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Technical Note

Micellar-enhanced ultrafiltration (MEUF) with mixed surfactants for removing Cu(II) ions

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Abstract

A nonionic surfactant, polyoxyethylene Octyl phenyl ether (Triton-X), is added to a micellar-enhanced ultrafiltration process to lower the critical micellar concentration (CMC) of an anionic surfactant, sodium dodecyl sulfate (SDS). The effects of adding Triton-X on the copper removal efficiency, the permeate SDS concentration, the copper binding capacity of SDS micelles, and membrane fouling are investigated.

Our results show that the addition of Triton-X at concentrations greater than its CMC can reduce the SDS dosage required for effective Cu removal, and at the same time, minimize the permeate SDS concentration. Although, no adverse effect on the copper binding capacity of SDS micelle is observed by the addition of Triton-X, the membrane fouling is worsen. Cleaning the membrane with DI water allowed restoring the membrane flux, indicating that the fouling caused by Triton-X was reversible.

Keywords: MEUF; Mixed surfactants; Copper removal; Membrane fouling

1. Introduction

Removal of heavy metals by micellar-enhanced ultrafiltration (MEUF) process was extensively investigated in the past decade (Huang et al., 1994a,b; Ahmadi et al., 1995; Liu et al., 2004). Metal is removed through adsorption onto surfactant micelles, which form at the surfactant concentrations greater than its critical micellar concentration (CMC), followed by subsequent removal of the metal–micelle complexes by ultrafiltration. Micelles of anionic surfactants are applied for removing positively charged heavy metals with the metal removal efficiency depending on the characteristics and concentrations of the metals and surfactants, solution pH and compositions, ionic strength, and parameters related to membrane operation (such as transmembrane pressure, filtration flow rate, membrane pore size, etc.) (Huang et al., 1994a,b; Akita et al., 1997; Gzara and Dhahbi, 2001; Liu et al., 2004).

Huang et al. (1994a) indicated that two important criteria, namely surfactant concentrations of greater than its CMC and surfactant to metal molar ratio (S/M ratio) of greater than certain value (denoted by these authors as the critical S/M ratio), have to be met to achieve an efficient metal efficiency by MEUF. For SDS which has CMC of 8.27 mM, the critical S/M ratio is 5 for obtaining metal removal efficiency of greater

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than 99% for the most of metals investigated (Huang et al., 1994a).

To treat industrial wastewater containing very low metal concentration using MEUF, meeting above-mentioned criteria makes the process less attractive. For example, treating wastewater containing Cu(II) concentration of 0.2 mM which is the median Cu(II) concentration in the wastewaters from electroplating industry in Taiwan according to the survey by the Eco-Technology Development Center, CTCI Foundation, Taipei, Taiwan, meeting the critical S/M ratio of 5 will only require 1 mM of SDS concentration. However, SDS concentrations greater than 8.27 mM, i.e. CMC of SDS, will be needed for meeting the second criterion. Therefore, possible ways of reducing the CMC values will be of interested in applying MEUF for treating industrial wastewater containing metals with relatively low concentration.

To overcome the above-mentioned problem, one can increase ionic strength of the solution or add nonionic surfactant as it has been shown that the CMC value of a surfactant can be reduced by increasing ionic strength of the solution or adding nonionic surfactant (Fillipi et al., 1999; Tung et al., 2002; Zhao et al., 2005). Increasing ionic strength will increase the concentration of total solids and conductivity in the effluent. On the other hand, addition of nonionic surfactant such as polyoxyethylene octyl phenyl ether which is trademarked as Triton™-X 100, can be a very effective way for lowering the CMC of SDS without increasing total solids content.

The idea of lowering the CMC of anionic surfactants by adding nonionic surfactant has been demonstrated and applied in the MEUF processes for treating metal alone or simultaneous removal of metal and organic contaminants (Park et al., 1989; Fillipi et al., 1999; Tung et al., 2002; Zhao et al., 2005). For example, Tung et al. (2002) has studied the application of SDS/Triton-X mixtures for simultaneously removal of Cu(II) and phenol. However, the effects of nonionic surfactant on the membrane fouling, the permeate SDS concentration, and the copper binding capacity of SDS micelles for metal, have not been reported in these studies. Therefore, the objectives of this study are to investigate the effects of Triton-X on (1) the metal removal efficiency, (2) the permeate surfactant concentration, (3) the copper binding capacity of SDS micelles, and (4) membrane fouling.

2. Experimental section

2.1. Chemicals

All chemicals were of reagent grade. The synthetic samples containing Cu(II) ions were prepared from 1000 mg l^{-1} ICP standard (J.T. Baker). An anionic surfactant, SDS, was purchased from ACROS, and a nonionic surfactant, Triton-X, was obtained from Sigma-Aldrich. Both surfactants were diluted with deionized water (DI water) to pre-determined concentration. HCl and NaOH, both having concentration of 1 N, were used for pH adjustment.

2.2. Apparatus and experimental methods

All experiments were carried out at room temperature (around 25 °C) in a batch stirred cell (Amicon 8200 stirred cell, Millipore, USA), with a 150-ml solution loaded initially. The solution was mixed with a stirring bar driven by a magnetic motor at 100 rpm. The test solution was placed in a water bath (fixed 25 ± 1 °C) for at least one hour, before it was loaded in the stirred cell. The applied pressure was controlled at 206.8 kpa (30 psi) by a compressed nitrogen gas tank. A hydrophilic UF membrane (YM10, Millipore, USA) which has a nominal molecular weight cutoff of 10 kDa was used. The clean water permeate flux, J_w, of new membrane was measured before each test, and was around 120 $dm^3\,m^{-2}\,h^{-1}$ after 5 min of operation at applied pressure of 206.8 kpa. Membrane was sonicated in DI water for 10 min after each experiment and was repeatedly used if the clean water flux was deviated within 5% of 120 $dm^3\,m^{-2}\,h^{-1}$. All experiments were carried out at pH 5.0 adjusted with NaOH and HCl. The pH in the feed and permeate were measured with an Orion pH meter.

2.3. Analyses

Three repeated tests were conducted for each experimental condition. The average permeate flux was calculated based on the time needed for collecting the first 50 ml of permeate, corresponding to a volume concentrated factor (VCF) of 1.5. The VCF is defined in Eq. (1) (Huang et al., 1994a)

$$\mathrm{VCF} = \frac{V_{\mathrm{ini}}}{V_{\mathrm{fin}}} \tag{1}$$

where V_{ini} and V_{fin} are the volumes of solution in the batch stirred cell initially and at the end of the test, respectively. Since the variation of the permeate Cu concentration is quite small during the course of filter run (data not shown), all 50 ml of permeate was collected and mixed for Cu concentration analysis using a flame atomic absorption spectrometry (Hitachi Z6100, Hitachi, Tokyo, Japan).

Initially, SDS concentration was analyzed according to the APHA Standard Method 5540C where methylene blue active substances (MBAS) were formed by adding methylene blue to the samples containing anionic surfactants, followed by extraction of MBAS using chloroform and colorimetrically analysis at wavelength of 652 nm (APHA, 1999). Since the analysis was interfered