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Separation of phenol from various micellar solutions using MEUF

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ABSTRACT

The separation of phenol from micellar solutions using micellar-enhanced ultrafiltration (MEUF) with polyether sulfone membrane was studied. Anionic sodium dodecylulfate (SDS), nonionic triton X-100 (TX-100) and three cationic surfactants, cetyl trimethyl ammonium bromide (CTAB), octadecyldimethylammonium bromide (OTAB) as well as cetylpyridinium chloride (CPC) were used. Several important parameters including distribution coefficient (D), concentration of phenol dissolved in the micelles (O_m) and concentration of surfactant in micelle phase (S_m) were determined to evaluate separation efficiency of phenol from various surfactant micelles with different hydrophilic head group and hydrophobic tail length. It was found that the rejection and D of phenol examined with CTAB micelles were the highest, while that with TX-100 were lower than SDS at feed surfactant concentration of 10 mM. The rejection and D of phenol as well as O_m with three cationic surfactants could be ranked as follows: OTAB > CTAB > CPC, which was contrary to the permeate flux. The rejections of three surfactants were extremely similar with the range of feed surfactant concentration from 1 mM to 30 mM, and S_m examined with OTAB and CPC was higher than that with CTAB.

1. Introduction

The wastewater containing phenol from different chemical and petrochemical industries is discharged into the environment we live in. The great adverse effect of wastewater cannot be ignored. Due to their toxicity, the presence of these compounds in wastewater has directly threatened human health and the ecosystem stabilization. Conventional separation processes, such as distillation, extraction and adsorption, fail to treat wastewater containing organic solutes effectively due to energy–intensity. In addition, traditional ultrafiltration is also ineffective in removing the dissolved low molecular weight organics such as phenol from water [1]. Thus, developing a low energy separation process has been becoming an urgent problem to be studied and solved.

Micellar-enhanced ultrafiltration (MEUF) is a promising separation technique that has been shown to be effective in removing small organic molecules [1–4] and toxic dyes [5–8] as well as heavy metals [9–12] from synthetic produced water. This method has such characters as low-press, better treating efficiency and simple operating, but the main shortcoming is membrane fouling and concentration polarization. The main shortcoming is membrane fouling and concentration polarization which severely limit the MEUF process. A decrease in the membrane permeability results from enhanced membrane fouling effects caused by gel layer formation and plugging of membrane pores. Concentration polarization may promote the convective transport of molecules through the membrane and decrease the filtration efficiency.

In MEUF process, as soon as the surfactant concentration in the aqueous stream exceeds a certain standard, namely critical micellar concentration (CMC), a great number of micelles with aggregate diameters larger than membrane aperture are formed due to aggregation of surfactant monomers. Micelles with solubilizing contaminants are rejected when aqueous stream passes through an ultrafiltration membrane [13]. In consequence, contaminants concentration in permeate stream is much lower than that in initial stream.

Especially, some studies about the MEUF of single phenol and multi-solute systems including phenol in aqueous stream have also been carried out. In the case of MEUF of single phenol system, these researches mainly emphasized the important operating factors of affecting the performance of MEUF in the removal of phenol, such as phenol and surfactant concentrations, operating pressure, temperature, electrolyte, and cross flow rate [1,14,15]. Kim et al. [1] have analyzed the effects of nonionic surfactants with different numbers of methylene groups and oxyethylene groups on the difference of rejection between phenol and benzene. However, the differences of separation of phenol in various surfactants micellar

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solutions (anionic, cationic, nonionic) have not been investigated. In addition, simultaneous removal of phenol and heavy metals (Cr^{3+}, Cu^{2+}) in micellar-enhanced ultrafiltration process have also been reported [16,17]. Witek et al. [16] indicate that the presence of Cr^{3+} in the system does not influence the rejection of phenol.

The aim of this work is to study separation efficiency of phenol from various surfactant micelles with different hydrophilic head group and hydrophobic tail length. In present work, several parameters including distribution coefficient (D), concentration of phenol dissolved in the micelles (O_m) and concentration of surfactant in micelle phase (S_m) were determined. Distribution coefficient is an important parameter of MEUF, which reflects relative affinity of the organic for micelles and measures the tendency of organic to solubilize in micelles. A high D value indicates that surfactants can bind a large number of organics leading to the increase in separation efficiency of organics. O_m and S_m, defined as the subtraction of solute concentrations in the retentate and permeate, contribute to understanding the distributions of organic and surfactant between water and micelle phases. In addition, these parameters also reflect the distributions of organic and surfactant in the retentate and permeate, which benefit further treatment of solutes such as recovery of surfactants to avoid secondary pollution.

In this study, phenol was chosen as a model of wastewater with organic contents. Negatively charged SDS, positively charged CTAB and uncharged TX-100, as three representative types of surfactants, were adopted in MEUF experiments. It was found that phenol interacted strongly with oppositely charged CTAB surfactant due to electrostatic interaction. Then, three cationic surfactants (CPC, CTAB, OTAB) with group difference, i.e., the same hydrophobic tail length but different hydrophilic head group and vice versa, were used to investigate effectiveness of removing phenol by MEUF.

2. Experimental

2.1. Chemicals

Anionic surfactant Sodium dodecylulfate (SDS, analysis purity) was purchased by Fuchen Chemical Reagent Factory, Tianjin, China. Nonionic surfactant TritonX-100 (TX-100, chemistry purity) and three cationic surfactants Cetylpyridinium chloride (CPC, analysis purity), cetyl trimethyl ammonium bromide (CTAB, analysis purity) and Octadecyldimethylammonium bromide (OTAB, purity 99%) were obtained from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. The properties of surfactants were shown in Table 1 [18–22]. Phenol (analysis purity) was purchased from Huihong Reagent Co., Ltd., Hunan, China. The chemicals were used without further purification. Distilled water was used in all experiments.

2.2. Membranes

A hydrophobic membrane made of polyether sulfone with molecular weight cut-off (MWCO) of 5 k, supplied by Yidong Membrane Engineering Equipment Ltd., Dalian, China, was used in all experiments. The effective area of the membrane is 0.4 m^2 and the pH range is 2–12. The maximum permissible temperature is 50 °C.

2.3. Methods

In the preparing process of feed solution, pre-determined amount of phenol and surfactants were weighted and dissolved into 3000 mL distilled water. After stirred fully and settled for 30 min to allow for formation of micelles and solubilization of phenol adequately, then the solution was treated through the ultrafiltration membrane. All of the experiments were carried out at room temperature of 26 ± 2 °C and a constant operating pressure of 0.15 MPa. The retentate was recycled into the feed tank and the permeate samples as well as the retentate samples were collected at certain intervals. In the experiments, the concentration of phenol added to the solution was kept constant at 1 mM while surfactants concentrations were varied from 1 mM to 30 mM. At the end of the ultrafiltration experiments, the concentrations of phenol and surfactants in permeate and retentate samples were determined. The schematic diagram of ultrafiltration installation was shown in Fig. 1.

After each run, the membrane was cleaned with tap water without pressure for about 1 h, and then the distilled water was filtered to wash away most of deposited surfactants and phenol at low pressure for 20 min. Finally, the membrane permeability was checked to ensure that it returned to the initial water flux within 95%.

2.4. Analysis

In aqueous solution of SDS/CTAB/OTAB and phenol, phenol concentration in the permeate and retentate solutions was determined by a UV spectrophotometer (Shimadzu UV-2550) at a wavelength of 270 nm.

The concentrations of CTAB and OTAB were analyzed by colorimetric method with methyl orange. The samples were measured by UV spectrophotometer at the wavelength of 470 nm, 509 nm to analyze the concentrations of CTAB and OTAB, respectively. In aqueous solution of TX-100/CPC and phenol, the concentrations of phenol and CPC were determined by HPLC having a 25 cm × 0.46 cm column Spherisorb ODS2 (particle size 5 μm). Operating conditions were as follows: mobile phase acetonitrile/water (75/25 by volume), injection volume 20 μL, flow rate 1 mL/min, temperature 30 °C, the UV wavelength 250, 270 nm for CPC and phenol, respectively.

2.5. Calculations

The rejections of phenol and surfactant as well as permeate flux are used to assess the filtration efficiency. Permeate flux as one of

Table 1
Characteristics of surfactants.

Name	MW [a] (g/mol)	CMC (mM)	HLB [b]	Aggregation number [c]	MW of micelle [d] (g/mol)	Solubility [e]
SDS	288	8.2	40	80	23040	s
TX-100	625	0.24	13.5	140	87500	s
CPC	358	0.88	26	95	34010	s
CTAB	364	0.9	15.8	–	–	s
OTAB	392	0.65	–	–	–	s

[a] Mean molecular mass according to the product declaration.
[b] HLB means hydrophile–lipophile balance.
[c] Aggregation number of micelle.
[d] Mean molecular mass of micelle.
[E] s means readily soluble in water.