CONTINUOUS SEPARATION OF PHENOL FROM AN AQUEOUS STREAM USING MICELLAR-ENHANCED ULTRAFILTRATION (MEUF)

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Micellar-enhanced ultrafiltration has been carried out to investigate the separation of phenol from an aqueous stream via hollow fiber membranes. First, phenol is solubilized into the micelles of cationic surfactant such as hexadecyltrimethylammonium chloride (CTAC) and hexadecylpyridinium chloride (CPC), and then the micellar solution is treated continuously through an ultrafiltration membrane module. In the present study we examine the effects of retentate concentration, molecular weight cut-offs, molar ratios of surfactant to phenol and other operating conditions on the rejection efficiency. The results show that the concentration of phenol in the permeate rapidly decreases as the surfactant aggregates to form micelles beyond its critical micelle concentration. Further, the rejection of phenol and surfactant by the membrane is enhanced when the operating condition is favorable to formation of a gel layer at the surface of the membrane which provides the presieving effect. Formation of a gel layer becomes pronounced when either the flux ratio of permeate to retentate or the micelle concentration in the feed increases.

Introduction

Conventional separation techniques, such as distillation and adsorption are so inefficient in the economic sense that they cannot be used to remove dissolved low-molecular-weight organics and multivalent ions from wastewater streams. Also, direct membranes separation process such as ultrafiltration cannot be used because of low rejection of the solutes since the size of the organics is much smaller than the pore size of the membrane. Micellar-enhanced ultrafiltration (MEUF) was firstly proposed by Scamehorn et al.1, 4, 5, 7, 19 to remove dissolved organics present in small or trace quantities from aqueous solution. Surfactants which consist of hydrophilic head and hydrophobic tail groups have the characteristics to form self-aggregates, so-called micelles, composed of 20-100 surfactant molecules only when they are present above the critical micelle concentration (CMC). Dissolved organics tend to be soluble in the micelles. Usually, the more hydrophobic the organic solute is, the more organic solute can be dissolved in the micelle. Aqueous solution containing the micelle with organic solutes is then treated in an ultrafiltration membrane having a pore size small enough to prevent the micelle from permeating through it. As a result, very pure permeate can be obtained while the organic solutes are concentrated in the retentate. In addition, MEUF has been found to be a very effective separation process for the removal of multivalent ions such as zinc, cupric and nitrate ions from aqueous streams.2, 14, 19, 21. Whereas organic solutes are soluble in the core and palisade region of the micelle, multivalent ions have a tendency to bind on the micelle surface having a charge opposite to that of the target ions.6

Recently, basic concepts of the MEUF have been extended to colloid-enhanced ultrafiltration (CEUF), including ligand-modified ultrafiltration (LMUF)7, polyelectrolyte-enhanced ultrafiltration (PEUF)18, 20 and ion-expulsion ultrafiltration (IEUF)1, 12. LMUF can provide high selectivity for the cupric ion with the aid of a copper-specific ligand, N-n-dodecyl-iminodiacetic acid. According to the results of Scamehorn et al.7, up to 99.2% selective rejection of the cupric ions was obtained by solubilizing the cupric ions complexed with the ligand into the micelles which are formed by hexadecylpyridinium chloride (CPC). The separation mechanism of the IEUF is based on the repulsive force of water-soluble polyelectrolytes such as sodium poly (styrenesulfonate) (PSS) or micelles composed of cationic surfactant, CPC, having like charges with those of the multivalent ions to be removed. Oppositely charged multivalent ions are expelled to the permeate side through the ultrafiltration membrane while the micelles or polymer macroions are blocked by the membrane on the basis of size exclusion. In PEUF, metal ions such as cupric and zinc ions can be separated by their binding around ionic colloids such as
PSS having charges opposite to those of the target ions. Although CEUF has found various applications in the removal of low-molecular-weight organic compounds and multivalent ions, researches to eliminate concentration polarization and thereby to identify the optimum operation conditions have not been fully undertaken. Furthermore, since most MEUF experiments have been carried out in a batch-type stirred cell membrane module, continuous separation using hollow fiber (or other cross-flow) membrane should be carried out for potential application as one form of colloid-enhanced ultrafiltration. The primary thrust of our research thus lies in the investigation of the effects of the operating conditions on the membrane performance. The operating conditions considered here are the pressure differences, the molecular weight cut-offs of the hollow fiber membranes, and the molar ratios of surfactant to solute. From the dependency of the flux and the rejection on the pressure difference and feed concentration of micellar solution we can predict qualitatively the effect of the concentration polarization, which has been one of the most serious obstacles to practical application of the membrane process.

1. Experimental

1.1 Materials

Among the numerous kinds of surfactants commercially available, we selected two kinds of cationic surfactants, CTAC and CPC which have the same length of hydrocarbon chain, 16 methylene groups with different head groups, for use as surfactants in the separation of phenol. All surfactants were of 98\% purity and were used as received. CPC was obtained from Aldrich Chemical Co. CTAC in the solution state was purchased from Fluka Co. CMC of the CTAC was reported to be 1.3 mM and CPC 0.9 mM\(^{15}\). ACS-grade phenol (Sigma Co.) was chosen as the low-molecular-weight organic compound to be removed from the aqueous stream. Distilled and deionized water was used throughout the experiment.

Among the most important parameters for the present study of MEUF are the sizes of micellar aggregates formed by the surfactant. The micelle size can be determined either theoretically or experimentally\(^{8, 9, 17, 22}\). A simple method for determining the micelle radius was proposed by Tanford based on the length of the hydrocarbon chain and the head group diameter\(^{16, 22}\). Recently, Issid et al. determined the micelle size of lithium dodecylsulfate by quasi-elastic light scattering in combination with the Stokes-Einstein relation and showed that the Tanford relation can provide a fairly accurate estimation of the micelle size\(^{9}\). Thus, we followed the Tanford relation to evaluate the size of the CTAC micelle. Upon calculating the lengths of the hydrocarbon chain of CTAC and adding the diameters of trimethylammonium and chloride ions, a value of 53.9 Å was obtained for the diameter of the CTAC micelle. Similarly, the estimated size of the CPC micelle was shown to be of the same order. The size of the CTAC micelle was also determined experimentally and the mean diameter was reported as 45.2 Å\(^{8}\). In addition, the micelle size can be deduced from the size of a macromolecule which has the same order of molecular weight as the micelle. For example, the aggregation number of CTAC micelles was determined experimentally by Roelants et al.\(^{17}\). According to their results, the aggregation number is 80-115 in the range of CTAC concentration used in our experiments. Thus, the equivalent molecular weight of the micelle is about 26,000-37,000.

The membranes employed here were made of polysulfone (Amicon Co.). For practical purposes, filtration membranes are usually classified by the molecular-weight cut-off (MWCO). We selected the membranes with three different MWCO’s (3,000, 10,000, and 30,000). Their pore sizes ranged from 15 Å to 40 Å in diameter according to the manufacturer’s data. The upper limit of pore size (or MWCO) should be smaller than the size (or equivalent molecular weight) of the micelle to be filtered. Thus, we chose the membrane with MWCO 30,000 as the upper limit. A membrane cartridge was composed of 250 hollow fibers of internal diameter 0.5 mm. The length of the cartridge was 20.3 cm and its surface area was 0.06 m\(^2\).

1.2 Ultrafiltration runs

The ultrafiltration runs were carried out in hollow fiber ultrafiltration equipment. The continuous ultrafiltration system consisted of feed solution reservoir, pump, rotameter and hollow fiber membrane module. A schematic diagram of the ultrafiltration system is shown in Fig.1. As recommended by the manufacturer, ultrafiltration experiments were carried out at a pressure below 1.8 kg/cm\(^2\), which was the critical operation pressure for the hollow fiber membrane. Transmembrane pressure difference was controlled by the back-pressure valve. Flux measurements for the distilled water and the micellar solution were carried out from low to high pressure difference and from low to high concentration. Operating pressure differences were varied from 0.25 kg/cm\(^2\) to 1.75 kg/cm\(^2\) at increments of 0.25 kg/cm\(^2\). All measurements and samplings were made 30 minutes after the steady state of filtration was established.
The observed rejection, \( R_{\text{obs}} \), is defined by

\[
R_{\text{obs}} = 1 - \frac{C_p}{C_f}
\]

where \( C_p \) and \( C_f \) are the permeate and the feed concentrations, respectively. Before the flux was measured, the hollow fiber membrane was washed thoroughly using distilled water in order to remove the fouling. When we changed from one feed solution to another of different concentration, we repeated washing and backflushing in order to minimize the effect of the preceding experiments. Feed solution of 2,000 mL volume was placed in the reservoir for each ultrafiltration run and was fed into the membrane module at a constant rate of 40.68 mL/min. In the present work, most of the experimental data were obtained with the molar ratio of surfactant to phenol fixed at 5. As we shall see in Figs. 9 and 10, where the rejection of phenol is plotted versus the surfactant concentration, the rejection increases rapidly as the surfactant concentration increases beyond its CMC. However, the rate of increase in the rejection is apparently reduced as the molar ratio of surfactant to phenol reaches around 5. This leads us to the choice of the molar ratio 5 for the effective separation of phenol.

The concentrations of the surfactant and the phenol were determined by HPLC using UV detector (Waters 486). CPC was detected at 260 nm and CTAC at 194 nm. The mobile phase was composed of HPLC-grade acetonitrile and water at a ratio of 7:3, and C18 µBondapak column was used.

2. Results and Discussion

We used membranes with the molecular weight cut-offs of 3,000, 10,000 and 30,000 to investigate the effect of pore size on permeate flux and concentration polarization. Variations of the permeate fluxes were monitored with a lapse of time from 30 min to 180 min as shown in Fig. 2. Permeate fluxes in MEUF were kept almost constant except those of MWCO 30,000 mem-

brane. A slight decrease of flux with time in MWCO 30,000 membrane indicates that membranes having large pores are vulnerable to clogging by micelles of comparable size, which we will discuss in detail later.

Permeate fluxes of the distilled water and micellar solution were measured also as the transmembrane pressure difference (\( \Delta P \)) across the membrane was increased from 0.25 kg/cm² to 1.75 kg/cm² at increments of 0.25 kg/cm². The feed solutions we used were composed of phenol and surfactant with a fixed molar ratio 5 of surfactant (CTAC or CPC) to phenol. However, we adopted five different micellar solutions to examine the existence of solute(surfactant/phenol) concentration. For illustrative purposes, the fluxes are plotted versus the pressure difference in Figs. 3 and 4, for the membranes with MWCO 3,000 and 30,000, respectively, which correspond to the two extremes of MWCO considered in this work. As expected, the flux of pure water is increased in proportion to the pressure difference regardless of MWCO of the membrane to be used. For micellar solutions, on the other hand, the linear dependence of flux on the pressure difference is shown to be valid only in the small \( \Delta P \) limit and the rate of increase of the flux in
response to change in the pressure difference is gradually reduced in the region of large $\Delta P$. Departure from the linearity of flux on the pressure difference in the large $\Delta P$ region is conspicuous for a membrane with large pores. It can be seen from Fig. 4 that the flux remains almost unchanged as the pressure difference is increased further beyond $\Delta P = 1.5$ kg/cm$^2$ for the membrane with MWCO 30,000. It is also noteworthy that the flux of the micellar solution exhibits a strong dependence on the feed concentration. As the feed concentration (or micelle concentration) increases, the total permeate flux decreases. This can be simply explained by the fact that the relatively strong osmotic pressure developed by the high concentration of the solute adjacent to the membrane surface causes a reduction in the net driving force, i.e., the net effective pressure difference across the membrane.

The comparison of the fluxes for the membranes of different MWCO’s can be interpreted in terms of the variation of permeability. According to Darcy’s law for porous media flow, the permeability ($\kappa$) is defined by

$$\kappa = \mu \ln \left( \frac{D_o}{D_i} \right) \frac{Q}{2\pi L \Delta P} \tag{2}$$

in which $D_o$ and $D_i$ are the outer and inner diameters of the hollow fiber respectively, $L$ the effective length of the hollow fiber, $\mu$ the viscosity of the fluid and $Q$ denotes the volumetric flow rate across a single fiber-membrane surface. As noted from Figs. 3 and 4, the flux is increased linearly in proportion to the pressure difference at the low $\Delta P$ limit, which clearly indicates that the permeability is independent of $\Delta P$ at this limit. At the high $\Delta P$ limit, however, the rate of increase of the flux with $\Delta P$ is considerably reduced, i.e., the permeability is a gradually decreasing function of the pressure difference. This is clear evidence for the formation of a gel layer (or concentration polarization) which reduces the permeate flux of the micellar solution. The concentration polarization becomes pronounced as the micelle density (or equivalently surfactant concentration) increases. It can also be seen from Figs. 3 and 4 that saturation of the permeate flux due to concentration polarization at the high $\Delta P$ limit becomes facilitated as the MWCO of the membrane increases up to 30,000, which is the largest value considered in this study. This is due to the fact that as the pore size increases, the permeate flux becomes large relative to the retentate flux for a given pressure difference, which is responsible for the concentration polarization.

We now consider the effect of pore size on the rejection of phenol, which is also an important parameter in addition to the permeate flux for the practical application of MEUF. In Fig. 5, the observed rejection of phenol is illustrated as a function of the feed phenol concentration for the three choices of MWCO, but with the molar ratio of surfactant to phenol still fixed at 5. It can be seen that the smaller the pore size is, the higher rejection of phenol when the retentate concentration is relatively low. However, at the high phenol and surfactant concentration in the retentate, the rejection exhibits a very weak dependence on the molecular weight cut-off (MWCO) or pore size of membrane. This is due to the fact that a gel layer is formed at the membrane surface when the solute (micelle) concentration is higher than a certain critical value as discussed earlier. Further, it is noteworthy that the rejection of surfactant by a membrane with large pores tends to be higher than that for small pores as the surfactant and phenol concentrations in the retentate increase, as seen in Fig. 6. This is contrasted with the rejection behavior at the low retentate concentration limit in which a membrane with small pores rejects phenol and surfactant more effectively than a membrane with large pores. This is owing to the presieving effects induced by the gel layer formed at the membrane surface or the higher degree of concentration.
polarization. It is evident, from the preceding discussion, that the presieving effect becomes pronounced when either the micelle density or the flux ratio of permeate to retentate increases. Thus, for a given feed concentration, the large MWCO membrane with high ΔP is favorable to the presieving effect. The presieving effect on phenol under high retentate concentration is relatively small compared with the effect on the surfactant (CTAC) as shown in Figs. 5 and 6.

Selection of the surfactant is important for the rejection efficiency, which depends on the solubilization capacity of the micelle. Cationic surfactant has been reported to be adequate for the MEUF so far as CMC, micelle size and phase transition are concerned. In our study, CTAC and CPC were chosen as surfactants for the separation of phenol. CTAC and CPC have the same carbon numbers in the hydrophobic tail part while they are different in the molecular structures of their hydrophilic head groups. The degree of solubilization of aromatic solubilizes is known to be influenced critically by the type of head group of the surfactant. The large solubilization capacity of the cationic surfactant-forming micelles for the aromatic hydrocarbons is due to the attractive interaction between π-electron cloud of arenes such as phenol and positively charged head groups (quaternary ammonium groups for instance). Comparison between the results in Figs. 5 and 7 shows that the difference in the solubilization capacity for phenol exists even among the cationic surfactants having positively charged head groups. When CTAC was replaced by CPC as a surfactant for micellization, the general features for the CTAC system were shown to be preserved. Although the rejection of CTAC is slightly lower than that of CPC, CTAC is more effective than CPC in the rejection of phenol. Under the same pressure difference, 1.5 kg/cm², CPC can be rejected up to 99% and CTAC up to 95.3%. However, phenol can be rejected up to 83.3% using CTAC, which is considerably more effective than the CPC system in which the phenol rejection is only up to 74.8%, as seen in Fig. 7. This is because the interaction between the quaternary ammonium head group and phenol is a little stronger than that between the pyridinium head group and phenol.

Let us then examine the rejection of phenol and CTAC as a function of the transmembrane pressure difference. In Fig. 8, the observed rejections of phenol and CTAC are plotted versus the pressure difference (ΔP) for the membranes with MWCO 3,000 and 30,000. The feed concentrations of phenol and CTAC are fixed at 10 mM and 50 mM respectively. It can be easily seen from Fig. 8 that the rejections of phenol and CTAC are less sensitive to the pressure difference ΔP than the flux. Although the rejection of surfactant increases gradually with ΔP due to the presieving effect of a gel layer, the enhancement of phenol rejection by increase in ΔP is far below our expectation. This can be explained as follows; first, the formation of a gel layer inhibits CTAC more effectively than phenol from permeating owing to the large difference in their sizes; second, in this particular case the feed concentration is sufficiently high that the presieving effect for phenol is almost saturated, as seen in Fig 7.

Finally, we consider the effect of molar ratio of CTAC to phenol on the rejections of phenol and CTAC. First, we examine the effect of CTAC on phenol rejection when the surfactant is present in the feed below its CMC. The results are shown in Fig. 9 in which the concentration of phenol in the permeate is plotted as a function of the feed concentration of CTAC ranging from 0 to 10 mM with the feed concentration of phenol fixed at 10 mM. Thus, in this plot the molar ratio of surfactant to phenol varies from 0 to 1. It can be seen easily from Fig. 9 that in the absence of CTAC, or equivalently with no CTAC-micelle present in which phenol can be soluble, most of the phenol permeates through the membranes. Further, as expected, the phenol rejection is almost inde-
pndent of the MWCO of the membrane in the absence of CTAC. However, the membranes we employed can still reject phenol as much as 4.4%-4.9%. The possible explanation is twofold; first, the distribution of pore sizes is nonuniform and the very small pores can provide resistance to phenol permeation; second, our system is not a total filtration since a part of the solution flows out as a retentate that does not experience any resistance. It should also be noted that the rejection remains unchanged until the CTAC concentration reaches 2.5 mM where the molar ratio is 0.25. Although the concentration 2.5 mM is certainly above the CMC of CTAC, enhancement of phenol rejection is not observed due to the small molar ratio of CTAC to phenol. It is thus evident that the solubilization capacity of the micelles is too small for the molar ratio of 0.25.

When the concentration of CTAC is increased further, phenol is solubilized in the palisade or interfacial region of the micelle. After the solubilization capacity of the micelle is saturated, phenol tends to bind to the outside of the micelle and the micelle begins to transform its shape from spherical to ellipsoidal shape (10). In Fig. 10, the rejection of phenol is plotted as a function of the molar ratio of CTAC to phenol for a membrane with MWCO 30,000. As noted from Fig. 10, the rejection of phenol rapidly increases up to 0.763, as the molar ratio reaches 2.5. Beyond the molar ratio of 2.5, the rate of increase in the rejection of phenol is gradually reduced. Finally, when the molar ratio becomes larger than 10, further increase in the surfactant concentration hardly contributes to the enhancement of phenol rejection. Although the corresponding results are not reproduced in this figure, the general features of phenol rejection discussed above for MWCO 30,000 are preserved for membranes with MWCO 3,000 and 10,000.

Conclusions

Continuous separation of phenol via ultrafiltration was carried out in hollow fiber membrane equipment in order to elucidate the effects of concentration polarization and MWCO's on rejection efficiency. The dependency of rejection efficiency and permeation flux on operating conditions such as pressure difference, time, feed concentration and molar ratio of surfactant to phenol was examined, using hollow fiber membrane with three different MWCO's. Our research leads to the following conclusions.

1) The concentration polarization becomes pronounced as either the micelle density or the flux ratio of permeate to retentate increases. Thus, for a given feed concentration the presieving effect induced by the gel layer on the rejections of phenol and surfactant is enhanced as either the pore size of membrane or the transmembrane pressure difference becomes large.

2) When the feed concentration is relatively low, the smaller pore size is the more effective in rejection of phenol. However, the rejection of phenol exhibits a very weak dependency on the MWCO's at the high retentate concentration, where the presieving effect is saturated.

3) Rejection of surfactant for the membrane with large pores tends to be higher than that for small pores as the feed concentration of surfactant increases. The presieving effect is much more noticeable for the rejection of surfactant than for the rejection of phenol.

4) The rejection of phenol is strongly dependent on the molar ratio of surfactant to phenol. However, there exists an optimum molar ratio beyond which no further appreciable increase in the solubilization capacity of the micelles is possible.

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Nomenclature

\[ C_p \] = permeate concentration \([	ext{mol/m}^3]\)

\[ C_f \] = feed concentrations \([	ext{mol/m}^3]\)

\[ D_o \] = outer diameter of the hollow fiber membrane \([\text{m}]\)

\[ D_i \] = inner diameter of the hollow fiber membrane \([\text{m}]\)

\[ L \] = effective length of the hollow fiber membrane \([\text{m}]\)

\[ Q \] = volumetric flow rate across a single fiber-membrane surface \([\text{m}^3/s]\)

\[ R_{\text{obs}} \] = observed rejection

\[ \Delta P \] = transmembrane pressure difference \([	ext{kg/m}^2]\)

\[ \kappa \] = permeability \([\text{m}^2]\)

\[ \mu \] = viscosity of the fluid \([\text{Pa s}]\)

<Abbreviations>

CEUF = colloid-enhanced ultrafiltration

CMC = critical micelle concentration

CPC = hexadecylpyridinium chloride

CTAC = hexadecyltrimethylammonium chloride

IEUF = ion-expulsion ultrafiltration

LMUF = ligand-modified ultrafiltration

MEUF = micellar-enhanced ultrafiltration

MWCO = molecular weight cut-off

PEUF = polyelectrolyte-enhanced ultrafiltration

UF = ultrafiltration

Literature Cited


