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# Evaluation of micellar enhanced ultrafiltration for removing methylene blue and cadmium ion simultaneously with mixed surfactants



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# ABSTRACT

Micellar enhanced ultrafiltration (MEUF) has been extensively applied to the separation of organic solutes or heavy metal ions from water, but the feasibility and efficiency of removing them simultaneously via MEUF have been seldom researched. In this study, simultaneous removal of methylene blue (MB) and cadmium ion  $(Cd^{2+})$  with MEUF by the binary mixture of sodium dodecylsulfate (SDS) and poly-oxyethylene octyl phenyl ether (TritonX-100) was investigated. The critical micelle concentration (CMC) of mixed surfactants was considered. Retentions of MB and  $Cd^{2+}$ , flux decay, and three parameters, namely distribution coefficient (*D*), micelle loading (*L*), and micelle binding constant (*K*) were discussed to assess the efficiency of MEUF process. The higher mole ratio of TritonX-100 was in favor of MB and  $Cd^{2+}$  removal. The presence of  $Cd^{2+}$  could promote the rejection of MB by increasing the micelles in the retentate but had no influence on the unit binding capacity of micelles and the relative affinity of MB for micelles. The presence of MB could also increase  $Cd^{2+}$  rejection with little influence on the unit binding capacity of micelles.

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# 1. Introduction

Organic contaminants and heavy metals in aqueous solution have posed great threats to environment and human health. Traditional methods for the removal of dissolved organic contaminants are adsorption, membrane separation, biodegradation and so on [1]. Chemical precipitation, ion exchange, electrochemical treatment, coagulation and flocculation are the well-known methods for the heavy metals removal [2]. Some methods, for examples, chemical precipitation and chemical coagulation, can be applied to remove both of organic matters and metal ions [3–6]. However, their drawbacks, such as requirement of stringent running conditions, relatively high cost and bulky sludge production, have limited their applications [7,8]. Besides, due to inefficiency and diseconomy, most of these traditional methods are unfeasible to treat wastewater with low concentration of organics and metal ions [9].

Micellar enhanced ultrafiltration (MEUF), which was firstly proposed by Dunn et al. [10], has emerged as a low energy require-

ment and high efficiency technology to remove organic solutes and metal ions from aqueous environment. In MEUF, surfactants are added to the contaminated water to a concentration higher than the critical micelle concentration (CMC). Then the surfactants form nanometric amphiphilic aggregates, namely micelles, whose interior hydrophobic core can solubilize low molecular weight organic matters and surface adsorb counter ions due to electrostatic interactions. Micelles along with trapped organic molecules or metal ions are separated from the aqueous stream via an ultrafiltration (UF) membrane with pore sizes smaller than those of the organic–micelle or metal ion–micelle complexes. Hence, highly purified permeate can be obtained by using MEUF.

Since the introduction of MEUF, plenty of organic pollutants and heavy metals were investigated to be removed by this process. Not only single surfactants, binary mixtures and even ternary mixtures of surfactants were employed in removing organics or heavy metals via MEUF [11,12]. One direct benefit of using mixed surfactants is the great reduction of the CMC value, which therefore reduces the amount of surfactants added and lower the surfactant concentrations in the permeate [13].

Apart from the traditional parameters, such as rejection and flux decay that describing the efficiency of MEUF process, distribution coefficient, micelle loading (showing the unit binding capacity of micelles) and the micelle binding constant (revealing the relative

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affinity of contaminants for micelles) were also proved to be useful in efficiency determination of MEUF process [13]. Yenphan et al. [7] used the distribution coefficient and the micelle binding constant to describe lead ion removal in mixed surfactant systems. They proved that an increase of surfactant concentration resulted in an increase of both lead ion and surfactant rejections because that more surfactant molecules joined in the formation of micelles and enhanced the affinity of lead ion for the micelle. In the study of removing nickel and cobalt simultaneously via MEUF, Karate and Marathe [14] found that maximum rejection of metal ions occurred in the early stage of ultrafiltration by comparing the change of rejection and distribution coefficient with the volume fraction, which was then confirmed by micelle loading and the micelle binding constant.

With the deterioration of environment and complication of contaminants in the waste stream, simultaneous removal of organic substances and heavy metals via MEUF has gradually been considered and deemed necessary. Tung et al. [15] used mixed surfactants of sodium dodecylsulfate (SDS) and polyoxyethylene octyl phenyl ether (TritonX-100) to remove Cu2+ and dissolve phenol simultaneously, which resulted in slightly enhanced rejection of copper ions and comparatively lower rejection of phenol than they were separated alone. Witek et al. [16] demonstrated that the presence of Cr<sup>3+</sup> in the SDS or cetyltrimethyl ammonium bromide (CTAB) micelle system did not influence the rejection of phenols. Misra et al. [17] observed that the presence of  $UO_2^{2+}$  had no significant effect on the rejection of dibutyl phthalate (DBP) in the SDS micelle system. No research, however, has been carried out to systematically examine the effectiveness of MEUF for the simultaneous removal of organics and heavy metals.

The focus of this work was to systematically evaluate the feasibility and efficiency of simultaneous removal of an organic pollutant MB and a kind of heavy metal  $Cd^{2+}$  via MEUF by binary surfactant mixtures of anionic surfactant SDS and nonionic surfactant TritonX-100. Critical micelle concentrations (CMC) of mixed surfactants were measured. Retentions of MB and  $Cd^{2+}$ , flux decay were tested at various conditions. Distribution coefficient (*D*), micelle loading (*L*), and micelle binding constant (*K*) were discussed to better understand the mutual influence of MB and  $Cd^{2+}$  in the SDS and TritonX-100/SDS systems.

# 2. Experimental

### 2.1. Chemicals

All reagents used were of analytical pure grade. Sodium dodecylsulfate (SDS) with purity of 99% was procured from Tianjin Kermel chemical factory. Polyoxyethylene octyl phenyl ether (Triton X-100) was supplied by Wako pure Chemical industry company, Japan. Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O was purchased from Shanghai Tingxin chemical factory, China. Methylene blue was supplied by Tianjin DaMao Chemical Agent Company. All the reagents were used without further purification. All aqueous solutions were prepared with ultrapure water from Lanconco Water Pro PS water purifier (Kansas, US).

### 2.2. Equipments

Table 1

Ultrafiltration experiments were carried out in a tangential hollow fiber ultrafiltration unit, which was provided by Yidong Membrane Engineering Equipment Ltd., Dalian, China. The membrane material, polysufone, is hydrophobic in nature. Specifications of the membrane are listed in Table 1.

#### 2.3. Experimental procedure

A laboratory-scale MEUF system employed is shown schematically in Fig. 1. The experiments were carried out at room temperature. The synthetic wastewater was obtained by adding certain amount of Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, MB and surfactants according to the experimental design into ultrapure water with pH unjusted. After adequate mixing, the wastewater was subjected to ultrafiltration, which was carried out in a batch manner under constant pressure of 0.03 MPa. The retentate was recirculated to the feed tank and permeate collected. The initial feed volume was equal to 3 L in all MEUF experiments and process was stopped when 400 mL was taken as concentrate.

The concentrations of MB and Cd<sup>2+</sup> in the feed solution were kept constant at 6 mg/L and 50 mg/L, respectively. In mixed surfactant systems, the concentration of SDS was fixed at 4 mM, and the ratios of TritonX-100 to SDS were 0.1, 0.3, 0.5, and 0.8.

#### 2.4. Analyses

The CMC of SDS solution and binary mixtures were obtained by surface tension measurement via an automatic interface tension meter (JYW-200A). The concentrations of MB and TritonX-100 were determined by Shimadzu UV-2550 (P/N206-55501-93) spectrophotometer at wavelength 663 nm and 274 nm, respectively, with ultrapure water as the reference solution. Concentration of Cd<sup>2+</sup> was determined by flame atomic absorption spectrophotometer (PerkinElmer, Modle AAnalyst 700). SDS was measured by the methylene blue spectrophotometric method at wavelength 652 nm.

#### 2.5. Membrane cleaning

After each run, the membrane was firstly washed by tap water till no foam was running from the concentrate outlet, then washed successively by 5 L 0.2 mol/L HNO<sub>3</sub>, 5 L 0.2 mol/L NaOH, and distilled water for 10 min, and finally 2 L ultrapure water. The



Fig. 1. Schematic diagram of laboratory-scale MEUF.

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Specifications for the us	ed hollow fiber ultrafiltration	membrane module.

Length (cm)	Diameter of the membrane module (cm)	Membrane effective surface area (m <sup>2</sup> )	MWCO (KDa)	Maximum operating pressure (MPa)	pH operating range	Operating temperature (°C)	Maximum pump power (W)
30	5	0.8	10	0.1	2–13	5-45	40

permeate flux of ultrapure water on the membrane is 20 L  $m^{-2}\,h^{-1}$  after membrane cleaning.

### 3. Theoretical basis

# 3.1. Retention

Separation efficiency in MEUF can be characterized by retention (R), which is defined as

$$R = 1 - \frac{[C]_P}{[C]_R}$$
(1)

where [C] is the concentration of contaminants, and the subscripts P and R represent permeate solution and retentate solution, respectively.

# 3.2. Permeate flux

The permeate flux during MEUF process is calculated as follows:

$$J = \frac{Q_t}{A} \tag{2}$$

where J (L m<sup>-2</sup> h<sup>-1</sup>) stands for the permeate flux, and  $Q_t$  (L h<sup>-1</sup>) and A (m<sup>2</sup>) denote the instant permeate volume and the effective surface area of the membrane, respectively.

# 3.3. Parameters

Micelles are dynamic aggregates of surfactants, which are in equilibrium with the surfactant molecules in water. However, the exchange time of one surfactant molecule between the micelle and the bulk, and the time from micelle formed to micelle breakdown, defined as residence time and micelle lifetime, respectively, are very short [13]. Thus, micelles can been redeemed as static, allowing some constants to be introduced. However, some assumptions should be stated: (1) the un-solublized organic matters or un-binded heavy metals pass freely through the membrane, and therefore the concentration of the contaminant in the permeate gives the concentration of the solute in monomer form; (2) the un-micellized surfactants pass freely through the membrane, and the surfactant concentration in the permeate is assumed to be 1CMC; and (3) no reactions exist between monomer surfactants and solute molecules.

Based on the hypothesizes above, important parameters, distribution coefficient, micelle loading, and micelle binding constant, were employed in this study to delve into the efficiency of MEUF process in removing organic matters and heavy metals simultaneously by using mixed surfactants.

Distribution coefficient (D) is described as the ratio of contaminant concentrations in the retentate and permeate [7,13,14], namely

$$D = \frac{[C]_R}{[C]_P} \tag{3}$$

Loading of micelles (*L*), which reveals the unit binding capacity of micelles, is defined by the following equation [13,14]:

$$L = \frac{[C]_R - [C]_P}{[S]_R - [S]_P} \tag{4}$$

where [S] stands for the surfactant concentration. For mixed surfactant systems,  $[S]_R$  is the combination of anionic surfactant and nonionic surfactant concentration in the retentate. Actually,  $[S]_P$  equals to 1 CMC according to the previous assumption.

Micelle binding constant (*K*), which stands for the relative affinity of contaminants for micelles, is expressed as [7,13,14]

$$K = \frac{[C]_M}{[C]_W S} \tag{5}$$

where the subscripts *M* and *W* denote the micelle phase and water phase, respectively, and *S* is the concentration of surfactants in micelle phase. Actually,  $[C]_M = [C]_R - [C]_P$ ,  $[C]_W = [C]_P$ , and  $S = [S]_R - CMC$ .

# 4. Results and discussion

#### 4.1. CMC of mixed surfactants

Demonstrated in Fig. 2 are the surface tension isotherms for SDS, TritonX-100 and their mixtures of various molar ratio (SDS/ TritonX-100 = 0.1, 0.3, 0.5, and 0.8) in aqueous solutions at room temperature and pH unjusted. The intercepts of the surface tension curves, for example, 7.9 mM for SDS and 0.53 mM for TritonX-100, suggest the critical micelle concentration (CMC) of each surfactant system. As illustrated in the figure, the CMCs of binary mixtures fall in between that of the individual surfactant, and the higher molar ratio of the nonionic surfactant leads to lower CMC value. Similar observations were also reported by Bielska and Szymanowski [13] for SDS+OMC-10 (oxyethy-lated coconut fatty acid methyl esters) systems, and Ghosh [18] for SDS + Tween-20 (polyoxyethylene-sorbitan monolaurate) and SDS + Brij-35 systems. The ethoxylated chains of the nonionic surfactant in the binary surfactant mixture coil around the charged head groups of the anionic surfactant, screening the electrostatic repulsions [12]. Thus, the micelle is easier to be formed, resulting in lower CMC compared to that of single surfactant. The CMC values for mixed surfactant systems with the molar ratio of 0.1, 0.3, 0.5, and 0.8 are 1 mM, 0.65 mM, 0.59 mM, and 0.56 mM, respectively. Such decreasing of CMC is significant, as lower CMC results in lower surfactant usage as well as decreased concentration of surfactants in the permeate (nearly 1 CMC) [13].

#### 4.2. Retention

The retentions of MB and  $Cd^{2+}$  are revealed in Table 2. Higher retentions of MB and  $Cd^{2+}$  are obtained when removing them simultaneously than that of obtained when treating them singly. The best retentions for MB (99.40%) and  $Cd^{2+}$  (98.06%) are obtained for the coexistence of MB and  $Cd^{2+}$ , and the mixed surfactants with the mole ratio of 0.3 for MB, and 0.5 for  $Cd^{2+}$ . However, the retentions begin to decrease when the mixed surfactants contained



**Fig. 2.** Surface tension isotherms for different surfactant systems (SDS ( $\bullet$ ), TritonX-100 ( $\bigcirc$ ), TritonX-100/SDS = 0.1 ( $\blacktriangledown$ ), TritonX-100/SDS = 0.3 ( $\Delta$ ), TritonX-100/SDS = 0.5 ( $\blacksquare$ ), TritonX-100/SDS = 0.8 ( $\Box$ )).

#### Table 2

Rejections of MB and Cd<sup>2+</sup> in using SDS alone and binary mixtures of SDS and TritonX-100.

Surfactants and contaminants <sup>a</sup>	r <sup>b</sup>	Rejections (%)	
		MB	Cd <sup>2+</sup>
SDS+MB	-	98.51 ± 0.31	-
$SDS + Cd^{2+}$	-	-	94.90 ± 0.39
$SDS + MB + Cd^{2+}$	-	99.20 ± 0.13	96.80 ± 0.26
SDS + TritonX-100 + MB	0.1	99.02 ± 0.19	-
	0.3	99.26 ± 0.22	-
	0.5	99.02 ± 0.29	-
	0.8	98.96 ± 0.46	-
SDS + TritonX-100 + Cd <sup>2+</sup>	0.1	-	96.73 ± 0.45
	0.3	-	96.97 ± 1.07
	0.5	-	97.54 ± 0.69
	0.8	-	97.31 ± 0.95
SDS + TritonX-100 + MB + Cd <sup>2+</sup>	0.1	99.25 ± 0.15	97.90 ± 1.00
	0.3	99.40 ± 0.30	$98.04 \pm 0.54$
	0.5	99.01 ± 0.41	98.06 ± 0.14
	0.8	98.89 ± 0.21	97.03 ± 1.33

<sup>a</sup> The concentration of SDS is always 4 mM, and the concentration of MB and Cd<sup>2+</sup> are 6 mg/L and 50 mg/L, respectively.

<sup>b</sup> In this table and the following figures, *r* stands for the molar ratio of TritonX-100 to SDS.

more TritionX-100. Thus, the nonionic surfactant should be added at a suitable ratio.

# 4.3. Flux decline

Permeate fluxes of MEUF processes with single and mixed surfactants in removing MB and Cd<sup>2+</sup> simultaneously versus filtration time are plotted in Fig. 3. The tendency of the curves for all cases suggests a rapid initial loss of flux followed by a relatively slow continuous loss of flux over longer time till reaching steady state. This phenomenon attributes mainly to the concentration polarization effect and membrane fouling [19-21]. The concentration polarization takes place as a result of a local increase of solutes concentration near the membrane surface. Membrane fouling, usually behaves as gel layer formation and pore blocking, occurs as a result of deposition and accumulation of solutes on the membrane surface and within the membrane pores [19]. In the initial stage of MEUF, a sharp decline of permeate flux takes place when the surfactants gather rapidly near the membrane surface, resulting in the concentration polarization effect and gradual formation of gel layer. As filtration process proceeds, the gel layer gets denser and denser, resulting in a slow flux decline. In the final stage, the membrane fouling is fixed and the permeate flux has reached the limit-



**Fig. 3.** Permeate fluxes of using single SDS and different molar ratio of mixed surfactants versus time in MEUF (SDS ( $\bullet$ ), TritonX-100/SDS = 0.1 ( $\bigcirc$ ), TritonX-100/SDS = 0.3 ( $\triangledown$ ), TritonX-100/SDS = 0.5 ( $\Delta$ ), TritonX-100/SDS = 0.8 ( $\blacksquare$ )).

ing value that will not change with time. The binary mixtures lead to a greater flux decline than that of SDS alone, and higher molar ratio of TritonX-100 tends to result in a lower permeate flux. Such phenomenon is also reflected in the case of filtration time. MEUF with SDS alone experiences the shortest filtration time, and longer filtration time can be observed with the increasing of TritonX-100 amount. The explanations of this observation can be illustrated in the following four aspects: (1) since the CMC of the surfactant system is reduced by the addition of the nonionic surfactant as discussed above, the amount of micelles in the aqueous solution is increased, resulting in higher extent of concentration polarization near the membrane surface [20]; (2) the charged micelles are screened off by the nonionic surfactant, leading to less space between micelles, and hence, a denser gel layer is formed [7]; (3) increasing amount of the nonionic surfactant can decrease the size of micelles, resulting in an increasing chance of membrane pore blocking [22]: and (4) the viscosity of the solution is enhanced by the addition of the nonionic surfactant, leading to increased hydraulic resistance against the flux [7,8,11].

Other factors, such as the adsorption of MB molecules on the membrane surface and membrane pores, formation of precipitations on the membrane as a results of MB + SDS [23,24] and  $Cd^{2+}$  + SDS [25] reactions, are not discussed here for they are not the main concerns for the flux decay.

# 4.4. Evaluation of the efficiency of MEUF

#### 4.4.1. Removal of MB

Fig. 4a manifested the distribution coefficient (D) of MB. The D of MB increases with increasing mole ratio of TritonX-100 when r is below 0.3, indicative of decreased CMC and therefore increased amount of micelles in the solution, rendering more hydrophobic cores for MB to solublize in. However, further increasing of the TritonX-100 (r > 0.3) does not result in higher concentrate degree. On the country, it pulls down the *D* value. This could be explained by the formation of compacter micelles and micelles with smaller apparent hydrodynamic diameter, resulting in decreased micelle solubilization capacity [21,22,24]. Further decreasing of *D* values may arise from the transformation of micelle shape from spherical to cylindrical or plate [24] by excessive amount of TritonX-100. Note that even when the D value is 50, which is less than the lowest D value in Fig. 4a, the retention of solutes can still reach 98% as illustrated in Fig. 5 [13]. Therefore, it may be concluded that the degree of micelle shape transformation in the above case is very slight, and the *D* value is very sensitive and hence amplifies such change.

The loading of the micelle (L) with MB and micelle binding constants (K) of MB are demonstrated in Fig. 4b and c, respectively. The two constants show the same trend with the increasing mole ratio of the nonionic surfactant. The L and K values drop sharply in the presence of TritonX-100. This observation bears testimony to the conclusion that the addition of the nonionic surfactant leads to increasing amount of micelles in the solution. Since unit binding capacity of micelles and the relative affinity of MB for micelles are reduced while D values is increased with the addition of the nonionic surfactant (in a certain mole ratio range), the only explanation is the increase of micelles' amount in the solution.

Also highlighted in Fig. 4a is that when in the presence of  $Cd^{2+}$ , greater *D* values of MB occurred compared to when MB is removed alone, indicative of (1) no competitiveness for micelle binding exists between MB and  $Cd^{2+}$  in surfactant aqueous solution and (2) the presence of  $Cd^{2+}$  promotes MB removal. The first conclusion is explained by the different removal mechanisms of MB and  $Cd^{2+}$ , for MB is by solublizing in the hydrophobic cores of micelles, while  $Cd^{2+}$  by electrostatic attractions between  $Cd^{2+}$  ions and negatively charged micelles. The second arises from decreased



**Fig. 4.** Changes of (a) distribution coefficient of MB, (b) loading of micelles for MB, and (c) micelle binding constant of MB in the absence ( $\bigcirc$ ) and presence ( $\bullet$ ) of Cd<sup>2+</sup> for TritonX-100/SDS systems, and in the absence ( $\Delta$ ) and presence ( $\blacktriangle$ ) of Cd<sup>2+</sup> for SDS systems.

repulsive force between negatively charged head groups of the surfactant when in the present of  $Cd^{2+}$ , resulting in the formation of micelles at lower surfactant concentration and therefore, more micelles formed [22,23]. However, the *L* and *K* values in the presence and absence of  $Cd^{2+}$  are almost similar for mixed surfactants, indicating that the unit binding capacity of micelles and the relative affinity of MB for micelles are not influenced by the addition of  $Cd^{2+}$ .

Comparing the *D* values of MB between using mixed surfactants and using the same total molar amount of pure SDS shown in the dominant graph and sub-graph in Fig. 4a, respectively, it is not difficult to find that, at a certain range, the former has an advantage over the latter, especially at the point of r = 0.3. This indicates that using mixed surfactants is more efficient than using the same mole amount of pure SDS. This result arises from the reduced CMC and hence more micelles for mixed surfactants compared with using the same mole amount of pure SDS. The above explanation is confirmed by L and K values, which are generally lower for mixed surfactants than those for pure SDS. The decreasing of L and K values suggests that the micelles are unsaturated for MB solublizing. Therefore, more amount of MB can be removed in such cases.

It must be pointed out that when using SDS alone, the D values are still very high despite the SDS concentrations are below 1 CMC (approximately 7.9 mM). This can be explained by the concentration polarization effect [24–26]. Although the amount of SDS in the bulk solution is very low that no micelles are formed in it, the SDS concentration near the membrane surface as a result of membrane filtration, gathering most of the surfactants near the membrane surface, is high enough to form micelles. Therefore, most of MB molecules are retained in the concentrated tank by solubilizing in the micelles. It may be noticed that, different from using mixed surfactants. D values for using pure SDS do not go down with further increasing of the surfactant dosage. This is because that the SDS concentrations used in this study is not high enough for micelle transformation. According to our earlier work, the transformation of micelle shape took place when the SDS concentration exceeded 8 mM [24].

# 4.4.2. Removal of $Cd^{2+}$

The parameters of removing Cd<sup>2+</sup> via MEUF are exhibited in Fig. 6. Consistent with the results for MB removal, the D values of Cd<sup>2+</sup> in using mixed surfactants also increase at first and then decrease with further increasing of the nonionic surfactant. According to our previous research, the degree of counter ion binding, which reveals the micelles' counter ion binding ability, decreased with the increasing molar ratio of TritonX-100/SDS [11]. So the increasing micelle amount and the decreasing micelle charge density, as the results of the addition of TritonX-100, jointly contributed to the changing of D values. Lower micelle charge density as a result of the nonionic surfactant overdose is mainly accounted for the drop of D values [7,22]. Unsurprisingly, the L and K values also experience sharp drop with the addition of TritonX-100 as illustrated in Fig. 6b and c. Higher micelle amount and lower micelle charge density are thought to be jointly responsible for this phenomenon.

Fig. 6a also highlights that whether in binary surfactant systems or pure SDS systems, *D* values of  $Cd^{2+}$  are always higher when in the presence of MB than those when without it. Presently, we have no clear explanation for the mechanisms of this phenomenon. Possible explanations include stronger electrostatic attractions between  $Cd^{2+}$  and micelles, and reduced CMC in the presence of MB. However, no obvious difference of *L* values in using mixed surfactants is observed in Fig. 6b, making the latter explanation more convincing. Tung et al. [15] also got the similar observation that the presence of 1 mM phenol could enhance the  $Cu^{2+}$  rejection



Fig. 5. Relationship of retention versus distribution coefficient for MB and Cd<sup>2+</sup>.



**Fig. 6.** Changes of (a) distribution coefficient of  $Cd^{2+}$ , (b) loading of micelles for  $Cd^{2+}$ , and (c) micelle binding constant of  $Cd^{2+}$  in the absence ( $\bigcirc$ ) and presence ( $\bigcirc$ ) of MB for TritonX-100/SDS systems, and in the absence ( $\triangle$ ) and presence ( $\blacktriangle$ ) of MB for SDS systems.

slightly in a SDS system, which they also thought was due to the slight reduction of CMC in the presence of organic solutes.

As can be seen in Fig. 6a, the *D* values of  $Cd^{2+}$  in mixed surfactant systems are higher than those of the same total molar amount of pure SDS systems when the total surfactant molar amount is lower than 6 mM. However, the situation is reversed when the total surfactant molar amount exceeds 6 mM. There are two paradoxical factors attribute this phenomenon. One is that the mixed surfactant system possesses more micelles, and the other is that the mixed surfactant system has lower micelle charge density than the same mole amount of pure SDS system. In the case of *r* below 0.5, the positive effect of the nonionic surfactant far outweighs the negative one, hence much more negatively charged binding sites are provided by the TritonX-100/SDS system than the same total molar amount of pure SDS. However, more amount of micelles as it brings about, further increasing of the nonionic surfactant gives

rise to lower and lower micelle charge density, allowing less Cd<sup>2+</sup> binding than the same total mole amount of pure SDS system. In the mean time, too much micelles caused by the increased amount of Tritonx-100 may finally lead to micelle transformation, which is not likely to happen in the case of the same molar amount of pure SDS until its concentration reaching 8 mM as we discussed above. Hence, a suitable mole ratio of nonionic surfactants is very important. In this case, 0.5 is assumed to be suitable.

# 5. Conclusion

The coexistence of MB and  $Cd^{2+}$  would promote the retentions of each other. The addition of  $Cd^{2+}$  in the solution could increase the distribution coefficient of MB by lowering the CMC of surfactants, but had no influence on the unit binding capacity of micelles and the relative affinity of MB for micelles. The presence of MB could also increase the distribution coefficient of  $Cd^{2+}$  and had little influence on the unit binding capacity of micelles. The best retentions for MB and  $Cd^{2+}$  are 99.40% and 98.06%, respectively.

Although the addition of the nonionic surfactant, TritionX-100, could effectively reduce the CMC of the surfactant solution, it could also lead to greater flux decline. Excessive amount of TritionX-100 would reduce the MB retention because of the formation of compacter micelles and micelles with smaller apparent hydrodynamic diameter, and would reduce Cd<sup>2+</sup> retention due to reduced micelle charge density. The best mole ratio of TritonX-100 to SDS is 0.3 for MB and 0.5 for Cd<sup>2+</sup>.

Therefore, it can be concluded that simultaneous removal of MB and  $Cd^{2+}$  via MEUF is feasible and efficient. In a certain range, the addition of the nonionic surfactant can improve the efficiency of this process.

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