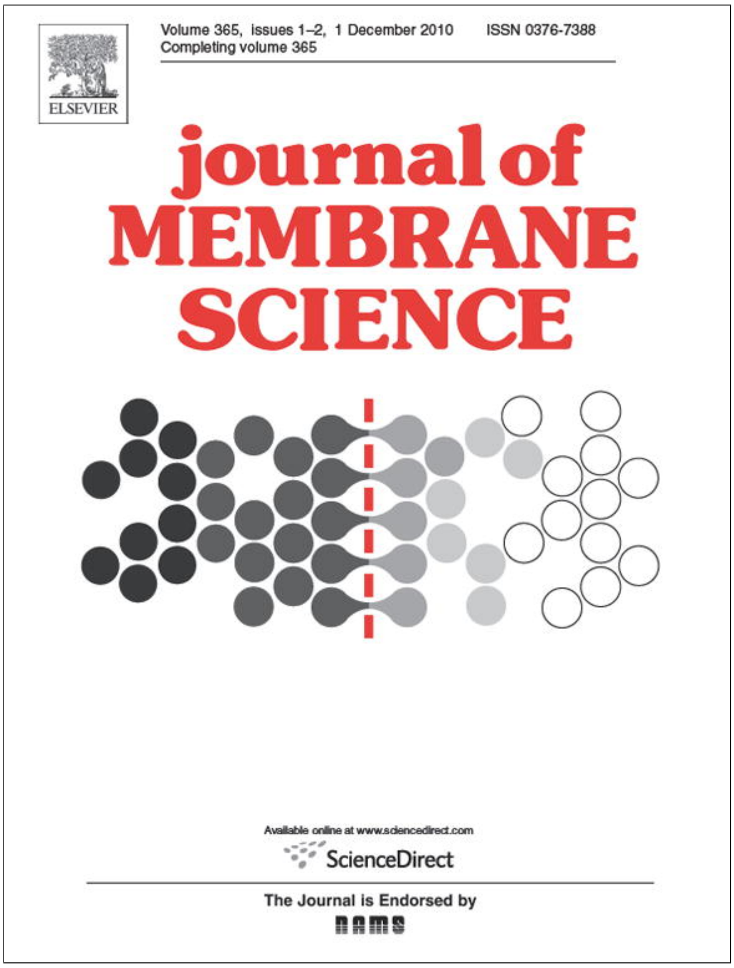

Volume 365, Issues 1–2, 1 December 2010 ISSN 0376-7388
Completing volume 365

ELSEVIER

journal of
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NAMS

Journal of Membrane Science 365 (2010) 138–144

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Micellar-enhanced ultrafiltration of methylene blue from dye wastewater via a polysulfone hollow fiber membrane

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ARTICLE INFO

Article history:
Received 26 May 2010
Received in revised form 17 August 2010
Accepted 28 August 2010
Available online 24 September 2010

Keywords:
Micellar-enhanced ultrafiltration
Methylene blue
SDS
Hollow fiber membrane
Permeate flux
Rejection

ABSTRACT

Micellar-enhanced ultrafiltration (MEUF) of methylene blue (MB) from dye wastewater was explored for obtaining colorless water, using a 10-kDa molecular weight cut-off (MWCO) polysulfone hollow fiber membrane and sodium dodecylsulfate (SDS) as an anionic surfactant. The effects of factors, such as operating pressure, feed SDS, MB and sodium chloride (NaCl) concentrations, on the permeate flux (J) and additional resistance (R_f) as well as the observed MB and SDS rejection were investigated. Moreover, the zeta potential of SDS micelle with feed SDS, MB and NaCl concentrations in the solution was also quantified. The rejection of MB and SDS decreased slightly with operating pressure increasing. It was observed that the permeate flux decreased while the additional resistance increased with increased SDS and MB concentrations in the feed. The addition of NaCl significantly increased surfactant retention and reduced the back contamination. The rejection of MB and SDS were 99.3 and 96.0%, respectively, with MB (6 mg/L), SDS (8 mM) and NaCl (200 or 300 mM) in the solution.

1. Introduction

Diverse synthetic dyes, widely used in the textile, printing, paper, and leather industries [1], are toxic as well as carcinogenic, mutagenic and teratogenic [2]. Large amounts of highly colored effluents are aesthetically displeasing and affect the nature of the water, impeding light penetration and reducing photosynthetic activity within the stream [3]. It is clear that dye wastewater must be treated sufficiently before it is discharged into a clean stream.

The conventional techniques for treating dye wastewater, are coagulation–flocculation [4,5], adsorption [6,7], oxidation or ozonation [8,9], biodegradation [10,11] and membrane separation [12,13], but each technique has disadvantages. The operating cost of coagulation–flocculation is high and the rejection of hydrophilic dye is very low. Adsorption often uses activated carbon as an adsorbent for removing dye from wastewater, but it is expensive and rejection depends on the type of dye used. In oxidation or ozonation process, even high doses of oxidant or ozone can barely remove all dye from wastewater [14]. The conventional biological technique is not very efficient due to the low biodegradability of dyes [15]. Two membrane separations, reverse osmosis (RO) and nanofiltration (NF) are now recognized as the best available techniques for the removal of several toxic dyes. However, with relatively “dense” membranes used in the RO and NF processes, the permeability is low and thus to obtain the desired throughput (permeate flux), a high operating pressure is required [16].

Micellar-enhanced ultrafiltration (MEUF), a surfactant-based separation process, has been shown to be effective and economical in removing dissolved organic solutes [17,18]. This technique combines the high selectivity of reverse osmosis and the high flux of ultrafiltration [19]. When surfactants are added into the aqueous stream at levels equal to or higher than their critical micelle concentrations (CMCs), surfactant monomers will assemble to form micelles [20,21]. The micelles are capable of solubilizing organic solutes. The micelle solution is then filtered through an ultrafiltration membrane with an appropriate molecular weight cut-off (MWCO) size. The micelles containing the solubilized pollutants can thus be removed by the ultrafiltration membrane [22].

The cationic dye methylene blue (MB) is extensively applied for coloring paper, as a temporary hair colorant, for dyeing cottons and wools, and as a coating for paper stock. MB is not strongly toxic, but it can cause some harmful effects. Acute exposure to MB will cause an increased heart rate, vomiting, shock, Heinz body formation, cyanosis, jaundice, quadriplegia, and tissue necrosis in humans [23,24]. Two reports have described the removal of methylene blue by MEUF [25,26]. In this work, we consider that the introduction of

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doi:10.1016/j.memsci.2010.08.052

Table 1
The characteristics of polysulfone hollow fiber membrane.

Type	Membrane material	MWCO (Da)	Contour size $\phi \times L$ (m)	Effective membrane area (m^2)	Operating pressure (MPa)	Operating temperature (°C)	pH
ZU503-22	Polysulfone	10k	0.05×0.3	0.8	<0.1	5–45	2–13

surfactant may cause back contamination, and resistance against the flux can also characterize ultrafiltration, so surfactant rejection and resistance had been further studied. The former literature [25] introduced the nonionic surfactant to SDS in order to reduce the permeate concentration of surfactant, in our study, it was found that the introduction of electrolyte (NaCl) also had the result that the rejection of SDS was promoted greatly, which was more economical and could reduce the back contamination of surfactant. Moreover, the effect of the parameters (SDS, MB dye and electrolyte concentration) on the zeta potential (surface electrostatic potential) of SDS micelle was quantified. The zeta potential of surfactant micelle is a very important index to measure the self-assemble performance of micelle, which can characterize the stability of SDS micelle in different aqueous environment. The more deviation from 0 mV of the zeta potential, the bigger the repulsive potential of the diffusion layer overlapping, and thereby the more stable the micelle.

In the present work, the MEUF of methylene blue using a polysulfone hollow fiber membrane and SDS as an anionic surfactant was studied. Hollow fiber membranes are widely used in various industries, including wastewater treatment. This type of membrane has a number of advantages, including stable performance, a high density within modules and low investment. The effects of important parameters, including operating pressure, feed SDS and MB concentration, NaCl concentration on the permeate flux (J) and additional resistance (R_f) as well as rejection of methylene blue and SDS were investigated.

2. Materials and methods

2.1. Materials

The cationic dye, methylene blue (MW 373.90) was purchased from SSS Reagent Co., Ltd., Shanghai, China. The anionic surfactant, sodium dodecylsulfate (MW 288.38) was procured from Kermel Chemical Reagent Co., Ltd., Tianjin, China. The critical micelle concentration of SDS is 8 mM in distilled water [27]. Sodium sulfate (guaranteed reagent) was offered from Sinopharm Chemical Reagent Co., Ltd., China. All chemicals were used without further purification. All feed solutions were prepared using distilled water.

2.2. Membrane

A hollow fiber membrane with a molecular weight cut-off (MWCO) of 10k, obtained from Yidong Membrane Engineering Equipment, Ltd., Dalian, China, was used for all the MEUF experiments, without further treatment. The membrane is made from polysulfone, which is hydrophobic. The permeate flux of the membrane was measured under standard test conditions and found to be 20 L/h. The properties of this membrane are given in Table 1.

2.3. Experimental setup

The ultrafiltration setup (ZM50-1) was purchased from Yidong Membrane Engineering Equipment, Ltd., Dalian, China. The ultrafiltration setup consisted of a cross-flow membrane container into which a polysulfone membrane was placed, a powerful feed pump used to feed the aqueous solution into the membrane container, a manometer and two rotameters for showing the permeate flux rate and retentate flow rate. Valves were installed in the rotameters to adjust the operating pressure by changing the permeate flux rate and retentate flow rate. In all experiments, the polysulfone hollow fiber membrane of molecular weight cut-off of 10 kDa and an effective area of 0.8 m^2 was used. The retentate was recirculated to the aqueous feed vessel. The schematic of the experimental setup is shown in Fig. 1.

2.4. Procedure

In all experiments, pre-determined amounts of MB and SDS were added into distilled water. After they were mixed adequately, the feed solution was ultrafiltered. In each experiment, the initial feed volume was 2 L and after 1.5 L of permeate was collected, the permeate and the retentate were sampled to determine the MB and SDS concentrations, simultaneously, the permeate flux indicated by the rotameter was recorded, and then the process was stopped.

After each ultrafiltration of the surfactant solution, the membrane was thoroughly washed to recover its permeability. First, tap water was used to rinse the residual SDS and MB from the membrane. Secondly, distilled water at 25 °C was recycled. Finally, ultrapure water was passed through the membrane and the membrane permeability was then measured.

The permeate flux was calculated as follows:

$$J = \frac{\Delta V}{\Delta t A} = \frac{J_1}{A} \tag{1}$$

where J denotes the permeate flux (m^3/m^2 s), ΔV is the change in volume of the permeate sample (m^3), Δt is the time difference (s), J_1 is the permeate flux shown by the rotameter (m^3/s) and A denotes the effective membrane surface area (m^2).

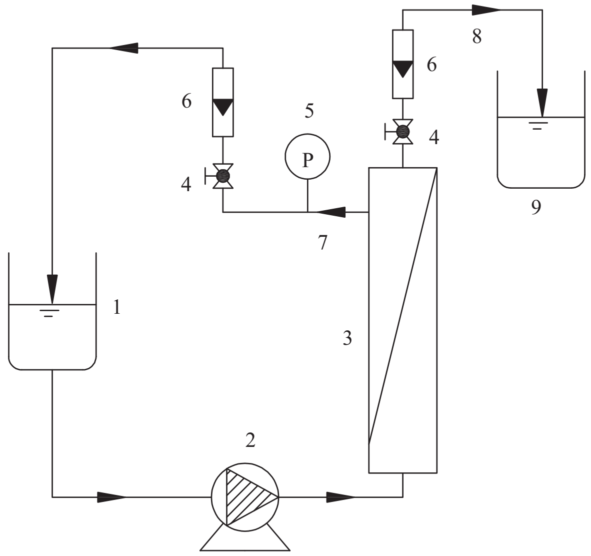

Fig. 1. Schematic of the experimental setup: (1) feed tank, (2) feed pump, (3) membrane cell, (4) control valve, (5) manometer, (6) rotameter, (7) retentate, (8) permeate, and (9) permeate tank.

When distilled water is filtered, the distilled water flux (J_w) follows the equation:

$$J_w = \frac{P}{\mu_w R_m}, \quad R_m = \frac{P}{J_w \mu_w} \tag{2}$$

where J_w is the distilled water flux ($\text{m}^3/\text{m}^2\,\text{s}$), P is the transmembrane operating pressure (Pa), μ_w is the viscosity of distilled water (10^{-3} Pa s at 25 °C), R_m is the hydraulic resistance of membrane itself (m^{-1}). R_m of the polysulfone hollow fiber membrane at various pressures can be calculated by Eq. (2).

In the resistance-in-series model, the permeate flux in an ultrafiltration process also follows the equation:

$$J = \frac{P - \Pi}{\mu_p R_t} = \frac{P - \Pi}{\mu_p (R_m + R_f)} \tag{3}$$

where J is the permeate flux ($\text{m}^3/\text{m}^2\,\text{s}$), $\prod$ is the osmotic pressure across the membrane (Pa), μ_p is the viscosity of permeate (Pa s), R_t is the total resistance (m^{-1}), and R_f is the additional resistance due to solute adsorption and concentration polarization (m^{-1}).

In the present work, the osmotic pressure was insignificant compared with the operating pressure, with reference to the flux calculation, and the viscosity of the permeate solution is similar to that of distilled water. Hence, the additional resistance (R_f) can be calculated in the following equation:

$$R_f = \frac{P}{J \mu_w} - R_m \tag{4}$$

2.5. Analysis

The concentrations of MB and SDS were determined by UV spectroscopy at wavelength of 663 and 652 nm, respectively, using a Shimadzu UV-2550 (P/N206-55501-93) spectrophotometer. Blank samples contained 1 CMC surfactant concentration for the MB concentration analyzed in the aqueous feed solution in order to reduce the influence of SDS on the MB absorbance. Because the effect of surfactant on the absorbance of MB in the permeate solution was found to be almost negligible, distilled water blank samples were used for the permeate MB concentrations. The determination of the anionic surfactant SDS in distilled water employs the methylene blue spectrophotometric method, based on the precipitation reaction of methylene blue and SDS and then with chloroform as an extractant. The zeta potential of SDS micelle was determined by dynamic light scattering (DLS) which was measured by a Zetasizer Nano ZS instrument (Malvern).

The separation efficiency of the membrane is defined by the following equation:

$$R = \left[1 - \frac{C_p}{C_f}\right] \times 100\% \tag{5}$$

where C_f and C_p denote the concentrations of MB or SDS in the feed and the permeate solution, respectively.

3. Results and discussion

3.1. Effect of operating pressure

3.1.1. Effect of operating pressure on the permeate flux and additional resistance

The study of effect of operating pressure was conducted at constant MB and SDS concentrations of 6 mg/L and 8 mM, respectively, at room temperature. It is evident from Fig. 2 that the permeate flux (J) increased almost linearly with operating pressure, ranging from $3.61 \times 10^{-6}\,\text{m}^3\,\text{m}^{-2}\,\text{s}^{-1}$ at 0.01 MPa to $11.81 \times 10^{-6}\,\text{m}^3\,\text{m}^{-2}\,\text{s}^{-1}$ at 0.09 MPa. From Eq. (3), it is not surprising that the permeate flux increased as operating pressure increased, because the operating pressure between retentate and permeate was the effective driving force for process, the increase of which could overcome the osmotic pressure and the resistance, thereby forcing more solution to filter through the membrane and leading to a higher permeate flux [28]. According to Eq. (4), the additional resistance (R_f) increased from $1.08 \times 10^{12}\,\text{m}^{-1}$ at 0.01 MPa to $4.46 \times 10^{12}\,\text{m}^{-1}$ at 0.04 MPa, then increased slowly to $4.74 \times 10^{12}\,\text{m}^{-1}$ at 0.09 MPa, as illustrated in Fig. 2, which was due to the transport of more solutes to the membrane surface with increased operating pressure, thereby increasing the effect of membrane adsorption and concentration polarization. The slow increase in additional resistance from 0.04 to 0.09 MPa indicated that the effect of membrane adsorption and concentration polarization was not significantly changed at higher pressure.

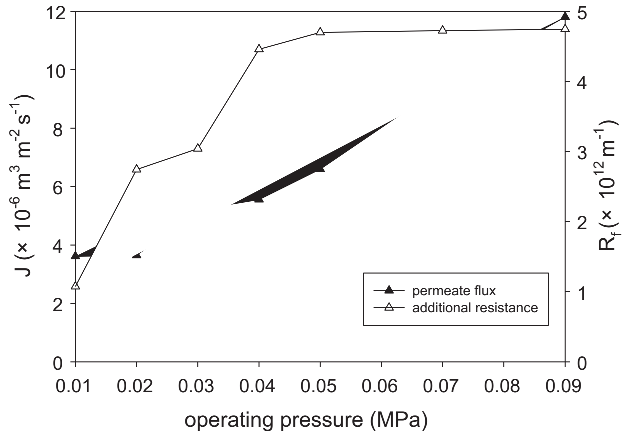

Fig. 2. Effect of the operating pressure on the permeate flux and additional resistance. Feed MB and SDS concentration, 6 mg/L and 8 mM, 25 °C.

3.1.2. Effect of operating pressure on the observed MB and SDS rejection

The effect of operating pressure on the rejection of MB and SDS was investigated, as presented in Fig. 3. From the figure it can be seen that the MB and SDS rejection decreased slightly with an increase of operating pressure, ranging from 99.62 and 62.5% at 0.01 MPa to 98.96 and 57.84% at 0.09 MPa, which was due to the following two reasons: at higher operating pressure, micelles might be compacted, thereby decreasing the micelle solubilization capability, and hence a lower quantity of MB dye would be solubilized within the micelles [14]; the increase of effective driving force caused the increment of the convective transport of solutes

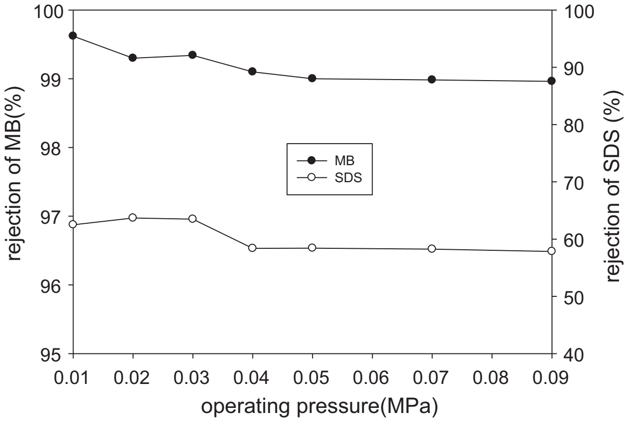

Fig. 3. Effect of the operating pressure on the MB and SDS rejection. Feed MB and SDS concentration, 6 mg/L and 8 mM, 25 °C.

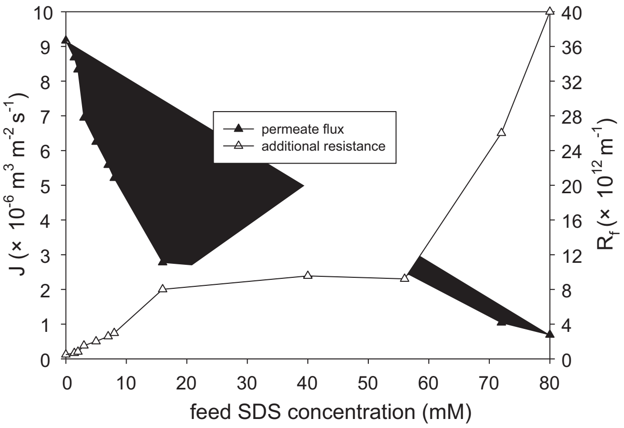

Fig. 4. Effect of feed SDS concentration on the permeate flux and additional resistance. Feed MB concentration, 6 mg/L; operating pressure, 0.03 MPa, 25 °C.

filtered through the ultrafiltration membrane to the permeate solutions.

3.2. Effect of feed SDS concentration

3.2.1. Effect of feed SDS concentration on the permeate flux and additional resistance

The feed MB concentration was fixed at 6 mg/L, at 0.03 MPa, at room temperature, and the feed SDS concentration varied between 0 and 80 mM. As shown in Fig. 4, it is obvious that the permeate flux (J) decreased sharply with an increase in the feed SDS concentration, from 9.17×10^{-6} m^3 m^{-2} s^{-1} at a SDS concentration of 0 mM to 0.69×10^{-6} m^3 m^{-2} s^{-1} at a SDS concentration of 80 mM. According to Eqs. (1)–(4), hydraulic resistance of membrane (R_m) at 0.03 MPa and room temperature was about 2.79×10^{12} m^{-1}, the additional resistance (R_f) increased from 0.48×10^{12} m^{-1} to 40.00×10^{12} m^{-1} with feed SDS concentration. At SDS concentrations below the CMC, the results were attributed to the following three reasons: (1) the presence of reactive precipitates of MB and SDS, which assembled and aggregated to form a cake on the membrane surface and in the membrane pores; (2) fouling of the membrane by adsorption of MB; and (3) a deposited layer near the membrane surface for the concentration polarization effect. At higher SDS concentrations, above CMC, the deposited layer of micelle aggregates offered more resistance against solvent flux through the membrane. Furthermore, the permeate flux decreased slowly with increasing SDS concentration from 16 to 56 mM because the resistance increased slowly with slight increase of the thickness of the deposited micelle layer.

3.2.2. Effect of feed SDS concentration on the observed MB and SDS rejection

Variation of the rejection of MB and SDS with feed SDS concentration is shown in Fig. 5. It is clear that the SDS retention increased sharply from 44.21 to 63.48% with feed SDS concentration increasing from 5 to 8 mM, then increases slowly to 92.25% for a feed SDS concentration of 72 mM, which was attributed to an increase in the aggregation number of SDS micelles.

From the figure, when the feed SDS concentration was lower than its CMC of 8 mM, although the surfactant micelles formation was almost negligible, the MB removal efficiency was also very high, about 99%, which was similar to the literature data [26]. This high rejection was attributed to the following three causes. The reason was the concentration polarization effect, leading to a deposited layer on the membrane surface, in which the SDS concentration might have exceeded the CMC value and therefore had formed micelles which would possibly solubilize some MB molecules. Secondly, the aqueous solution turned from blue to purple, precipitates along with MB could be removed by the membrane due to the precipitation reaction of MB with a small amount of SDS surfactants [29,30]. The third cause was that MB molecules adsorbed on the membrane surface and in the membrane pores during the ultrafiltration. As a result, membrane fouling was extensive.

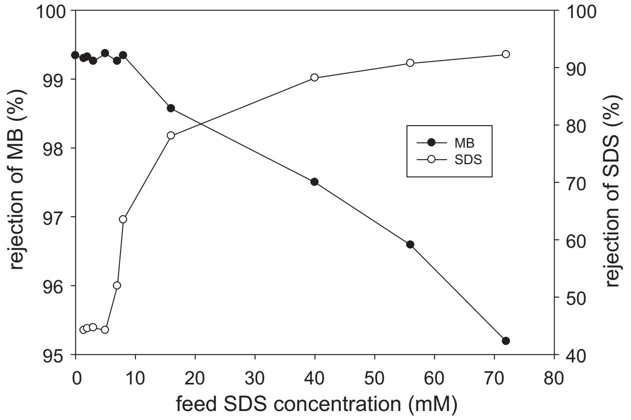

Fig. 5. Effect of feed SDS concentration on the MB and SDS rejection. Feed MB concentration, 6 mg/L; operating pressure, 0.03 MPa, 25 °C.

In fact, as the feed SDS concentration increases, the number of micelles will increase, so more MB molecules should soluble in micelles. However, it is observed from the figure that the MB filtration efficiency decreased from 99.34 to 95.19% when the feed SDS concentration ranged from 8 to 72 mM. The MB rejection decreased slightly, which was due to the filtration of SDS micelles through the membrane resulting from the distribution of pore sizes of ultrafiltration membrane. Furthermore, at SDS concentration of 80 mM, which is 10 times CMC of SDS, the SDS rejection was only 87.14% (lower than 92.25% at SDS concentration of 72 mM) and the MB concentration in the permeate solution was 20.0 mg/L (much higher than 6 mg/L in the feed). This was attributed to the change of micellar shape from spherical to cylindrical or plate like and thereby that could be easily crossed through the membrane pores causing considerable drop in the rejection of MB dye [31].

3.2.3. Effect of feed SDS concentration on the zeta potential

The shape of curves of zeta potential (ζ) vs. feed SDS concentration with or without MB (6 mg/L) in the solution is mostly similar (1.4–40 mM SDS), as displayed in Fig. 6. The magnitude of zeta potential with MB in the solution was lower than that without

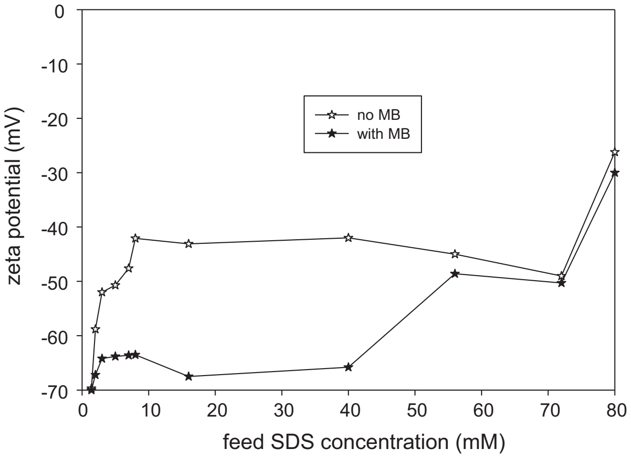

Fig. 6. Effect of feed SDS concentration on the zeta potential of SDS micelle, 25 °C.

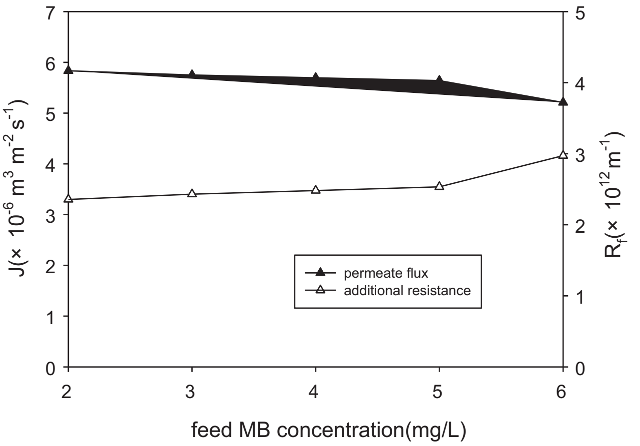

Fig. 7. Effect of the feed MB concentration on the permeate flux and additional resistance. Feed SDS concentration, 8 mM; operating pressure, 0.03 MPa, 25 °C.

MB, which suggested that the surface charge density of micelles was promoted with MB, due to the dissociation of MB into cationic ions that could insert into the head groups of surfactant leading to the stern layer on micelles compressed and the reduction of electrostatic repulsive force between head groups of surfactant, thereby the CMC decreases and the aggregation number of micelles increases slightly. Both the magnitude of zeta potential increased as the feed SDS concentration in the range of 1.4–8 mM, which implied the reduction of the aggregation number of micelles. This was good agreement with the literature [32], in which the hydrodynamic diameter of SDS micelles decreased with increasing SDS concentration. During the process of micellization of surfactants, the large and incompact micelles become the small and compact micelles. It is shown in the figure that the magnitude of zeta potential decreased slightly from −42.1 mV at 8 mM to −49.0 mV at 72 mM in the absence of MB in the solution, and then ascended to −26.2 mV at 80 mM, while it decreased slightly from −63.5 mV at 8 mM to −65.8 mV at 40 mM, then ascended to −30 mV at 80 mM in the presence of MB. The results indicated that the effect of MB on zeta potential was insignificant with SDS concentration from 56 to 80 mM, and the dramatic ascending of magnitude of zeta potential at 80 mM of SDS validated the change of the SDS micellar shape as described above, leading to the decrease of surface charge density of micelles.

3.3. Effect of feed MB concentration

3.3.1. Effect of feed MB concentration on the permeate flux and additional resistance

To observe the effect of MB feed concentration, the SDS concentration in the feed was fixed at 8 mM and an operating pressure of 0.03 MPa was applied to the cell, at room temperature. The experiments were carried out by varying the feed MB concentration from 0 to 6 mg/L. As observed from Fig. 7, the permeate flux decreased slightly as the feed MB concentration increased, from 6.94×10^{-6} m^3 m^{-2} s^{-1} for 0 mg/L to 5.21×10^{-6} m^3 m^{-2} s^{-1} for 6 mg/L. The reduction in permeate flux at the higher MB concentration was attributed to increase adsorption of MB and deposited layer near the membrane. Accordingly, the additional resistance (R_f) increased slightly from 1.53×10^{12} m^{-1} to 2.97×10^{12} m^{-1} as the feed MB concentration increased.

3.3.2. Effect of feed MB concentration on the observed MB and SDS rejection

Fig. 8 shows that the MB rejection was always above 99%, which indicated that the MB concentration in the feed hardly affected the percentage rejection of MB. The high rejection of MB was due to the solubilization of most MB molecules in SDS micelles. While the SDS rejection remained at about 60.0% with feed MB concentration from 2 to 6 mg/L, which were higher than 54.9% without MB in the solution. This was attributed to the slight decrease of CMC and increase of the aggregation number of micelles in the presence of MB dye that could make the formation of SDS micelle easier.

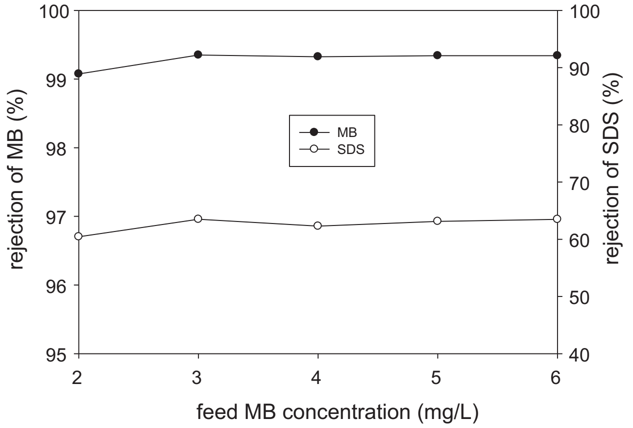

Fig. 8. Effect of the feed MB concentration on the MB and SDS rejection. Feed SDS concentration, 8 mM; operating pressure, 0.03 MPa, 25 °C.

3.3.3. Effect of feed MB concentration on the zeta potential

The effect of feed MB concentration on the zeta potential of SDS micelle is illustrated in Fig. 9, the SDS concentration was fixed at 8 mM. It can be seen from the figure that the magnitude of zeta potential decreased from −41.1 mV at 0 mg/L of MB to −63.5 mV at 6 mg/L of MB in the solution, which was attributed to the slight decrease of CMC and increase of the aggregation number of micelles with the feed MB concentration increasing, resulting in the increase of surface charge density of micelles.

3.4. Effect of electrolyte

3.4.1. Effect of electrolyte on the permeate flux and additional resistance

Real dye effluent always contains high concentrations of electrolytes, so the effect of electrolyte on the MEUF process was studied. In this study, NaCl was chosen as an electrolyte in order to evaluate the influence of electrolyte. The oper-

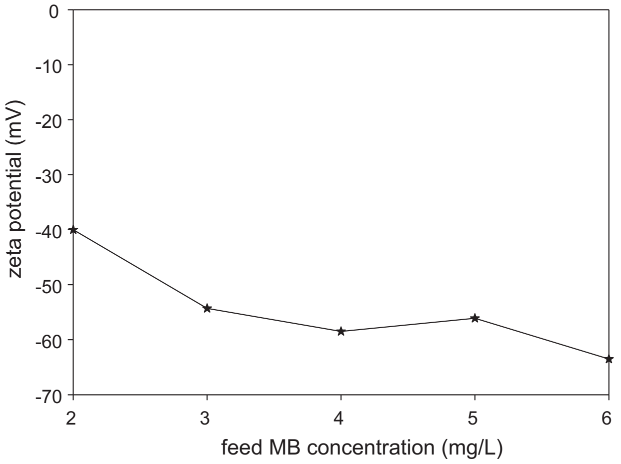

Fig. 9. Effect of the feed MB concentration on the zeta potential of SDS micelle. Feed SDS concentration, 8 mM, 25 °C.

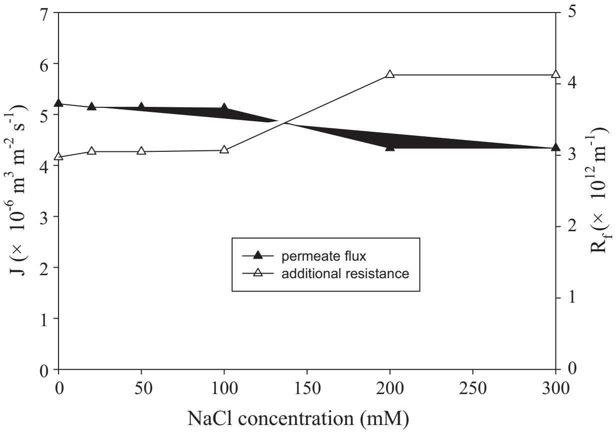

Fig. 10. Effect of NaCl concentration on the permeate flux and additional resistance. Feed MB and SDS concentration, 6 mg/L and 8 mM; operating pressure, 0.03 MPa, 25 °C.

ating pressure was fixed at 0.03 MPa and the feed MB and SDS concentrations were fixed at 6 mg/L and 8 mM, respectively, at room temperature. From Fig. 10, the permeate flux (J) decreased slightly from $6.94 \times 10^{-6}\,\mathrm{m^3\,m^{-2}\,s^{-1}}$ without NaCl to $4.34 \times 10^{-6}\,\mathrm{m^3\,m^{-2}\,s^{-1}}$ at 200 mM or 300 mM NaCl. Correspondingly, the additional resistance (R_f) increased slightly from $1.53 \times 10^{12}\,\mathrm{m^{-1}}$ to $4.13 \times 10^{12}\,\mathrm{m^{-1}}$ with NaCl concentration. This was due to the decrease in the CMC of the surfactant and increase in the aggregation number of micelles as the NaCl concentration increased, resulting from the reduction of repulsive forces between the charged head groups of the surfactant that fighting against the formation of surfactant monomers. Therefore, more micelles deposited on the membrane surface and blocked the membrane pores, increasing R_f by membrane fouling and concentration polarization.

3.4.2. *Effect of electrolyte on the observed MB and SDS rejection*

It can be seen from Fig. 11 that as the NaCl concentration increased, the MB rejection remained almost constant at a value of 99.3%. For an ionic surfactant, adding electrolyte to the aqueous solution would reduce the repulsive forces between the charged head groups of the surfactant, resulting in the easier formation of the surfactant micelle. Therefore the surfactant CMC decreased and the amount of the micelle increased. While the repulsive force was reduced, the solubilization capability of micelle was changed: the solubilization of hydrocarbons that were solubilized in the inner core of the micelle was promoted but solubilization of polar solutes that were solubilized in the outer portion of the palisade layer was lowered [17,27]. In fact, the MB molecules were solubilized in both the inner core and the palisade layer of the micelle so that the rejection of MB was independent on the NaCl concentration. As observed from the figure, the SDS rejection increased gradually with NaCl concentration, from 63.48% without NaCl to 96.0% at 200 mM or 300 mM NaCl, which could also be explained by the decrease of its CMC and increase in the aggregation number of the micelles. Clearly, addition of electrolyte could reduce the back pollution, which was also economical.

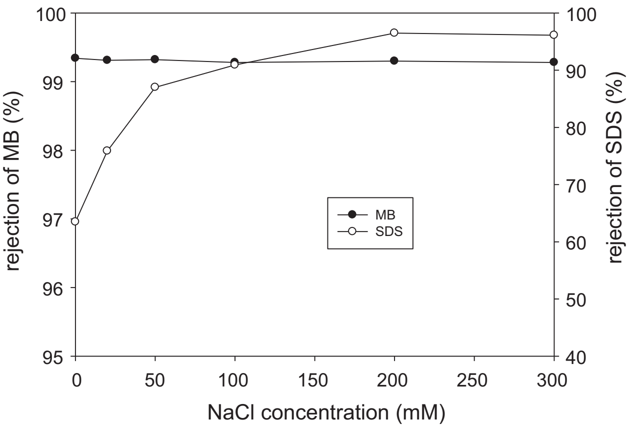

Fig. 11. Effect of NaCl concentration on the MB and SDS rejection. Feed MB and SDS concentration, 6 mg/L and 8 mM; operating pressure, 0.03 MPa, 25 °C.

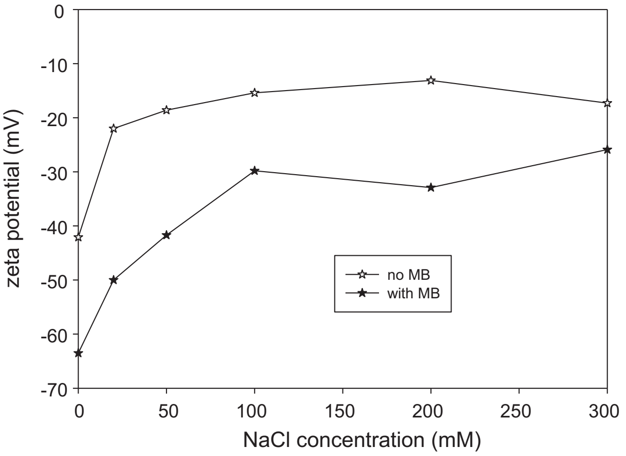

Fig. 12. Effect of NaCl concentration on the zeta potential of SDS micelle. Feed SDS concentration, 8 mM, 25 °C.

3.4.3. *Effect of electrolyte on the zeta potential*

The effect of NaCl concentration on the zeta potential is displayed in Fig. 12, with SDS concentration fixed at 8 mM. It can be seen from the figure that the magnitude of zeta potential with MB (6 mg/L) was lower than that without MB in the solution, because small amount of MB cationic ions could reduce the repulsive forces between the surfactant (SDS) head groups, leading to the slight decrease of CMC and increase of the aggregation number of micelles, which agreed with the observation in Fig. 6. In the presence of electrolyte, the cationic ions influence the zeta potential of SDS micelle on two aspects: they can weaken the repulsive force between the head groups of surfactant monomers resulting in the decrease of CMC, thereby easier aggregation of micelle and bigger aggregation number of micelle, as a result, the surface charge density of micelle increases, and the zeta potential of SDS micelle is more negative; on the other hand, the introduction of cationic ions will force more cationic ions from diffusion layer into adsorbent layer of SDS micelle, hence, the zeta potential is less negative. Integrating the two effects, it can be seen from the figure that the magnitude of zeta potential increased without or with MB in the solution, from −42.1 and −63.5 mV at 0 mM of NaCl to −15.0 and −29 mV in the range of 100–300 mM of NaCl, respectively, which indicated that the later effect of NaCl was stronger than the former effect on the zeta potential.

4. Conclusion

The permeate flux (J) and the additional resistance (R_f) as well as the observed MB and SDS rejection had been studied and analyzed under the important conditions (operating pressure, feed SDS, MB dye and NaCl concentration), using a polysulfone hollow fiber membrane in the MEUF process. J and R_f both increased, while the rejection of MB and SDS decreased slightly with the operating pressure increasing. J decreased with feed SDS, MB and NaCl concentration while R_f increased. The MB rejection decreased slightly from 99.34 to 95.19% when the feed SDS concentration increased from 8 to 72 mM. The SDS rejection increased from 54.90% in the absence of MB to 60% in the presence of MB in the solution. The addition of NaCl had no significant effect on MB rejection but could promote the surfactant rejection significantly from 63.48% without NaCl to 96.00% at 200 or 300 mM NaCl, since the electrolyte could reduce the CMC of the surfactant and increase the aggregation number of SDS micelles. Therefore, electrolyte in the dye wastewater could reduce the back contamination in MEUF, which was also economical. The zeta potential of SDS micelle was also investigated with MB, SDS and NaCl concentration in the solution. The magnitude of zeta potential decreased with MB concentration increasing in the solution and increased without or with MB in the solution as NaCl concentration increasing.

Acknowledgements

This study was financially supported by the National Basic Research Program (973 Program) (2005CB724203), the Program for New Century Excellent Talents in University from the Ministry of Education of China (NCET-08), the National Natural Science Foundation of China (50978088, 51039001), the Hunan Key Scientific Research Project (2009FJ1010) and the Hunan Provincial Natural Science Foundation of China (10JJ7005).

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