Korean J. of Chem. Eng., **13**(5), 448-452 (1996)

REMOVAL OF METAL IONS BY ULTRAFILTRATION OF A MICELLAR SOLUTION CONTAINING ANIONIC SURFACTANT

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(*Received 28 December 1995 • accepted 16 July 1996*)

Abstract – Heavy metals in wastewater were removed by ultrafiltration of a micellar solution containing surfactant such as sodium dodecyl sulfate. Experimental results showed that permeate flux was primarily controlled by the operating parameters such as transmembrane pressure difference, flow rate and feed concentration. The average permeate flux increased at a higher transmembrane pressure, feed velocity, and at a lower solution concentration. The transmembrane pressure had a relatively small effect on metal removal whereas the level of surfactant-to-metal ratio (S/M) had a substantial effect. The optimal ratio of S/M for a best removal of metal ions was measured around 5 and 8 in the presence of sodium dodecyl sulfate, and the affinity resulted in the order of Cr>Co>Ni>Mg.

Key words: Ions, Ultrafiltration, Micellar, Surfactant

INTRODUCTION

Industrial wastewater streams frequently contain high concentrations of dissolved toxic metal cations (often called heavy metals) that cause a major environmental hazard. Sources of such wastewater are including metal plating industries, semiconductor manufactures, mining operations, chemical processes, and many others. Improved methods of removing these heavy metals from water would be of great value.

Membrane separation technology, such as reverse osmosis (RO) and ultrafiltration (UF), can significantly reduce the waste volume without phase change, which results in low energy consumption. Surfactant-based UF, which combines the high flux of UF with the high selectivity of surfactants, has been applied to separate dissolved heavy metals and toxic organics from water using synthetic surfactant like sodium dodecyl sulfate (SDS) [Huang et al., 1994].

The underlying principle is to increase the size of pollutant molecules so they can be removed when passed through a membrane with an appropriate pore size. At concentrations above the critical micellar concentration (CMC), 60-200 surfactant molecules will attach to each other, forming macromolecules or micelles. Therefore, metal cations associated with negatively charged micelles, which have a molecular weight in the range of 2,000 and 10,000, can be selectively removed by an UF membrane with considerably higher permeate flow rates at lower pressure ranges than by RO [Huang et al., 1994].

Successful separation is basically dependent on the type of surfactant and metal, surfactant-to-metal ratio (S/M), binding characteristics of surfactant to contaminants, and operating pressure. Selective removal of metal cations from wastewaters with surfactant-based UF can also be achieved by applying an appropriate level of S/M and a compatible type of membrane.

The goals of the present research were to determine the effects of surfactant, metal types, and S/M ratio on the system performance of crossflow surfactant-based UF.

THEORY

1. Surfactant

Amphiphilic substances are those that posses both hydrophilic and hydrophobic parts in the same molecule (i.e. water-attracting and water-repelling parts, respectively). One of the characteristic properties of amphiphilic substances is that they tend to assemble at interfaces. They are therefore often referred to as surface active agent. The formation of large aggregates, or micelles, is another characteristic property of amphiphilic substances [Jonsson and Jonsson, 1991].

A surfactant molecular consists normally of an alkyl chain and a hydrophilic head-group. Surfactants are categorized into four groups depending on the charge of the head-group: nonionic (0), anionic (−), cationic (+) and zwitterionic (±) surfactants.

2. Critical Micelle Concentration

The monomer concentration is normally very low in amphiphilic solutions. At a specific concentration, the critical micelle concentration (CMC), the association to form large aggregates (micelles) begins. Many physicochemical properties, such as osmotic pressure, surface tension, conductivity and solubilization, change abruptly at the CMC.

3. Micelles

Micelles are aggregates with the polar head-groups oriented towards water and with hydrocarbon chains hidden in the interior. At low concentrations micelles are spherical aggregates, but ionic surfactants have a tendency to grow and form rod-shaped micelles at higher surfactant concentrations.

A micelle composed of ionic surfactants is highly charged. For the condition of electroneutrality to be satisfied, the con-

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centration of ions with charge opposite to that of the surfactant in the vicinity of the micelle surface must be higher than the concentration in bulk solution. Thermodynamically, these counterions may also be considered to be adsorbed at the micelle-solution interface. These adsorbed counterions are either bound in the sternlayer of the micelle, or present in excess in the electrical double layer surrounding the micelle.

Consider now the ultrafiltration of a micellar solution containing ionic surfactant, multivalent counterions, and monovalent counterions. If the micelles are completely rejected by the membrane, electroneutrality constrains the adsorbed counterions to be rejected. Otherwise, a great number of positive charges from counterions would permeate through the membrane rather than negative charges, and an electrical potential would be rapidly set up across the membrane which would prevent the passage of any more adsorbed counterions through the membrane. As a result, the adsorbed counterions are rejected by the membrane if the micelles are rejected.

The selection of a surfactant is an important issue in designing separation processes based on micellar-enhanced ultrafiltration [Kandori and Schechter, 1990]. The ideal surfactant is one which has a very small CMC, at which the amount of the surfactant in the filtrate can be minimized. It has a great affinity for the solute, and does not solubilize unwanted solute.

EXPERIMENTAL

1. Chemicals

Among the numerous kinds of surfactants commercially available, we have selected an anionic surfactant to trap cations in a dilute solution. The surfactant used in this study, sodium dodecyl sulfate (SDS), was obtained from Duksan Pharmaceutical Co. and used as received. Analytical reagent-grade $CoCl_2\cdot 6H_2O$, $MgCl_2\cdot 6H_2O$, $NiCl_2\cdot 6H_2O$ and $CrCl_3\cdot 6H_2O$ were used as received. Cations were generated by dissolving salts in water. Water used in all experiments was distilled and deionized.

2. Equipment

The flow sheet of an ultrafiltration apparatus is reported in the previous work [Yang et al., 1996]. An Amicon model HIP 3-20 hollow-fiber cartridge (Amicon Corp., Danvers, Massachusetts) was used. The fiber (ID 0.05 cm, effective length 15.3 cm) was made of polysulfone which has a molecular-weight-cut-off (MWCO) of around 3000 daltons. And the total effective membrane area was 6000 cm^2. The unit was connected to a 3-liter jacketted tank. The feed solution was circulated by a peristaltic pump with a variable speed motor, and the feed flow was measured with a flowmeter. The pressure was measured with a pressure gauge.

3. Experimental Conditions and Procedure

The experimental conditions are as follows. The S/M ratios of feed solution were 0.5, 3.0, 5.0 and 8.0; the feed flow velocity was 3.2207×10^{-2} m/sec; and the feed transmembrane pressure difference were 0.5, 0.8, 1.0 and 1.2 bar. The feed solution temperature in all experiments was kept at 25°C by a thermostat. During a run, both permeate and retentate were recycled back to the feed tank to keep the feed concentration constant.

The experimental procedure is as follows. First, a fresh hollow fiber module was used to determine the intrinsic resistance of membrane R_m. Permeate fluxes for pure water, J_w, were measured under various transmembrane pressure differences and flow velocity. Second, the feed-water was replaced with the tested solution. Permeate fluxes for test solutions, J_t, were measured under all operating conditions at steady state. After collection of 10 ml of permeate for analysis, some moles of surfactant was added into the feed tank. The collected permeate at each interval was put back into the feed solution to keep the concentration of each metal as constant as possible. The retentate was collected at atmospheric pressure. Metal concentrations in the feed and permeate samples were determined using an ICP.

CMC measurements were performed using a dye solubilization method and an interfacial tension method [Ahma et al., 1994]. In the dye solubilization method, 10^{-4} M chloride pynacyanol solution was prepared in distilled water. One ml of this solution was added to 5 ml of soap solutions at different concentrations. A color change occurred at the point where micelles just formed.

After each run, the membrane module was cleaned by a combination of high circulation and backflushing with pure water. The cleaning procedure was repeated until the original water flux had been restored.

RESULTS AND DISCUSSION

The experimental data of the permeability are presented in Fig. 1. The permeability was directly proportional to transmembrane pressure difference. For the finding of permeate flux, the resistance-in-series approach [Yen and Cheng] was employed in this research. It can also be seen that the permeability decreased with surfactant concentration in the same manner in a previous result [Ahma et al., 1994]. The flux reduction has been explained by concentration polarization caused by retained micelles.

Fig. 2 shows the permeability of a water as a function of

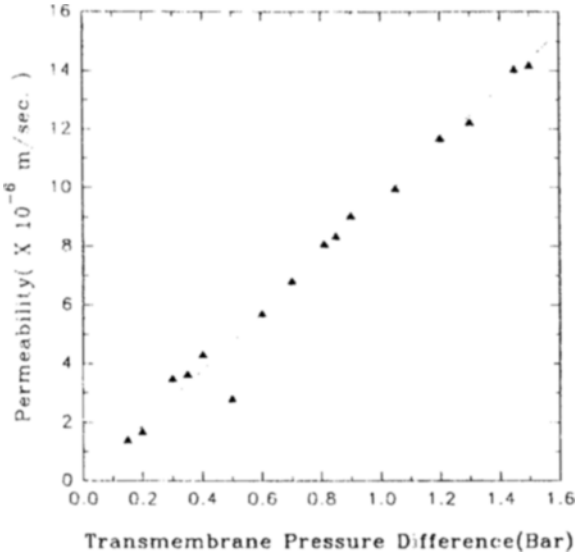

Fig. 1. Permeability of water in the hollow fiber filter with MWCO=3,000 at the feed velocity of 3.2207×10^{-2} m/s at 25°C.

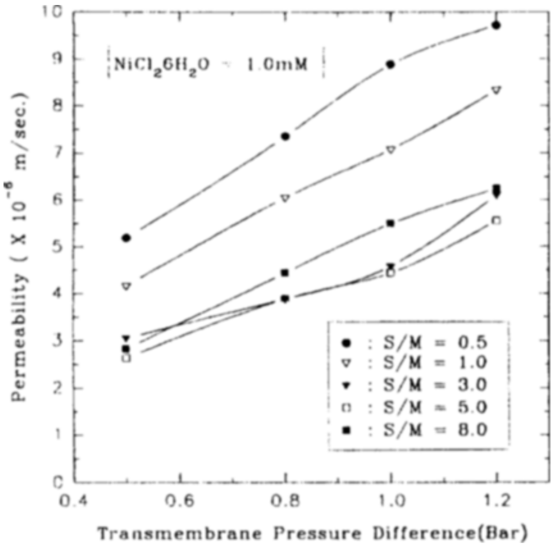

Fig. 2. Permeability of water as a function of transmembrane pressure difference for various S/M ratios at the Ni salt concentration of 1.0 mM.

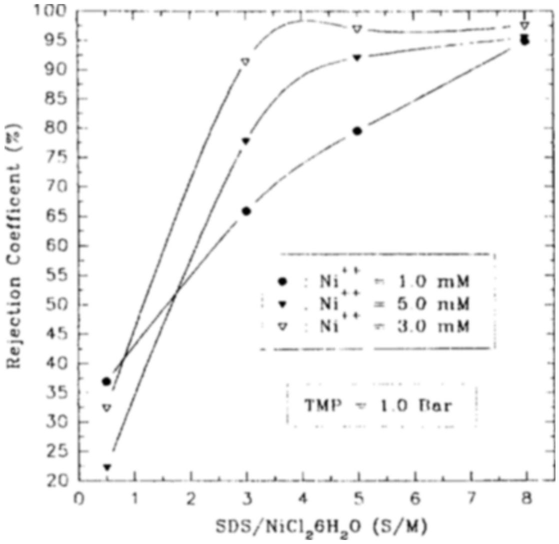

Fig. 3. The rejection coefficient as a function of S/M ratio at the TMP of 1.0 bar.

transmembrane pressure difference for various S/M ratios at the nickel salt concentration of 1.0 mM. This result indicates that interaction between solute and ultrafiltration is vital. These interactions could lead to adsorption within the pores, near the mouths of the pores, and more generally anywhere on the surface. This phenomenon normally reduces permeability of macromolecular species. Since there is no electrostatic repulsion between the species the adsorbed layer can be closely packed so that the layers formed in the pores reduce the permeability significantly. Three possible reasons have been suggested in explanation of the deposition of surfactant and layer formation: (i) adsorption is a multi-layer phenomenon influenced by shear stress; (ii) surfactant molecules may have been partially solubilized in the membrane resulting in membrane swelling in the region of the pores; and (iii) due to fouling it could be possible that the critical micelle concentration could be reached at the membrane surface where pores blocking could then result from the presence of micelles [Field et al., 1994].

Fig. 3 shows the rejection coefficient of nikel ion as a function of S/M ratio at the transmembrane pressure difference of 1.0 bar. The efficiency of a UF process to retain a specific component was mainly characterized by the rejection coefficient [Scamehorn et al., 1993], R(%), defined as

$$R(\%)=(1-C_P/C_F)\times 100$$

where C_P is the concentration of the components in the permeate and C_F is the concentration of the components in the feed.

As seen in the figure, the rejection coefficient of nickel ion increased with S/M ratio. The increase of the rejection coefficient at an increasing concentration of surfactant seems to result from the increased amount of micellized surfactant aggregates (dimers, trimers, n-mers, etc.) which bind metal cations in the feed solution. A higher rejection coefficient of micellized surfactants appeared to be a sequence of membrane fouling due to adsorption. Thus a mechanism of size exclusion could be sufficient to explain micelle rejection if there was a significant reduction of the pore diameter of the membrane. An interesting point for now is the permeation of micelles through the membrane. Several factors which determine the passage of micelles through the membrane are membrane size, surfactant structure, and electrolyte concentration. As the alkyl chain is shortened, micelles tend to pass through the membrane. Shortening the chain length decreases both the size of the micelles and the aggregation number decrease.

Fig. 4 and 5 show the change of rejection coefficient of nickel ions as a function of transmembrane pressure difference at two different concentrations of nickel ion and for various SDS/metal salts ratios. As seen in the figures, the rejection coefficient of metal ion increased with S/M ratio and it was very stable with the transmembrane pressure difference.

The rapid increase of viscosity at higher surfactant concentrations indicated that the micelles are becoming longer and rod-like, not smaller as suggested by Scamehorn et al. [1993]. This is, general in fact, the trend that can be expected with increasing surfactant concentrations. At the beginning of the ultrafiltration, a monomer layer is probably adsorbed onto a membrane. This might allow a significant metal concentration to be retained in the layer of the surfactant heads. In addition, pore sizes are probably reduced and adsorbed surfactant tails must confer hydrophobic forces to the membrane-solution interface.

Using the molecular weight cutoff as a qualitative characterization of rejection, we expect monomer to be passed completely by the 3000 MWCO membrane and micelles to be rejected completely. The latter was observed well. This was likely due to a combination of effects including repulsive electrostatic interactions between free and adsorbed monomers and reduction of the average effective pore size due to monomer adsorption.

As seen in comparison with Fig. 4 and 5, a higher rejection coefficient was observed at a higher Ni^{++} concentration even

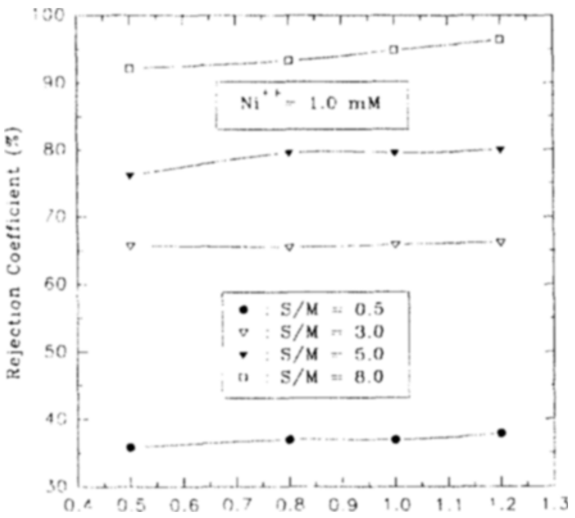

Fig. 4. The rejection coefficient as a function of transmembrane pressure difference for various S/M ratios at the Ni salt concentration of 1.0 mM.

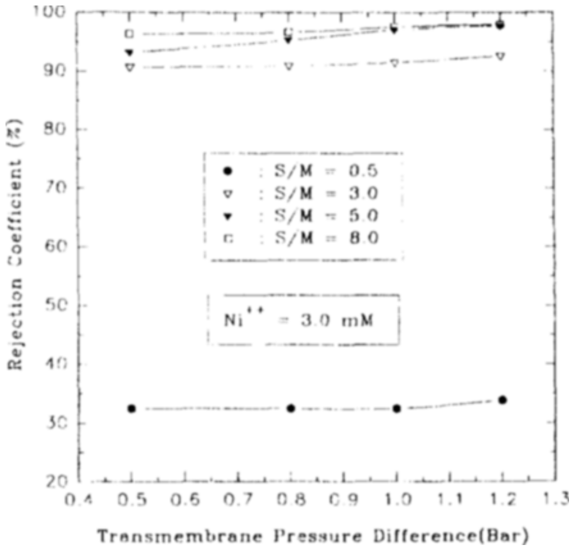

Fig. 5. The rejection coefficient as a function of transmembrane pressure difference for various S/M ratios at the Ni salt concentration of 3.0 mM.

when the S/M ratio is small. These results clearly illustrate the effect of the monomer-micelle equilibrium on surfactant rejection in a hollow fiber membrane system. Effectively, about 90% of the surfactant monomer was rejected by the membrane pores. Because all micelles were sieved, total surfactant rejection was, of course, much higher, especially when the concentration at the membrane surface was large and was comprised mostly of rejected micelles. As a retentate is further concentrated, the S/M ratio in MEUF (micellar enhanced ultrafiltration) would remain constant in the retentate as both concentrations increase. The permeate metal concentration should be independent of surfactant concentration and proportional to metal concentration in the retentate. Therefore, as the metal concentration increases in the retentate along a path, at a constant SDS/metal ratio, the permeate metal concentration should increase in direct proportion to the retentate metal concentration.

As shown in Fig. 4, about 36% rejection coefficient was observed at a S/M ratio is 0.5. We believe that this resulted from the formation of a gel layer next to the membrane due to the concentration polarization effect. Surfactant monomer can be rejected to some extent in MEUF. In this case, there may be an accumulation of surfactant in this gel layer exceeding the CMC and micelles can be present in this region, even when the bulk retentate has no micelles present.

In the range of large surfactant concentrations, the free metal ion concentration in the permeate was significantly lower than its concentration in the feed. This seems to mean that the membrane did not carry out a simple micelle filtration, since a part of the free metal ions in the aqueous phase was also rejected. As the retentate surfactant concentration relative to the retentate metal concentrations increased, the permeate metal concentration decreased. This was due to the increase of the fraction of surfactant in micellar form by increased relative concentration of the surfactant. A large fraction of total surfactant present in micellar form will tend to increase the separation efficiency.

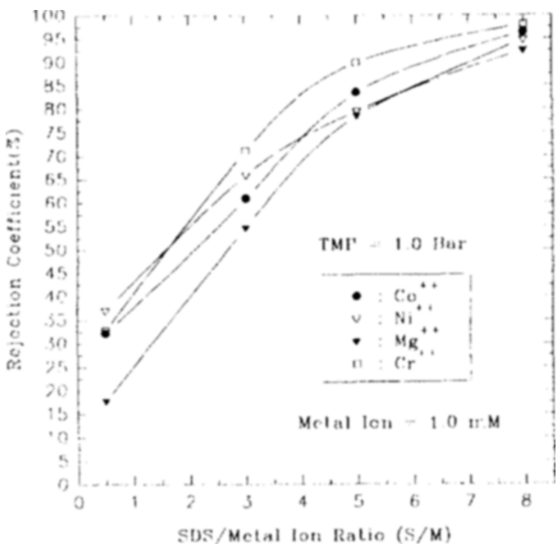

Fig. 6. Effect of S/M ratio on the rejection coefficient at metal salt concentration of 1.0 mM and TMP of 1.0 bar.

For a comparison reason, membrane rejection coefficients were determined for solutions of cobalt, magnesium, nickel, chrome for various S/M ratios ranging from 0.5 to 8.0. The rejection coefficient data for different tests are presented in Fig. 6. The effect of metal types and concentrations on the rejection coefficient at a metal ion concentration of 1.0 mM was showed. As shown in the figure, valence was the dominant factor determining the efficiency of removal of a multivalent ion from water using MEUF. The rejections were in the order of Cr>Co>Ni>Mg. The maximum rejection coefficient of 90-99% was obtained at ratios from 5.0 to 8.0. At this condition the affinity to metal ion on the micelles showed a slight difference and increased in the following order; Cr>Co>Ni>Mg. The main reason of the small difference was believed to be the complexation of the cations with anions in solution.

The necessity of some excessive surfactants for micellization was explained with anionic surfactants, SDS nature and the effect of steric factors on the micellization.

The effect of the surfactant concentration while holding the retentate metal concentration constant is shown in Fig. 6. Metal ions at a concentration of 1.0 mM can be considerably removed by SDS at a S/M above 5. Each metal was not effectively removed at a below S/M of 5 because the concentration of SDS did not reach its CMC. So a higher S/M than 5 was needed to remove all the metal ions at a lower concentration. This might be caused by a different interaction between the micelles and the membrane surface. The trend of SDS for the removal of individual metal was similar for each metal.

As seen in Fig. 6, selective removal of four heavy metal ions is of no ease even when the different S/M ratio is used. For example, a mixture of magnesium (or nickel)-cobalt-chrome can use the S/M ratio of between 3 and 5, and a mixture of magnesium-nickel under 3, however their rejection coefficients are very small and ineffective. A high operating transmembrane pressure difference (TMP of 1.0 bar) did not increase the metal rejection coefficient significantly. At the transmembrane pressure difference of 1.0 bar, the trend of rejection coefficient of each metal were more similar to that of nickel. It was shown in Fig. 3 that a higher rejection coefficient of S/M ratio of 8.0 was above 95%. The metal ions can be removed with a surfactant concentration below its CMC. This means that metal was removed by forming metal complexes at a surfactant concentration below the CMC and by forming both metal complexes and metal micelles at a surfactant concentration above the CMC.

The optimal S/M for SDS on total removal of metal ions present in a mixture was around 8. All metal ions present in a mixture can be substantially removed by SDS at a S/M of 8. This means that roughly eight surfactant molecules were needed to bind a metal ion at a surfactant concentration above its CMC. SDS had a capability for total and selective removal, to some extent, of metal ions present in a simulated wastewater with relatively high permeate flux.

From a practical viewpoint, micelles were completely rejected. Thus, the surfactant concentration in the permeate was very small compared with the total surfactant in micellar form in the retentate under the conditions. It is necessary for MEUF to be a feasible industrial separation method.

CONCLUSIONS

Metals in a simulated wastewater were substantially removed by a micellar-enhanced-ultrafiltration using surfactant such as sodium dodecyl sulfate. The results from this work can be summarized as follows.

1. Permeate flux was primarily controlled by the operating parameters, such as transmembrane pressure difference, flow rate and feed concentration.
2. Successful separation was basically dependent on the kinds of metal, surfactant-to-metal ratio and operating pressure.
3. In the presence of all four metals, sodium dodecyl sulfate showed the following affinity: Cr>Co>Ni>Mg.
4. The optimal surfactant (sodium dodecyl sulfate)-to-metal ratio for considerable metal removal was around 5 and 8 for all metals.
5. This study showed that transmembrane pressure difference had a relatively small effect whereas surfactant-to-metal ratio had a substantial effect on metal removal.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the financial support from Korea Electric Power Research Institute (KEPRI) and Nuclear Environment Management Center in Korea Atomic Energy Research Institute (KAERI)

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