Separation of o-Cresol Using Polymer/Surfactant Complexes

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Abstract: In the present work, Colloid-Enhanced Ultrafiltration (CEUF) was investigated using complexes formed by sodium dodecyl sulfate (SDS) and hydroxypropylcellulose (HPC) to test the performance of removing o-cresol (0.1 mM) from dilute aqueous solutions. In order to study CEUF, stirred-cell experiments were conducted and a dye solubilization method was employed. The results showed that the critical aggregation concentration (c.a.c) of SDS was about 2 mM for the HPC/SDS/water system. When the proposed system was employed for removing o-cresol, CEUF required very small surfactant concentrations, about 10% of the SDS concentrations normally used in MEUF. In addition, the rejection and permeate flux are strong functions of [SDS] and it is necessary to find the optimum SDS concentration when we operate CEUF.

Keywords: colloid-enhanced ultrafiltration, hydroxypropylcellulose, sodium dodecyl sulfate, o-cresol

1. Introduction

Micellar-enhanced ultrafiltration (MEUF) is a separation process using surfactants and membranes which can remove dissolved organic solutes or multivalent ions from water [1-5]. In MEUF, the surfactant can be selected depending on the target material to be removed. For the separation of organics in aqueous solutions, either a cationic or anionic surfactant can be used as long as the interior of the micelle contains a hydrocarbon chain and forms a hydrophobic environment. Then, organic solutes dissolve or solubilize in the micelles by hydrophobic association and interactions, in some cases, with the surfactant head groups. In most MEUF studies, cationic surfactants have been employed for the removal of organics due to the disadvantages of using anionic surfactants; that is small micelle size, high CMC, and relatively low solubilization capacity [2]. For example, the cationic surfactant hexadecylpyridinium chloride (CPC) was used for the removal of 4-tert-butylphenol [2], cresols [6] and phenol [4]. On the other hand, anionic surfactants must be employed for the removal of multivalent heavy metals, due to the separation mechanism. That is, the micelle has a highly negative electrical potential on the surface where the metal cations adsorb or bind due to electrostatic attraction. For these reasons, an anionic surfactant sodium dodecyl sulfate (SDS) was utilized in MEUF for the removal of Cu²⁺ [7], Zn²⁺ [3], and Cd²⁺ [8].

In a number of industrial operations, wastewater contains unacceptable concentrations of both dissolved organics and heavy metals. In order to remove the dissolved organics and metal ions (cations) simultaneously, it is essential to employ an anionic surfactant in MEUF. In fact, a study [3] was previously performed to test the ability of MEUF for the simultaneous removal of phenolics (phenol and o-cresol) and a divalent metal cation (Cu²⁺ or Zn²⁺). According to this study, the removal of the organic solute was not significantly affected by the presence of the metal and vice versa. This result is quite attractive since a single MEUF unit can replace two unit operations for the removal of both metals and organics. In operating MEUF, however, the monomeric or free surfactant

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molecules which are approximately equivalent to the critical micelle concentration (CMC) can penetrate through the membranes. This leakage of the surfactant is not favorable since we waste the surfactant to the permeate in MEUF. In addition, for the operation of MEUF, a relatively large concentration of surfactant should be used. Consequently, the economic feasibility of the MEUF process is strongly dependent on the ability to recover these surfactants. To solve this problem, it is necessary to minimize the leakage of the surfactant into the permeate. Another way may be the use of very small surfactant concentrations in the MEUF process. In this case, the recovery of the surfactant would be less important from an economic point of view.

Recently, colloid-enhanced ultrafiltration (CEUF) which was employed using polymer/surfactant complexes has been proposed by several workers [9,10] to solve the leakage problems. In these studies, water-soluble (anionic and cationic) polymers were added to the surfactant system and polymer/surfactant complexes were formed. Since the polymer can play the role of a "scavenger" for surfactant species that enter the permeate, the leakage of the surfactant could be reduced. More importantly, the formation of a polymer/surfactant complex occurs with lower concentrations of a surfactant (so-called critical aggregation concentration, c.a.c.) than the ordinary CMC. This phenomenon is economically advantageous since reducing the CMC of a surfactant results in a smaller monomeric surfactant concentration in the permeate. Actually, the previous study [9,10] shows that both molecular organic pollutants and surfactant ions could be effectively removed using ionic polymer/surfactant systems. To our knowledge, however, non-ionic polymers have not been employed for studying on the removal of organics by CEUF. In particular, when anionic surfactants are used with a non-ionic polymer, it is possible to remove organics and metal cations simultaneously. In other words, an anionic surfactant can form micelles (probably hemi-micelles) on the surface of the polymer. Metal cations are then adsorbed on the surface of the micelles and the organic solutes can be solubilized in the interior of the micelles. Therefore, the separation of both organics and metal ions from an aqueous stream can be attained with less surfactant leakage into the permeate.

In the present work, the performance of CEUF for the removal of organics was tested using the complex of a non-ionic polymer and an anionic surfactant. The study was performed as the first phase in researching the simultaneous removal of organics and metal cations. Stirred-cell ultrafiltration experiments were conducted as an evaluation method for the performance of CEUF. In addition, the interaction of the surfactant and the polymer was investigated using the dye solubilization method. In this study, selected was hydroxypropylcellulose (HPC) since cellulose and its derivatives are biodegradable and less toxic. o-Cresol was used as the target solute, and sodium dodecyl sulfate (SDS) was selected as the complex forming surfactant with the polymer.

2. Experimental

2.1. Materials

As the water soluble non-ionic polymers, two types of hydroxypropylcellulose (HPC) with a weight-average molecular weight of 400000 (Polymer I, TCI) and 100000 (Polymer II, Aldrich) were used. Stock solutions of HPC were dialyzed in tube membranes (Spectra/Por, Spectrum, MWCO: 12000) against Milli-Q water (Millipore) for 5 days to remove salts and other low molecular weight materials before the concentration was determined by drying the samples to a constant weight at 105 °C. Sodium dodecyl sulfate (SDS) and o-cresol were obtained from Sigma Chemical Co. They were more than 99% pure and were used as received. Oil Orange S5 (benzophenone) for the solubilization study was obtained from Aldrich.

2.2. Dye Solubilization Measurements

The solubilization of the dye Oil Orange S5 was studied for the determination of the solubilization power of the complex and the critical aggregation concentration (c.a.c.) of SDS. First, aqueous solutions of HPC/SDS with different concentrations of SDS with a fixed polymer concentration were prepared. An excess of dye was then added, and the solutions were equilibrated for 2 days at 30 °C in a shaker bath. The excess of dye was separated off by centrifugation and the absorbance of the supernatant was spectrophotometrically measured at 495 nm.

2.3. Ultrafiltration Experiments

The ultrafiltration experiments were performed in a 400 mL batch, stirred cell (Fisher Scientific). The cell was wrapped in tubing containing circulating water to maintain a temperature at 30 °C. The pressure was maintained by nitrogen gas at 200 kPa (29 psig). The membranes were acetate cellulose, 76 mm diameter, membranes (Molecular/por Type C) from Spectrum. The molecular weight cut-off (MWCO) of the membranes used in the ultrafiltration runs was 20000 and the flux of pure water through the membranes was 40 L/h·m². Initially, the cell was filled with 300 mL of the feed solution containing known
concentrations of o-cresol (in some cases, Cu²⁺), HPC, and SDS. The agitation speed was maintained at approximately 840 rpm. 40 mL of the permeate was collected and the average permeate flux was measured. At any time, the permeate and the retentate concentrations were determined experimentally. The concentration of SDS was determined by employing the ethyl violet spectrophotometric determination method [11,12]. The concentration of o-cresol was measured by GC after the solute was completely extracted by toluene and the concentrations of Cu²⁺ were determined by AA.

3. Results and Discussion

Figure 1 shows the results of the solubilization of the dye Oil Orange SS given as a plot of the absorbance at 495 nm versus the total SDS concentration for the HPC/SDS/water system. As given in Figure 1, the solubilization of the dye in the aqueous HPC solutions begins approximately with 2.0 mM of the total SDS. Accordingly, it can be inferred that the interaction, or the adsorption of the surfactant molecules starts with approximately 2.0 mM of SDS and the critical aggregation concentration (c.a.c) is about 2 mM. Figure 1 also shows that the CMC for SDS in pure water is determined as 8.0 mM using the same dye solubilization technique, which agrees well with previous literature [13]. With a further increase in [SDS], the absorbance increased almost linearly, which implies that the solubilization capacity was also increased. In addition, it was observed that the critical aggregation concentration of SDS is not a function of the polymer concentration as long as [HPC] is higher than 0.3 wt %.

In Figure 2, the ultrafiltration results for the removal of o-cresol (0.1 mM) are given as a function of the total retentate concentration of SDS. In the figure, the percentage rejection is defined as

\[ \text{Rejection} = \left( 1 - \frac{[\text{solute}]_{\text{res}}}{[\text{solute}]_{\text{in}}} \right) \times 100 \]  (1)

As shown in Figure 2, the rejection of o-cresol with the polymer/SDS system is higher than that with the SDS micellar system. This is due to the lower aggregation concentration of SDS in the polymer/SDS system (2 mM) compared to that in the SDS micellar system (8 mM). With the same total [SDS], fewer free surfactant molecules exist in the polymer/SDS system which indicates that more surfactant molecules participate in the aggregation, i.e., the polymer/SDS complexes provide more solubilization power. In addition, the results show that there are three SDS concentration regions in the rejection for the polymer/SDS system. With low concentrations of [SDS], the rejection increases linearly up to nearly 60% and then the rejection drops down with a further increase in the [SDS]. This result is probably due to the release of the free SDS molecules in the solution. In other words, when the surface of the polymer is saturated with SDS molecules, an additional increase in the SDS concentration results in the
formation of free SDS molecules. Since free SDS molecules can penetrate into the permeate, it appears that the solute (o-cresol) pass through the membrane with the SDS n-mer (dimers, trimers, etc.) formed in the retentate. However, from the points, i.e., 15 mM (for Polymer I system) and 30 mM (for Polymer II system) of [SDS], the rejection increases again as the [SDS] increases. This behavior is ascribed to the formation of normal micelles. Once normal micelle forms at [SDS] > CMC, an increase in [SDS] will increase the rejection of the solute. In addition, the results reveal that the saturation concentration of SDS for Polymer I system differs from that for Polymer II system. This is probably due to the difference in the chemical properties of the polymer surface such as the molar substitution of the hydroxypropyl group.

The relative fluxes for the ultrafiltration runs are shown in Figure 3. In this figure, the relative flux is defined by \([\text{the flux of the system}]/[\text{the flux of pure water}]\). As expected, the relative flux for the low molecular weight polymer (Polymer II) system was higher than that for the Polymer I system. This is due to the differences in the viscosity of the solution since flux is inversely proportional to the viscosity of a solution in ultrafiltration.

In general, the flux decreases with an increase of surfactant concentration in MEUF [14] and CEUF [9]. Interestingly, however, in CEUF employing the SDS/HPC system, the relative flux increased when the [SDS] in the retentate increased. In addition, an abrupt increase in the relative flux was observed at 10-15 mM of [SDS]. This could be attributed to the unusually high viscosity of the HPC/SDS system at 30 °C, as shown in Figure 4. In order to understand this phenomena, we required a model proposed for the SDS/polymer system. In a previous study [15] on a similar system, a model was proposed for the interactions between SDS and hydroxypropylmethylcellulose (HPMC). According to this model, at a critical aggregate concentration, SDS starts to adsorb to the polymer chain in a cooperative manner in the form of small micelles (clusters). Then, the adsorbed clusters increase in size with the surfactant concentration up to a certain limiting value, and a cluster is shared by two or more polymer molecules creating a three-dimensional network when the polymer concentrations are high enough. In addition, with high concentrations of SDS ([SDS] > CMC), normal micelles also form into which HPC may distribute. Therefore, it appears that a similar aggregation model can be applied to the present HPC/SDS system. That is the low permeate fluxes at low [SDS] were due to three-dimensional network formation in the retentate. In addition, it can be also inferred that the abrupt increase in the flux with 10-15 mM of [SDS] was ascribed to the distribution of the polymer from a three-dimensional network (the reduction in viscosity) and the formation of normal micelles.

In Figure 5, the concentration of SDS in the permeate as a function of the concentration of SDS in the retentate is given for the ultrafiltration runs. In general, the permeate SDS concentration can be assumed to be the concentration of free, SDS molecules in the retentate [1,2,6]. As can be seen in Figure 5, the
concentration of SDS in the permeate increases as the retentate SDS concentration increases up to nearly 4 mM regardless of the presence of HPC. On the other hand, the permeate SDS concentrations approach to limiting plateau values with increasing the retentate SDS concentrations above 10 mM. In the case of the pure SDS system, the limiting plateau value will be approximately the CMC (8 mM). Even with the HPC/SDS system, the limiting value would approach the CMC of SDS since the normal micelles form at [SDS] > 30 mM. However, at 5-30 mM of [SDS], the permeate SDS concentration for the HPC/SDS system was smaller than the value for the pure SDS system by about 20-30%, thus less amount of SDS permeates through the membrane in the CEUF employing the HPC/SDS system. However, the role of the polymer HPC as a "scavenger" was not so effective compared with the results for the ionic polymer/ionic surfactant system. In the case of the cationic-polymer/SDS system the interaction between the polymer and the surfactant was strong, thus the leakage of the surfactant molecules into the permeate could be greatly reduced [9,10]. Nevertheless, it is very attractive to employ the HPC/SDS complex in CEUF for the removal of o-cresol since the system needs only 5-20 mM of SDS to obtain a good rejection of o-cresol (In reality, when we employ MEUF with 50-200 mM of [SDS], the rejection of o-cresol is about 40-85% [3,14]), and the [SDS] in the permeate in the CEUF would be only 2-5 mM. Furthermore, the present work was conducted as the first phase in researching the simultaneous removal of organics and metal cations. For the simultaneous removal, it is necessary to utilize a non-ionic polymer in the CEUF. To test the ability of CEUF for the simultaneous removal, a CEUF run was performed and the result for the removal of o-cresol and Cu$^{2+}$ was given in Table 1. As shown in Table 1, the rejection for the o-cresol and Cu$^{2+}$ was 68% and 91%, respectively. Indeed, the simultaneous removal of organics and a divalent metal cation can be successfully attained by CEUF employing the HPC/SDS system. In fact, we are performing the study for obtaining the optimum operating conditions for the simultaneous removal of organics and metal cations by CEUF. The variables for this work include the molecular weight cut-off of the membranes, applied pressure, and the concentration of the HPC/SDS complex. The results will be published later.

### 4. Conclusions

In the present study, the performance of CEUF employing the HPC/SDS complex was investigated for the removal of o-cresol using stirred-cell ultrafiltration experiments. From the dye solubilization experiments, it was found that the critical aggregation concentration (c.a.c) of SDS is about 2 mM for the HPC/SDS/water system and the c.a.c. is not a function of the polymer concentration as long as [HPC] is higher than 0.3 wt %. When the CEUF runs were conducted with the HPC/SDS system, the rejection of o-cresol (0.1 mM) was higher than that with MEUF utilizing SDS micelles. In addition, the rejection and permeate flux are strong functions of [SDS] and it is necessary to find the optimum SDS concentration when we operate CEUF with the HPC/SDS system. On the other hand, when the present system is employed for obtaining the same level of o-cresol rejection, CEUF requires only about 10% of the [SDS] which is used in MEUF.

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References