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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 polyoxyethylene 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 exhibited lower CMC value but more intensified flux decay. Within a certain range, the addition 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.

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 requirement 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 Cu^{2+} 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^{3+} 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. $Cd(NO_3)_2{\cdot}4H_2O$ 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

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 $Cd(NO_3)_2{\cdot}4H_2O$, 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^{2+} 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^{2+} 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_3, 5 L 0.2 mol/L NaOH, and distilled water for 10 min, and finally 2 L ultrapure water. The

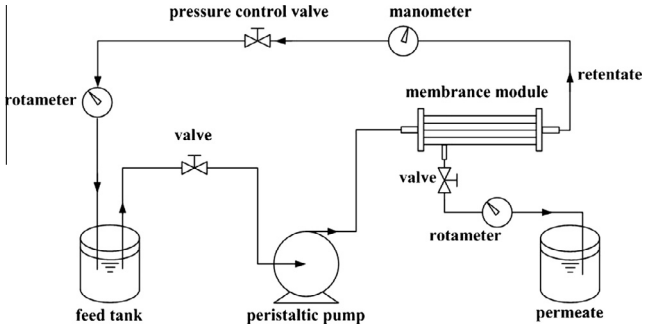

Fig. 1. Schematic diagram of laboratory-scale MEUF.

Table 1
Specifications for the used hollow fiber ultrafiltration membrane module.

Length (cm)	Diameter of the membrane module (cm)	Membrane effective surface area (m^2)	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