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Simultaneous Separation of Mixture of Metal Ions and Aromatic Alcohol using Cross Flow Micellar-Enhanced Ultrafiltration and Recovery of Surfactant

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Abstract: Separation characteristics of two systems of binary mixtures, namely, (i) copper and calcium; (ii) copper and beta naphthol were studied using micellar-enhanced ultrafiltration (MEUF). Sodium dodecyl sulfate (SDS) was taken as the anionic surfactant. An organic polyamide membrane of molecular weight cut-off 5 kDa was used in cross flow MEUF experiments. Suitable feed surfactant concentration was found to be about 25 kg/m^3. The effects of the feed composition, the transmembrane pressure drop, and the cross flow rate on the permeate flux and observed retention of each solute were studied. For single solute systems, the observed retention of both copper and calcium were about 99% for a solute concentration up to 1.0 kg/m^3 but the retention reduced to 90% to 92% when solute concentration was increased to about 3 to 4 kg/m^3. Retention of copper and calcium was in the range of 88 to 97% for various compositions in their binary mixture. Retention of beta naphthol was in between 82 to 84% in its mixture with copper, whereas, about 92% separation of beta naphthol was achieved in the single solute system. Binding isotherms of both calcium and copper and beta naphthol and copper were evaluated in their binary mixture using extended Langmuir isotherm. A two-step chemical treatment was adopted to recover the surfactant.

Keywords: Metal ions, aromatic alcohol, anionic surfactant, micellar-enhanced ultrafiltration, permeate flux, observed retention, precipitation

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INTRODUCTION

Waste streams containing metal ion are one of the major sources of environmental pollution. These are generated from metal finishing, refineries, photographic processing industries, etc. Most of the heavy metals are toxic and potential environmental hazards. Therefore, the treatment and the quality of the industrial effluent have now become important social issues, leading to stricter environmental protection regulations. The traditional methods for the treatment of metal ion containing waste are mainly, adsorption (1), ion exchange (2), precipitation (3), flocculation (4), etc. The most popular method is adsorption. But this is quite a slow process due to mass transfer limitations. Rate governed, membrane based processes can be attractive alternatives in this regard. In order to remove small molecular weight metals from the solution, membranes are required with quite lower pore sizes, typically used for reverse osmosis and nanofiltration. These processes are energy intensive with high capital and operating costs. These problems can be overcome by micellar enhanced ultrafiltration (MEUF). In MEUF, small pollutants are bound (for ionic pollutants) or solubilized (for organic pollutants) in large surfactant micelles which can be separated by ultrafiltration membranes with larger pore size. Separation of metal ions as well as organic pollutants using MEUF is a field of active research during last fifteen years (5–12). Application of MEUF for removal of various metal cations include Cd^{2+} (13), Ni^{2+} (14), Cs^{+}, Sr^{2+}, Mn^{2+} (15), Pb^{2+} (16), Cu^{2+} (17), Al^{3+} (18), Cr^{3+} (19), etc. But most of these studies are for a single component system. An industrial effluent may contain more than one ionic pollutant. Scant literature data are available for treatment of binary mixture of metal ions (e.g., Sr^{2+} and Mn^{2+}, Sr^{2+}, and Zn^{2+}, etc.) using MEUF (15).

A review demonstrates the recent development in the separation of emulsified organic compounds from surfactant solutions for surfactant reuse and/or surfactant contaminant disposal. Three major principles have been employed for separating organic compounds and/or surfactants from aqueous solutions, namely, organic compound inter-phase mass transfer, surfactant micelle removal, and manipulation of surfactant solution phase behavior (20).

Dissolved organic substances (DOS) are also another source of water pollution. Removal of trace amount of DOS from aqueous stream using MEUF is reported (21–26). Several industrial effluents (including coal refining, textiles, dyes, and synfuel processing), contain unacceptable concentrations of DOS as well as multivalent metal ions (e.g., heavy metals). Generally two-stage separations are required for the effective removal of DOS and heavy metals. MEUF has the potential of simultaneous removal of DOS and heavy metals and can combine two unit operations into one. Few research works on simultaneous removal of DOS and metal ions are reported (27, 28). Simultaneous removal of phenol or ortho cresol and zinc or nickel ions using MEUF is reported by Dunn et al. (27). Witek et al. (28) reported simultaneous separation of phenolic compounds along with chromium ion. In these works, only the feasibility of the separation of the solutes is reported. But, viability of MEUF process depends on the permeate flux, which is the throughput of the system. Apart from that, the variation of the permeate flux and solute retention with the operating conditions and recovery of surfactant are also important design criteria. In the present work, an attempt is made to fill this gap.

The presence of ionic surfactants in the treated effluent at higher concentration adversely affects the quality of the produced water. Apart from that, ionic surfactants are costly. Therefore, recovery and reuse of the surfactant are important in the context of MEUF. Various methods are investigated to recover surfactants efficiently (6, 13).

In the present work, separation characteristics of two systems,

i. binary mixture of metal ions (copper and calcium),
ii. binary mixture of heavy metal (copper) and DOS (beta naphthol) using MEUF are studied in continuous cross flow mode.

Suitable feed surfactant concentration is experimentally found for the selected membrane. Effects of various operating conditions, e.g., feed concentration of solutes, transmembrane pressure drop, and cross flow rate on the observed retention and permeate flux are studied in detail. The solubilization isotherms of copper and calcium and beta naphthol (BN) and copper in their binary mixture on SDS micelle are developed using the extended Langmuir isotherm. A two-step chemical treatment process, available in literature, involving calcium chloride and sodium carbonate is tested for the recovery of the surfactant from the permeate as well as from the retentate stream (6, 29). Optimum consumption of chemicals is also found. A schematic representation of solubilization of organic solute as well as metal ions and the consequent filtration by MEUF is presented in Fig. 1. The block diagram describing the MEUF including the chemical treatment methods for surfactant recovery is shown in Fig. 2.

EXPERIMENTAL

Materials

The chemicals, sodium dodecyl sulfate (MW 288.38), copper sulfate (MW 249.68), sodium carbonate (MW 130), beta naphthol (MW 144.17) and chloroform (MW 119.38) were obtained from Merck Ltd., Mumbai, India. Calcium chloride (MW 111) was procured from S. D. Fine Chem. Ltd., India. Hyamine 1622 (0.004 M) and disulfine blue (MW 566.7) were obtained from Merck KGaA, 64271 Darmstadt, Germany and dimindium bromide (MW 380.3) was procured from Loba Chemie, Mumbai, India.

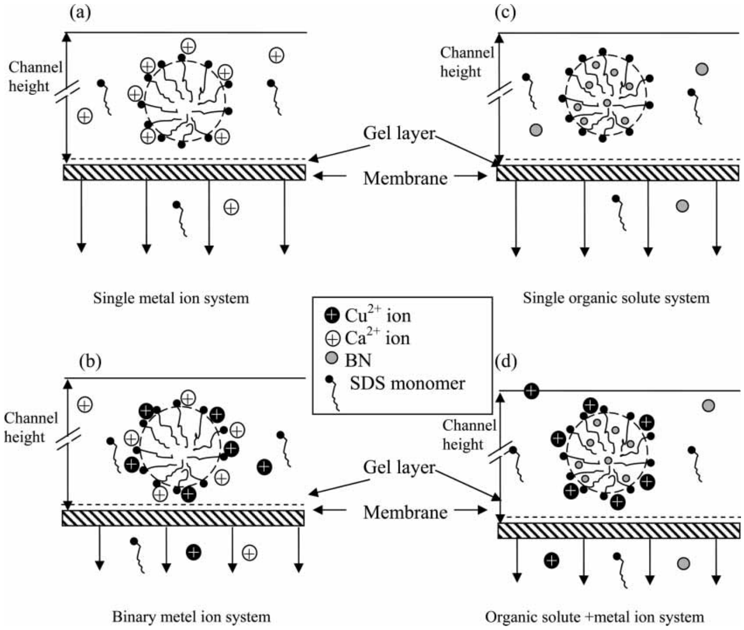

Figure 1. A schematic representation of solubilization of organics and metal ions and filtration by MEUF.

Membrane

A thin film composite (TFC) membrane with polyamide skin of molecular weight cut-off 5 kDa was used for all the MEUF experiments. The

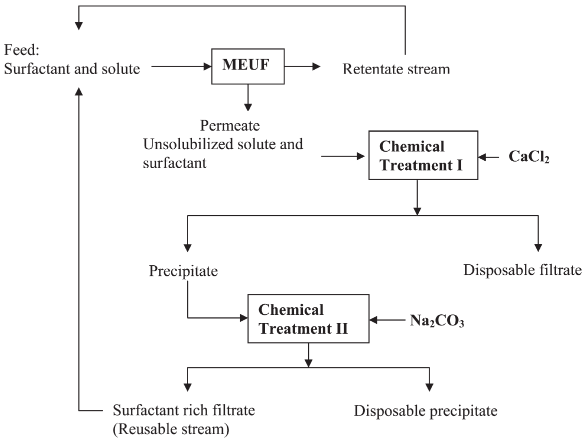

Figure 2. Schematic of MEUF and recovery of surfactant.

membrane was supplied by M/s, Permionics Membranes Pvt. Ltd., Gorwa, Vadodara, India. The membrane was hydrophilic in nature and used without any further treatment. Membrane permeability was measured using distilled water and was found to be 3.62×10^{-11} m/Pas.

Experimental Set Up

Cross Flow Cell

A rectangular cross flow cell, made of stainless steel, was designed and fabricated. A schematic of the experimental set up was shown elsewhere (5). The cell consisted of two matching flanges. The inner surface of the top flange was mirror polished. The bottom flange was grooved forming the channel for the permeate flow. A porous stainless steel plate was placed on the lower plate to provide mechanical support to the membrane. Two silicon rubber gaskets were placed over the membrane. The effective length of the membrane was 37.2×10^{-2} m and width was 5.0×10^{-2} m. The channel height depended on the thickness of the gasket and after tightening of the flanges was found to be 3.5×10^{-3} m. The micellar solutions of different solutes were placed in a stainless steel feed tank of 10×10^{-3} m^3 capacity. A plunger pump was used to feed the micellar solution into the cell. The retentate stream was recycled to the feed tank. After the experiment, the membrane permeability was checked by using distilled water and found to be constant indicating the plugging of the membrane pores by adsorption/clogging is negligible. The permeate stream was also recycled to maintain a constant concentration in the feed tank. A bypass from the pump delivery to the feed tank was provided. The two valves in the bypass and the retentate lines were used to vary the pressure and the flow rate through the cell, independently.

Design of Experiments

Selection of Feed Surfactant Concentration

To select the suitable feed surfactant concentration, two sets of experiments were conducted. The first set of experiments were conducted using SDS solution in the concentration range of 5 to 35 kg/m^3 (5, 10, 15, 20, 25, 30, and 35 kg/m^3) at 276 kPa pressure and 1.67×10^{-5} m^3/s cross flow rate. These experiments were performed at fixed Cu^{2+} and Ca^{2+} concentrations (highest metal ion concentration) of 4 and 3 kg/m^3. The second set of experiments were conducted keeping SDS concentration constant (25 kg/m^3) and varying metal ion concentrations from 0.05 to 4 kg/m^3. This method of selection of surfactant concentration was outlined by Huang et al. (30) and Chhatre and Marathe (31).

Micellar Enhanced Ultrafiltration Experiments

MEUF experiments were conducted with the selected surfactant concentration. Seven feed concentrations of both copper and calcium were taken in the range of 0.04 to 4 kg/m^3, in the single solute system. Five combinations of compositions for copper and calcium and six compositions for copper and beta naphthol in their binary mixture were selected, to observe the effect of solute concentration in the feed. To observe the effects of transmembrane pressure drop and cross flow rate, three pressures in the range of 276 to 552 kPa and three flow rates in the range of 1.67×10^{-5} m^3/s. to 3.33×10^{-5} m^3/s were selected. The experimental conditions are given in Table 1.

Chemical Treatment for the Recovery of the Surfactant

The recovery of the surfactant from the permeate stream before final disposal was carried out by two successive processes, chemical treatment I (surfactant precipitation) and II (dissolution of surfactant) as shown in Fig. 2. The reactions involved in both the steps are presented as:

Reaction occurring during chemical treatment I:

$$2C_{12}H_{25}SO_4^-Na^+(aq) + CaCl_2(aq) \rightleftharpoons Ca^{2+}(C_{12}H_{25}SO_4^-)_2(s) \downarrow + 2NaCl(aq)$$

Table 1. Experimental conditions for the cross flow cell

SDS (kg/m^3)	Cu^{2+} only (kg/m^3)	Ca^{2+} only (kg/m^3)	BN only (kg/m^3)	(Cu^{2+} + Ca^{2+}) in mix. (kg/m^3 + kg/m^3)	(Cu^{2+} + BN) in mix. (kg/m^3 + kg/m^3)	Pressure (kPa)	Cross flow rate × 10^5 (m^3/s)
25	0.05, 1, 2, 2.5, 3, 3.5 and 4	0.04, 1, 1.5, 2, 2.5 and 3	0.04, 0.09, 0.24, 0.4, 0.5 and 1	0.05 + 3, 1 + 2.5, 2 + 2, 3 + 1 and 4 + 0.04	0.05 + 1, 1 + 0.5, 2 + 0.4, 3 + 0.24, 3.5 + 0.09 and 4 + 0.04	276	1.67
25				2 + 2	3 + 0.24	276, 414 and 552	1.67
25				2 + 2	3 + 0.24	276	1.67, 2.5 and 3.33

Reaction occurring during chemical treatment II:

$$Ca^{2+}(C_{12}H_{25}SO_4^-)_2(aq) + Na_2CO_3(aq) \rightleftharpoons 2C_{12}H_{25}SO_4^-Na^+(aq) + CaCO_3(s)$$

A series of experiments were carried out to obtain the optimum ratio of calcium chloride to SDS for maximum precipitation of the surfactant in chemical treatment I and the ratio of sodium carbonate to calcium dodecyl sulfate in chemical treatment II for the maximum regeneration of SDS. The recovery of SDS from the retentate stream was performed using the same procedure.

Procedure

MEUF Experiments

In cross flow experiments, a fresh membrane was compacted at a pressure of 690 kPa for 3 h using distilled water. Flux values at various operating pressures were measured and the membrane permeability was determined from the slope of the flux versus the pressure plot. For MEUF experiments, feed was pumped to the cell and cumulative volumes of the permeate were collected at different times for analysis. Permeate flux values at different points of time were calculated from the slopes of cumulative volume versus time plot. The duration of a cross flow experiment was 1 h. After each experiment, the membrane was thoroughly washed, in situ, by distilled water for thirty minutes. The cross flow channel was dismantled thereafter, and the membrane was dipped in distilled water for 30 min. It was then washed carefully with distilled water to remove traces of surfactant. The cross flow cell was reassembled and the membrane permeability was measured again. It was observed that the membrane permeability remained almost constant between successive runs. All the experiments were conducted at a room temperature of $32 \pm 2^\circ C$. The observed retention of each solute was defined as $R_o = 1 - (C_p/C_o)$, where, C_p and C_o where the solute concentrations in the permeate and feed, respectively.

Chemical Treatment

Three typical permeate samples of MEUF experiment, were selected for the chemical treatment I. A series of solutions were prepared keeping SDS concentration (at the permeate level) constant but with varying $CaCl_2$ concentrations in 100 ml volumetric flasks. All the experiments were conducted at 30°C. All the solutions were cooled to freezing temperature for thirty minutes to force precipitation as surfactant solutions stay supersaturated for long period. These solutions were then kept in a constant temperature bath at 30°C for four days and were shaken periodically. After complete precipitation, the solutions were filtered. The equilibrium concentration of

SDS in the filtrate was measured by standard technique (as discussed in the next section). The amount of precipitated SDS was calculated by material balance. The precipitated SDS in chemical treatment I was treated with the solution of Na_2CO_3 at different concentrations in chemical treatment II. Percent redissolution of calcium dodecyl sulfate was calculated in the same way as in chemical treatment I.

Analysis

Measurement of Copper and Calcium Concentration

Copper and calcium present in various samples were estimated by Orion Aplus^{TM} Benchtop Ion Meter (supplied by M/s, Thermo Electron Corporation, Beverly, MA, U.S.A.) using ion specific electrodes.

Measurement of BN Concentration

BN concentrations in feed and permeate were measured by a UV spectrophotometer (make: Thermo Spectronic, USA; model: GENESYS 2). The wavelength at which maximum absorption occurred was 274 nm.

Measurement of SDS Concentration

SDS concentration was determined by a two-phase titration according to Epton (32). The titrant was Benzothonium Chloride (often called hyamin 1622), a cationic surfactant, the indicator was an acidic mixture of a cationic dye (dimindium bromide) and an anionic dye (disulfine blue VN). The titration was carried out in a water chloroform medium. The pink color of the chloroformic phase was discharged at the end-point; the chloroform layer became grey and with one further drop of the hyamin the chloroform layer turned to blue. SDS concentration was determined using the following equation:

$$\text{SDS concentration} = \frac{a \times (\text{M}) \text{ of hyamin} \times 288.38}{5\,\text{ml of sample}} \tag{1}$$

where a was the volume (ml) of hyamin 1622 required for titration.

RESULTS AND DISCUSSION

Selection of Feed Surfactant Concentration

As outlined in an earlier section, the feed concentration of SDS is selected using various combination of surfactant to metal ion concentration.

Variation of metal ion retention with the surfactant to metal ion ratio is shown in Fig. 3. It is observed from Fig. 3 that the retention of metal ions increases sharply with the S/M ratio upto about 92% and marginally thereafter. S/M ratio is 6.25 for Cu^{2+} and 8.33 for Ca^{2+}, beyond which the retention of metal ions is almost invariant. The corresponding SDS concentration turns out to be about 25 kg/m^3. It may be noted here that the experimental results presented in Fig. 3 are for the maximum metal ion concentration present in the feed. Therefore, the selected surfactant concentration gives better retention of metal ions even at lower concentrations. It is also observed from this figure that for SDS concentration beyond 25 kg/m^3, although the retention of metal ions increases slightly, two problems arise. These may be observed from the inset of Fig. 3. First, beyond S/M ratio 6.25 for Cu^{2+} and 8.33 for Ca^{2+}, the permeate concentration of the surfactant increases sharply. For example, for S/M ratio of 9.0, permeate concentration of SDS is about 3 kg/m^3 for Cu^{2+} solution and for S/M ratio of 12, SDS concentration in permeate is about 3.2 kg/m^3 for Ca^{2+} solution. This is due to the fact that at a higher surfactant concentration in feed, smaller sized micelles permeate through the membrane and permeate concentration goes beyond critical micellar concentration (CMC: 2.33 kg/m^3) (6). The hydrodynamic radius of SDS micelles is 1.9 nm and it increases with electrolyte concentration (33). With further increase in feed surfactant concentration, more micelles permeate through the membrane resulting into monotonic increase in permeate concentration, as shown in Fig. 3. Since, the surfactant itself is costly and increases COD (chemical oxygen demand) load of effluent, its concentration in the permeate should be slightly lower than CMC. Secondly, as surfactant concentration in the feed increases, the permeate flux decreases

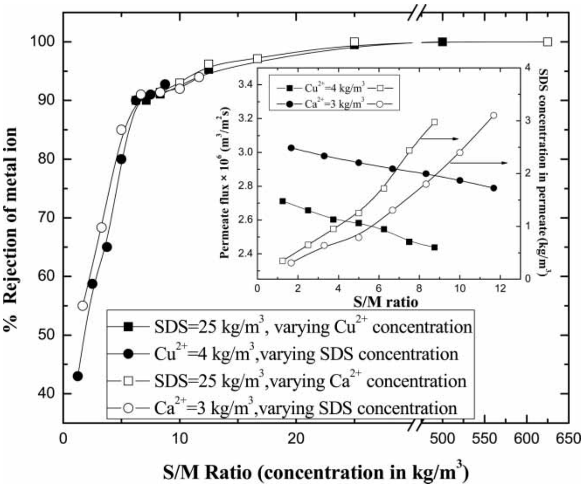

Figure 3. Variation of retention of metal ions with S/M ratio.

as evident from the inset of Fig. 3. For example, the permeate flux decreases from 2.7 to 2.4 × 10^{-6} m^3/m^2s as S/M ratio increases upto 9.0, for Cu^{2+} solution. These trends can be explained using the concentration polarization phenomena. As the feed surfactant concentration increases, the thickness of the deposited layer of the micelles increases leading to more resistance against the solvent flux resulting in flux decline. Thus, higher surfactant concentration (i.e., at higher S/M ratio) leads to lowering in permeate flux accompanied by increase in surfactant concentration in permeate. Therefore, a suitable trade off concentration of the surfactant should be selected. For the present case, from Fig. 3, 25 kg/m^3 is selected as feed concentration of surfactant which results in permeate flux of about 2.7 × 10^{-6} m^3/m^2s and permeate concentration about 1.8 kg/m^3 for Cu^{2+} solution. All MEUF experiments were conducted with this feed concentration of surfactant.

MEUF of Single Component System

Effects of feed concentration of solute on the permeate flux and observed retention are shown in Fig. 4. It is observed from this figure that both the permeate flux and the observed retention decreases with the feed concentration of solute. It may be observed that the permeate flux of 25 kg/m^3 SDS solution is about 6 × 10^{-6} m^3/m^2s (refer Fig. 3), whereas an addition of 1 kg/m^3 solute brings down the flux by almost 50%. It is 3.2 × 10^{-6} m^3/m^2s for calcium and about 2.85 × 10^{-6} m^3/m^2s for copper at the same operating conditions. This signifies that the gel layer concentrations of the SDS micelles are reduced on the addition of the cations. Both copper and calcium ions, being positively charged can bridge more net negatively charged micelles, leading to an early onset of the gel-

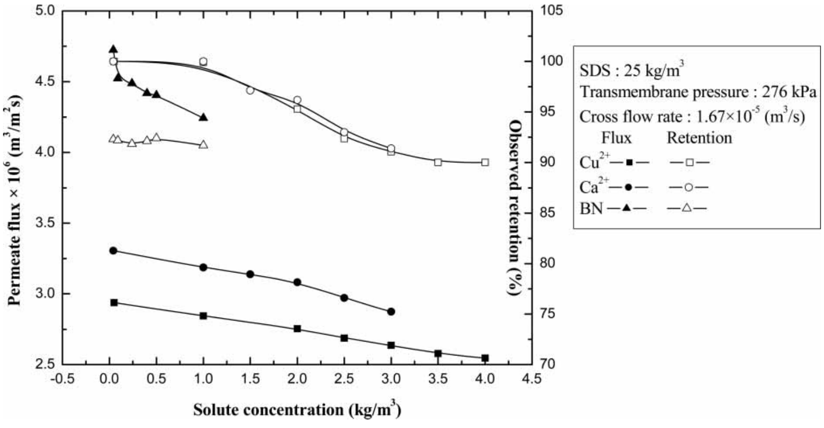

Figure 4. Effect of feed concentration on permeate flux and solute retention in the single component system.

layer over the membrane surface (6, 8, 22, 34). This effect is more pronounced as the solute concentration increases. From Fig. 4, it is clear that copper has a higher capacity to reduce the gel layer concentration compared to calcium. Hence, the permeate flux is less in case of copper. Since the surfactant concentration remains constant, the binding capacity of the micelles remains invariant. Hence, an increase in solute concentration, leads to the permeation of unbound solutes in the permeate side, leading to decrease in the observed retention (refer Fig. 1). The observed retention decreases from about 99% to about 90–92% as the solute concentration increases from 1 to 4 $\mathrm{kg/m^3}$. In case of beta naphthol, the permeate flux decreases with the solute concentration. Being an organic molecule, beta naphthol is solubilized in the hydrophobic core of micelles leading to an increase in size of micellar aggregates (6). This phenomena is augmented at higher concentration of beta naphthol, resulting in decrease in gel layer concentration (34). This leads to a decline in the permeate flux at higher beta naphthol concentration. With increase in solute concentration, more beta naphthol permeates through the membrane (refer to Fig. 1) and the observed retention remains almost unchanged (about 92%) in the concentration range considered here.

MEUF of Binary Mixture of Copper and Calcium

Five compositions in the binary mixture are selected for MEUF study. The compositions are selected such that both the solutes vary from low to high range in terms of concentration. The concentrations (in $\mathrm{kg/m^3}$) of solutes are $\mathrm{Cu^{2+}}$:$\mathrm{Ca^{2+}} = 0.05{:}3;\ 1{:}2.5;\ 2{:}2;\ 3{:}1;\ 4{:}0.04$. Variation of permeate flux and observed retention for these five compositions of mixture are plotted in Fig. 5. It is observed that the permeate flux decreases as the total concentration of the salts increases. This indicates that the capability of both the solutes to reduce gel concentration is working here in tandem which decreases the flux values further (compared to single solute system) (33). About 10% of the flux decline is observed in the range of concentration studied here. It is clear from the figure that the retention of copper ions decreases from about 97 to 88% as the concentration of copper increases in the feed. Similarly, the retention of calcium decreases from about 97.2 to about 92% as the concentration of calcium increases in the feed. The reasons have already been discussed earlier. Interestingly, it may be noted that the retention of both the solutes are slightly less in the mixture (compared to single solute system). For example, for a mixture of 2 $\mathrm{kg/m^3}$ of each solute, the retention of copper is about 90% whereas that for calcium is 94.5%. At the same conditions and feed concentration, the retention in case of the single solute system, is about 95% for both solutes (Fig. 4). The slight decrease in the retention may be explained by the competitive solubilization of the two solutes (refer Fig. 1). Solubilization of calcium is favored over that of copper. The effects of cross

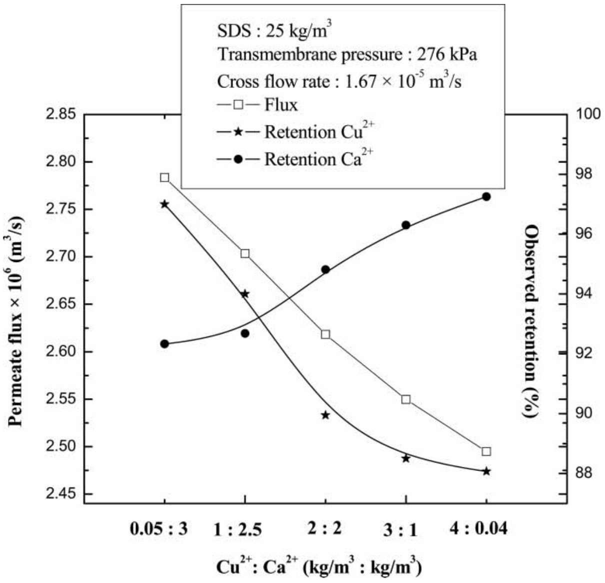

Figure 5. Effect of feed concentration on permeate flux and solute retention in Cu Ca mixture.

flow rate and transmembrane pressure drop on the mixed solute system are observed from Figs. 6 and 7, respectively. It is clear from these figures that the retention of both the solutes remains almost unaffected with the cross flow rate or transmembrane pressure drop. These results simply imply that the retention of solutes is solely governed by the extent of solubilization of the cations on the micelles, not by the operating conditions of MEUF. On the other hand, the permeate flux increases almost linearly with the cross flow rate and the operating pressure difference. With increase in cross flow rate, the gel layer thickness of the micelles over the membrane surface decreases, increasing the permeate flux (8). For example, the permeate flux increases from 2.62 to $2.75 \times 10^{-6}\,\mathrm{m^3/m^2s}$ when the cross flow rate increases from 1.67 to $3.33 \times 10^{-5}\,\mathrm{m^3/s}$. From Fig. 7, the permeate flux increases with the transmembrane pressure drop due to an increase in the driving force. The increase is about 10% when pressure increases from 276 to 552 kPa.

MEUF of Binary Mixture of Copper and BN

Six compositions in the binary mixture are selected for MEUF study. The compositions are selected such that both the solutes vary in lower to higher range. The concentrations (in $\mathrm{kg/m^3}$) of solutes are Cu^{2+}:BN = 0.05: 1; 1:0.5; 2:0.4;

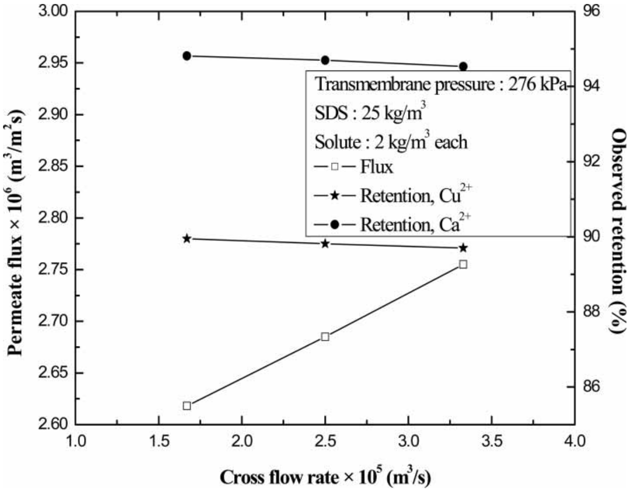

Figure 6. Effect of cross flow rate on permeate flux and solute retention in Cu ca mixture.

3:0.24; 3.5:0.09; 4:0.04. Variation of permeate flux and observed retention for these six compositions of mixture are plotted in Fig. 8. It is observed from this figure that the permeate flux decreases as the copper concentration increases. The decrease in flux is about 16% in the concentration range considered herein. Interestingly, it may be noted that almost the same amount of flux decline occurs for the pure copper system in the same concentration range (Fig. 4). Therefore, the flux decline in the mixture of copper and beta

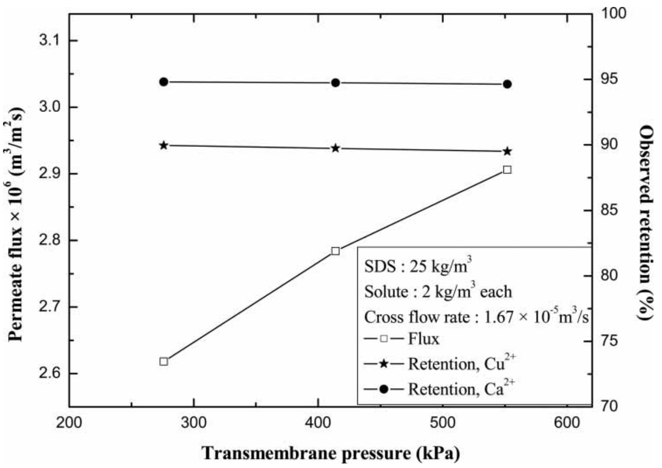

Figure 7. Effect of transmembrane pressure on permeate flux and solute retention in Cu Ca mixture.

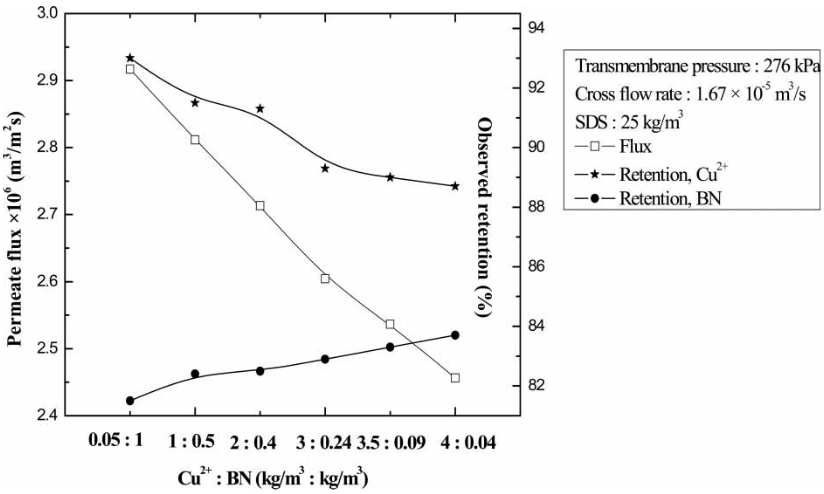

Figure 8. Effect of feed concentration on permeate flux and solute retention in Cu BN mixture.

naphthol is dominated by the presence of copper; the reason for which is discussed earlier. It is clear from the figure that the retention of copper ions decreases from about 93 to 89% as the concentration of copper increases in the feed. Similarly, the retention of BN decreases from about 84 to about 82% as the BN concentration increases in the feed. The reasons have already been discussed earlier. As observed in the case of the copper-calcium system, retention of both the solutes are slightly less in the mixture (compared to single solute system as shown in Fig. 1). For example, for a mixture of (3:0.24 kg/m^3) solute, the retention of copper is about 90% whereas that for BN is 83%. At the same conditions and feed concentration, the retention in case of single solute system, is about 92% for both solutes (Fig. 4). In a copper beta naphthol system, copper ions are quickly adsorbed in the outer surface of oppositely charged micelles. This may cause steric hindrance to the solubilization of beta naphthol within micellar core. Therefore, the retention of beta naphthol decreases slightly compared to a pure component system (refer to Fig. 4). Solubilization of copper is favored over that of BN. As observed in the case of the copper calcium mixture, in case of copper beta naphthol system also, the solute retentions are found to be independent of operating conditions and the permeate flux increases marginally with cross flow rate and operating pressure drop in the range studied here.

Solubilization Isotherm of the Solutes on Micelles in Binary System

The solubilization isotherm data of the two component mixture is fitted with the modified bisolute Langmuir isotherm with the interaction factors (35, 36). The modified Langmuir model can be represented as follows:

$$\frac{(C_{0,1} - C_{p,1})}{(S_0 - CMC)} = \frac{Q_1 \cdot b_1 \cdot C_{p,1}}{1 + b_1 \cdot C_{p,1} + b_2 \cdot C_{p,2}} \tag{2}$$

$$\frac{(C_{0,2} - C_{p,2})}{(S_0 - CMC)} = \frac{Q_2 \cdot b_2^* \cdot C_{p,2}}{1 + b_1^* \cdot C_{p,1} + b_2^* \cdot C_{p,2}} \tag{3}$$

where, $C_{0,1}$ and $C_{0,2}$ are the feed concentration of component 1 and 2 respectively. $C_{p,1}$ and $C_{p,2}$ are their concentration in the permeate. Component 1 is copper in case of copper calcium as well as copper beta naphthol system. Component 2 is calcium for the first and beta naphthol for the second system. The parameters of Eqs. (2) and (3) are evaluated by optimization of the experimental data using BCPOL subroutine of IMSL library. These parameter values are presented in Table 2. Variation of permeate concentration of solutes with weight fraction of copper in feed stream in binary system is shown in Figs. 9 and 10 for Cu Ca and Cu BN mixture, respectively. The results presented in Figs. 9 and 10 signify that the model equations (2) and (3) are quite successful in describing the solubilization of the organic and inorganic solutes within micelles present in the feed stream. At lower concentrations of Cu^{2+} ions, the permeate is almost free of Cu^{2+} ions whereas with increase in Cu^{2+} ion concentration in the feed, the micelles are almost saturated and hence free Cu^{2+} ions start permeating through the membrane, resulting in an increase of permeate Cu^{2+} ion concentration. Similar trends are evident for other solutes (Ca^{2+} and BN) as well. The characteristic curves presented in Figs. 9 and 10, also demonstrate the performance capacity of MEUF system. Given a feed composition (either Cu^{2+}-Ca^{2+} or Cu^{2+}-BN system), the permeate concentration of both the species can be interpreted from these figures. On the other hand, if the permeate composition is specified by the pollution control regulation; the composition of feed stream corresponding to maximum solute concentration to be treated can also be obtained.

Chemical Treatment for Recovery of Surfactant from the Permeate Stream

Chemical Treatment I (Surfactant Precipitation)

Three typical MEUF permeate streams (one for pure copper, one for pure calcium and the other for pure BN) are selected to test the efficacy of the surfactant recovery from the permeate. In the first treatment, calcium chloride is added to the permeate stream resulting in a precipitation of calcium dodecyl sulfate. Figure 11 shows the variations of %SDS precipitation from the permeate for different $CaCl_2$ to SDS concentration ratio. It can be clearly observed from the figure that when $CaCl_2$ to SDS ratio is 0.19 (stoichiometric

Table 2. Interaction parameters for modified bisolute Langmuir isotherm.

Mixture	Q_1 (mg/mg)	Q_2 (mg/mg)	$b_1 \times 10^2$ (l/mg)	$b_2 \times 10^2$ (l/mg)	$b_1^* \times 10^2$ (l/mg)	$b_2^* \times 10^2$ (l/mg)	r^2
Cu^{2+} and Ca^{2+}							
Cu^{2+} in mixture	0.1		9.0	2.97			0.94
Ca^{2+} in mixture		0.11			8.37	54.0	0.98
Cu^{2+} and BN							
Cu^{2+} in mixture	0.14		9.1	1.63			0.99
BN in mixture		0.03			4.21	15.27	0.99

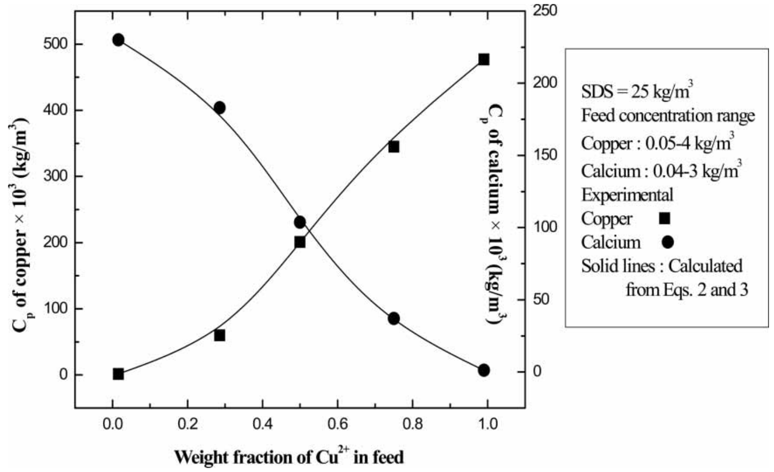

Figure 9. Variation of permeate concentration of solutes with weight fraction of copper in feed in Cu Ca system.

ratio) about 84% SDS is precipitated. With increase in this ratio, SDS precipitation increases for both the cases and beyond 0.384, SDS precipitation becomes almost constant (about 90%) with $CaCl_2$ concentration. This corresponds to about 99.1% removal (including both membrane filtration and subsequent precipitation from permeate) of SDS with respect to the surfactant concentration in the feed of MEUF.

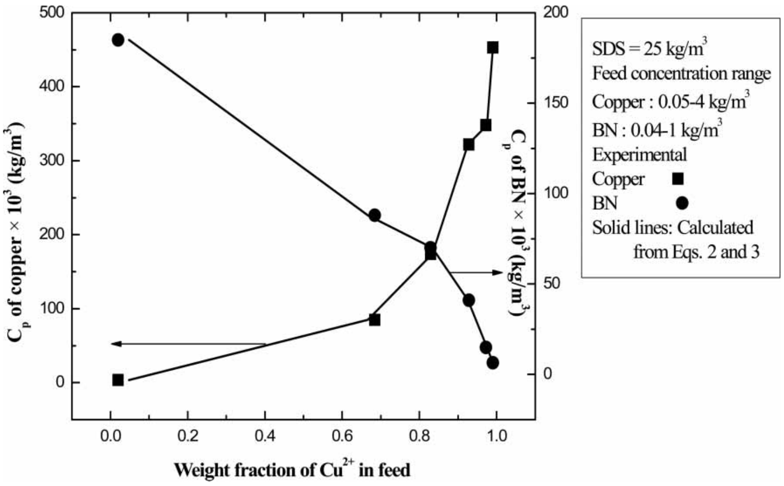

Figure 10. Variation of permeate concentration of solutes with weight fraction of copper in feed in Cu BN system.

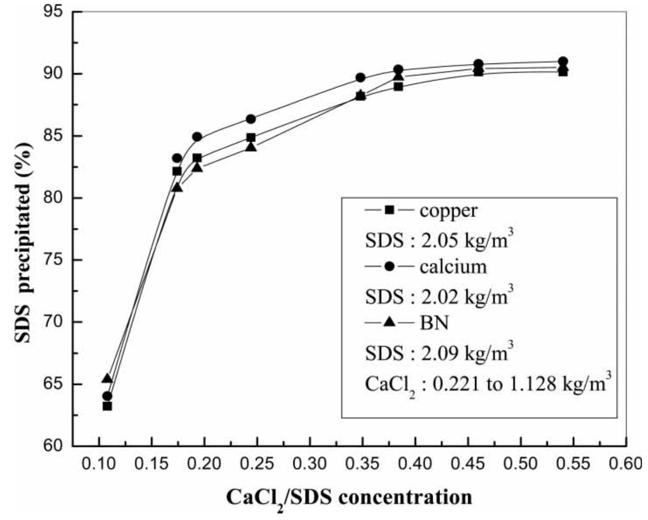

Figure 11. Variation of SDS precipitation with $CaCl_2$ to SDS ratio.

Chemical Treatment II (Redissolution of Surfactant)

Calcium dodecyl sulfate obtained from chemical treatment I, cannot directly be recycled to the main feed of MEUF. It is necessary to get back the surfactant in the aqueous medium. So, calcium dodecyl sulfate should be transformed to a

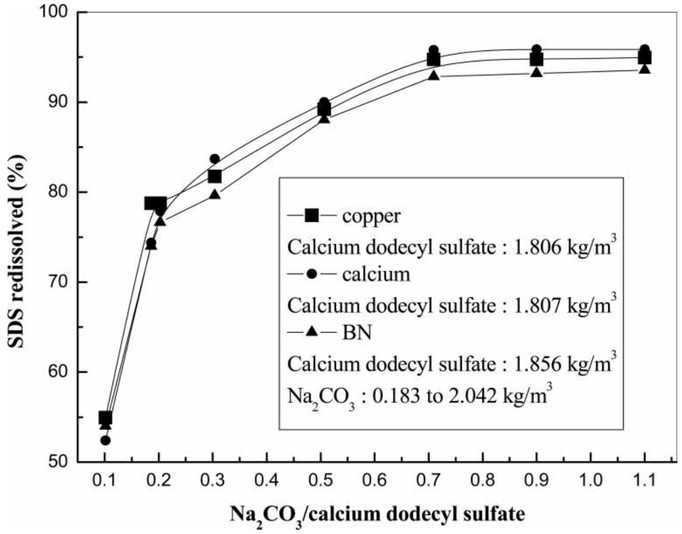

Figure 12. Variation of SDS redissolved with Na_2CO_3.

Table 3. Performance of chemical treatment I and II for a typical retentate concentration.

Mixture	Copper calcium	Copper BN
Copper (kg/m^3)	2.0	
Calcium (kg/m^3)	2.0	
Copper (kg/m^3)		3.0
BN (kg/m^3)		0.24
Retentate SDS concentration (kg/m^3)	25.0	25.0
$CaCl_2$/SDS (w/w)	0.384	0.384
SDS precipitated (%)	99.7	94.5
Na_2CO_3/calcium dodecyl sulfate (w/w)	0.71	0.71
SDS recovered with respect to retentate (%)	90.1	86.5

water-soluble sodium salt. In this case, solution of sodium carbonate (Na_2CO_3) is added to the precipitate obtained from chemical treatment I. The relevant reactions are presented in appendix. The effects of concentrations of Na_2CO_3 on the percentage redissolution of calcium dodecyl sulfate have been studied as a function of Na_2CO_3 to calcium dodecyl sulfate concentration ratio. The results are shown in Fig. 12. With increase of Na_2CO_3 to calcium dodecyl sulfate ratio, the percentage dissolution of calcium dodecyl sulfate increases for both the cases and beyond 0.71, the percent redissolution of SDS becomes almost constant (about 93%). This data corresponds to the recovery of SDS about 84% with respect to the permeate stream.

Chemical Treatments for the Recovery of Surfactant from Retentate Stream

The two-step treatment process as described earlier is applied to recover SDS from the retentate stream using the optimum concentrations of both the chemicals ($CaCl_2$ and Na_2CO_3). Two typical MEUF experiments of the binary mixture are considered for this study. The results are presented in Table 3. It is observed from Table 3 that about 99.7% SDS is precipitated and about 90% SDS can be recovered from the retentate stream, and hence, can be reused.

CONCLUSIONS

Simultaneous separation of copper and calcium and copper and beta naphthol from their aqueous binary mixture was studied using MEUF. The feed surfactant (SDS) concentration was selected as 25 kg/m^3 for 5 kDa membrane. A wide range of concentration of both solutes was studied. The concentration range was 0.04 to 4.0 kg/m^3 for copper calcium system; for copper beta naphthol system, the concentration of beta naphthol was from 0.04 to 1 kg/m^3 and that of copper was from 0.05 to 4 kg/m^3. Retention of copper and calcium was in the range of 97 to 88% and 97 to 92% respectively. For the copper beta naphthol system, the retention of copper was found to be in the range of 93 to 89% and that for beta naphthol was from 81 to 84%. These retentions were slightly less than those of pure component systems. Retention values were found to be independent of MEUF operating conditions, e.g., cross flow rate and transmembrane pressure drop. Solubilization isotherms of the solutes were evaluated using extended Langmuir isotherm. A two-step chemical treatment process (available in literature) was used for surfactant recovery. In the first step, the optimum weight ratio of $CaCl_2$ to SDS was found to be 0.38 and with second step, Na_2CO_3 to $Ca(DS)_2$ was found to be 0.71. About 93% SDS was recovered from permeate and 90% from retentate.

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