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Removal of cadmium ions using micellar-enhanced ultrafiltration with mixed anionic-nonionic surfactants

Jin-hui Huang*, Guang-ming Zeng, Yao-yao Fang, Yun-huan Qu, Xue Li

College of Environmental Science and Engineering, Hunan University, Changsha 410082, China

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ABSTRACT

Micellar-enhanced ultrafiltration (MEUF) was used to remove cadmium ions from wastewater efficiently. In this study the nonionic surfactants polyoxyethyleneglycol dodecyl ether (Brij35) and polyoxyethylene octyl phenyl ether (TritonX-100) were for micellar-enhanced ultrafiltration to lower the dosage of the anionic surfactant sodium dodecyl sulfate (SDS). The surfactant critical micelle concentration (CMC) and the degree of micelle counterion binding were investigated. The effects of nonionic surfactant addition on the efficiency of cadmium removal, the residual quantities of surfactant, the permeate flux and the secondary membrane resistance were investigated. A comparison between MEUF with SDS and MEUF with mixed anionic–nonionic surfactants was undertaken. The results show that the addition of Brij35 or TritonX-100 reduced the CMC of SDS and the degree of counterion binding for the micelles. Due to these variations the Cd^{2+} rejection efficiency was at a maximum when the Brij35:SDS and the TritonX-100:SDS molar ratio was 0.5. The Cd^{2+} rejection efficiency in MEUF with SDS is higher than for MEUF with mixed surfactants when the total dose of surfactant is constant. The permeate flux of MEUF with SDS is higher than that for MEUF with mixed surfactants while the secondary resistance of MEUF with SDS is less than that of MEUF with mixed surfactants.

1. Introduction

Cadmium-containing wastewater has always attracted widespread attention because of its significant threat to the environment and to human health. The current popular techniques for treating cadmium-containing wastewater are chemical precipitation, adsorption, bleaching powder oxidation, ion exchange and biotechnology etc. These techniques, however, have deficiencies, such as secondary pollution by deposition, inconvenient operation, high cost and difficulty of recycling cadmium. As a surfactant-based separation process, micellar-enhanced ultrafiltration (MEUF) has been shown to be an effective technique for the removal of cadmium ions from industrial effluents. Sadaoui et al. studied the removal of Cd^{2+} [1–3], Cd^{2+} and Cr^{3+} [4], Cd^{2+}, Cu^{2+}, Ni^{2+} and Zn^{2+} [5], Cd^{2+} and Pb^{2+} [6] from waste streams by MEUF. Junga et al. [7] studied MEUF for the removal of Cd^{2+}, Cu^{2+}, Zn^{2+} and Pb^{2+} from soil-washing effluent. This was an extended application of MEUF to intricate contaminants and circumstances. MEUF has thus been shown to be effective in removing Cd^{2+} from wastewater. MEUF can also remove many other metal ions, including Cd^{2+} [1–7], Ni^{2+} [5,8], Zn^{2+} [5], Cr^{3+} [4,9–11], Mn^{2+} [12], Pb^{2+} [6,13], $CrO_4{}^{3-}$, Cu^{2+} [5], Fe^{3+} [9,14] and $Fe(CN)_6{}^{3-}$ [15]. The advantages of this method are low energy requirements for the ultrafiltration process and its high removal efficiency, due to the effective trapping of solutes by the micelles.

In MEUF, the micelles of an ionic surfactant in an aqueous solution bind ions on the surface of oppositely charged micelles via electrostatic interactions. To form ionic surfactant micelles, the amount of anionic surfactant should be greater than its critical micelle concentration (CMC). Traditionally, the large quantities of anionic surfactant used for the separation make the separation process expensive, and a high concentration of residual surfactant remains in the permeate. Lowering the CMC of anionic surfactants by adding nonionic surfactants has been demonstrated and applied in the MEUF processes for treating metal ions. MEUFs were carried out with SDS/NPE to remove Cr^{3+} [16], with SDS/TritonX-100 to remove Cu^{2+} and dissolved phenol [17,18] and with CPC/Tween 80 to remove TCE and Cr^{3+} [19].

These studies focused on the effects of surfactant concentration, the composition of mixed surfactants, applied pressure, salt addition, membrane geometry, the rejection of surfactants and relative flux [17–19]. The addition of nonionic surfactants has been shown to reduce the anionic surfactant dosage required for effective metal ion removal and simultaneously minimize

Abbreviations: CMC, critical micelle concentration; MEUF, micellar-enhanced ultrafiltration; MWCO, molecular weight cut-off; TMP, transmembrane pressure.

* Corresponding author. Tel.: +86 731 8821413; fax: +86 731 8821413.
E-mail address: huangjinhui_59@163.com (J.-h. Huang).

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the anionic surfactant concentration in the permeate [18,19]. These studies, however, did not investigate interactions between micellar characteristics such as the CMC, the degree of counterion binding to micelles, the efficiency of metal ion removal, nor did they draw a comparison between MEUF with pure anionic surfactant and MEUF with mixed anionic or nonionic surfactants.

Our previous studies focused on the optimization of important separation parameters in MEUF with SDS as surfactant to remove Cd^{2+} from synthetic wastewater. These parameters included the operating time, the concentration of SDS, transmembrane pressure, solution pH, the concentration of feed electrolyte and the mixing of SDS and Brij35 [2,3]. The focus of these experiments was to investigate micellar characteristics and compare two MEUF processes, and therefore, the optimization of the separation conditions was ignored.

In this study, the nonionic surfactants polyoxyethyleneglycol dodecyl ether (Brij35) and polyoxyethylene octyl phenyl ether (TritonX-100) were used in the MEUF process to study their effect on the removal of cadmium ions from wastewater. The objectives are (1) to characterize the variation of the CMC of SDS and the degree of counterion binding to micelles; (2) to investigate the effects of molar ratio variations of the nonionic surfactant to SDS with regards to the rejection of Cd^{2+}, the permeate residual SDS concentration, the permeate flux and the membrane resistance; (3) to investigate the connection between micellar characteristics such as the CMC, the degree of counterion binding to micelles and the metal ion removal ability; (4) to conduct a comparative experiment between MEUF with SDS and MEUF with Brij35/SDS or TritonX-100/SDS mixed surfactants.

2. Materials and methods

2.1. Chemicals

All agents were analytical pure grade (99%) and used as received. The properties of the surfactants used are shown in Table 1. The synthetic samples containing cadmium ions were prepared from cadmium nitrate, $Cd(NO_3)_2{\cdot}4H_2O$, which was purchased from Shanghai Tingxin chemical factory in China. The deionized water used in all experiments was produced by a deionized water apparatus type 90007-03 purchased from Labconco.

2.2. Membrane

The experimental hollow fiber ultrafiltration membrane was supplied by Tianjin Motian membrane engineering technology company in China and used without further treatment. The characteristics of the membrane are shown in Table 2.

In this study, the permeate flux of the ultrafiltration membrane is defined as

$$J_i = \frac{Q_i}{A} \tag{1}$$

where J_i is the permeate flux (l/(m^2 h)), Q_i is the feed flux (l/h), A is the area of membrane (m^2).

Table 2
Characteristics of membrane.

Dimensions × L (mm × mm)	50 × 386
MWCO	6000
Area (m^2)	0.3
pH	2–13
Material	Polyether sulfone
Inner/out diameter (mm)	0.24/0.4
TMP (MPa)	≤0.15

The Cd^{2+} rejection efficiency is expressed as

$$R = \left(\frac{1 - C_e}{C_0}\right) \times 100\% \tag{2}$$

where R is the Cd^{2+} rejection efficiency (%), C_0 is the concentration of Cd^{2+} (mg/l) in the feed solution and C_e is the concentration of Cd^{2+} in the permeate (mg/l).

The total resistance of the ultrafiltration membrane in MEUF includes the membrane resistance and a secondary resistance which is caused by pollution of the membrane. These are defined as

$$R_m = \frac{\Delta p \times 1000}{\mu_w J_w} \tag{3}$$

$$R_f = \frac{\Delta p \times 1000}{\mu_s J_s - R_m} \tag{4}$$

where R_m is the resistance of the membrane (m^{-1}), R_f is the secondary resistance (m^{-1}), Δp is the transmembrane pressure (Pa), μ_w is the viscosity coefficient of water (Pa h), μ_s is the viscosity coefficient of the solution (Pa h), J_w is the permeate flux of water (l/(m^2 h)) and J_s is the permeate flux of the solution (l/(m^2 h)).

2.3. Experimental setup

2.3.1. Evaluation of CMC and the degree of counterion binding for mixed systems

The CMC of SDS was measured by a conductivity method. A significant change of slope in the conductance versus concentration curve occurs at a certain concentration which allows the calculation of the CMC of SDS.

The degree of counterion binding reveals the ability of micelles to bind to counterions and may be obtained by the electrical conductivity and the concentration curve [20]. It is defined as

$$k_0 = \frac{1 - k_a}{k_b} \tag{5}$$

where k_0 is the degree of counterion binding for mixed micelles, k_a is the slope of the concentration curve when the concentration is higher than the CMC and k_b is the slope of the concentration curve when the concentration is lower than the CMC.

2.3.2. Micellar-enhanced ultrafiltration

Synthetic wastewater-containing cadmium ions was prepared from cadmium nitrate and surfactants were added to the syn-

Table 1
Properties of surfactants.

Surfactants	Molecular structure	Molecular mass	CMC (g/l)	Source
Sodium dodecyl sulfate (SDS)	$C_{12}H_{25}NaSO_4$	288.38	2.16	Tinajin Miou chemical factory in China
Polyoxyethyleneglycol dodecyl ether (Brij35)	$C_{12}H_{25}(C_2H_4O)_{23}OH$	1189	0.36	Koch Light Laboratories in England
Polyoxyethylene octyl phenyl ether (TritonX-100)	$C_8H_{17}C_6H_4(C_2H_4O)_8OH$	628	0.12	Koch Light Laboratories in England