ELSEVIER

Chemical Engineering Journal 144 (2008) 35–41

Chemical Engineering Journal

www.elsevier.com/locate/cej

Separation of cation–anion mixture using micellar-enhanced ultrafiltration in a mixed micellar system

Chandan Das, Pintu Maity, Sunando DasGupta, Sirshendu De *

Department of Chemical Engineering, Indian Institute of Technology, Kharagpur, Kharagpur 721302, India

Received 14 March 2007; received in revised form 20 December 2007; accepted 4 January 2008

Abstract

Aqueous solution containing copper (cation) and potassium permanganate (anion) was treated by ultrafiltration using mixed micellar system comprising of sodium dodecyl sulfate and cetylpyridinium chloride. Simultaneous separation characteristics of both cation and anion, as well as permeate flux were studied for various operating conditions, namely, transmembrane pressure drop and cross-flow rate. The study was carried over a wide concentration range of both solutes. In the mixture, copper concentration was in the range from 0.05 to 4.0 kg/m^3 and that of potassium permanganate was 0.05 to 0.25 kg/m^3. Retention of copper was in the range of 90–100% and that of potassium permanganate was 96–99%. Permeate flux was found to be less in the mixed micellar system compared to single surfactant system. A four step chemical treatment process was proposed to recover and reuse the surfactants.

Keywords: Mixed micellar system; Cation; Anion; Retention; Surfactant recovery

1. Introduction

Waste water from various industries, e.g., metal plating, leachate from metal mines, coal refining, etc., contains dissolved ions which are potential source to environmental pollution. With stricter environment protection regulations, research efforts are directed for efficient treatment of such individual waste water. Traditional methods for treatment of waste water containing ionic pollutants include, adsorption [1], ion exchange [2], precipitation [3], flocculation [4], etc. These equilibrium governed processes are extremely slow [5]. Therefore, energy efficient membrane separation processes are emerging as potential separation technique in this regard. Typical membrane based process for separation of ionic pollutant is reverse osmosis. However, it requires quite high operating pressure (more than 25 atm) resulting in high capital and operating cost. In micellar enhanced ultrafiltration (MEUF), metal ions are solubilized in the oppositely charged micelles. This system can run at much lower operating pressure (6–8 atm) leading less consumption of energy. Application of MEUF for removal of cationic pollutants (Cu^{2+}, Pb^{2+}, Ni^{2+}, Al^{3+}, Mn^{2+}, Co^{2+}, Cd^{2+}) is available in literature [6–12]. Most of these studies are for single component system, i.e. waste water containing one ionic pollutant. Removal of anionic pollutants like, chromate, nitrate, permanganate, etc. using MEUF is also reported [13–15]. Few references for treatment of binary ionic mixture using MEUF are available [10–15]. Again these are for same kind of ionic pollutants, i.e., either binary mixture of cations [10–12] or anions [13–15]. Use of MEUF to treat waste water containing both cationic and anionic pollutants is not available in the literature. A system of mixed micelles containing cationic as well as anionic surfactants is required for this purpose. Micelles of cationic surfactants solubilize the anionic pollutants and those for anionic surfactants solubilize the cationic pollutants. MEUF using mixed micellar system is reported in the literature for removal of single cation only [16–19]. But in all these studies, mixed micelles are generated from an ionic surfactant and a non-ionic surfactant. The primary aim of all these works was to reduce the critical micellar concentration on the ionic surfactant by the non-ionic surfactant so that the solubilization capacity of ionic micelles increases.

In the present work, simultaneous separation of both cations (copper ions) and anions (permanganate ions) using MEUF has been attempted with mixed micelles of sodium dodecyl sulfate (SDS) and cetylpyridinium chloride (CPC). The effects of operating conditions, namely, transmembrane pressure drop,

---

* Corresponding author. Tel.: +91 3222 283926; fax: +91 3222 255303.
E-mail address: sde@che.iitkgp.ernet.in (S. De).

1385-8947/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2008.01.006

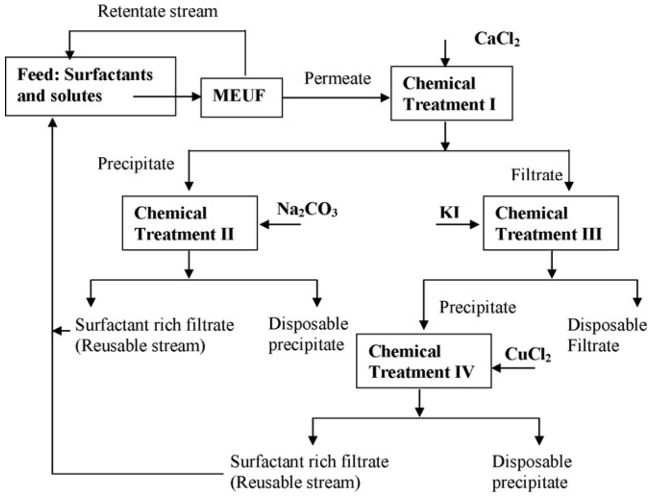


Fig. 1. Schematic of MEUF and recovery of surfactant.

cross-flow rate and composition of the feed (having both pollutants) are studied on the retention characteristics of each solute and permeate flux of the system. The performance is compared with the single solute system in the same range of operating conditions. A four step chemical treatment method is proposed to recover surfactants from the permeate stream for reuse. A schematic of the process is shown in Fig. 1.

2. Experimental

2.1. Materials

The chemicals, sodium dodecyl sulfate ($C_{12}H_{25}NaO_4S$, MW 288), copper sulfate ($CuSO_4{\cdot}5H_2O$, MW 250), sodium carbonate (Na_2CO_3, MW 106), potassium permanganate ($KMnO_4$, MW 158), potassium iodide (KI, MW 166), cupric chloride ($CuCl_2{\cdot}2H_2O$, MW 170) and chloroform ($CHCl_3$, MW 119) were obtained from Merck Ltd., Mumbai, India. The surfactant CPC ($C_{21}H_{38}ClN{\cdot}H_2O$, MW 358) was procured from SISCO Research Laboratories, Mumbai, India. Calcium chloride ($CaCl_2$, MW 111) was procured from S. D. Fine Chem. Ltd., India. Hyamine 1622 (0.004 M) ($C_{27}H_{42}NO_2Cl$, FW 448) and disulfine blue ($C_{27}H_{31}N_2NaO_6S_2$, MW 567) was obtained from Merck KGaA, 64271 Darmstadt, Germany and dimindium bromide ($C_{20}H_{18}BrN_3$, MW 380) was procured from Loba Chemie, Mumbai, India.

2.2. Membrane

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

2.3. Experimental set up

2.3.1. 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 [20]. 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 after the tightening of the flanges was determined by the thickness of the gasket and was found to be 3.5×10^{-3} m. The micellar solution of different solutes was 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. 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.

2.4. Design of experiments

2.4.1. Selection of surfactant concentrations in feed

The feed anionic surfactant concentration was determined by conducting six experiments using only SDS solution in the range of concentration of 5–40 kg/m^3 (5, 10, 15, 20, 30, 40 kg/m^3) at 276 kPa pressure and cross-flow rate of 1.67×10^{-5} m^3/s. The concentration of cationic surfactant in the feed was determined by conducting five experiments using CPC solution only in the range of concentration of 2–30 kg/m^3 (2, 5, 10, 20, 30 kg/m^3) at same a pressure and cross-flow rate as that of SDS experiments.

2.4.2. Micellar enhanced ultrafiltration experiments

MEUF experiments were conducted with selected surfactant (CPC and SDS) concentration. Seven feed concentrations of copper were taken in the range of 0.04–4 kg/m^3 and six feed concentrations potassium permanganate (PP) were taken in the range of 0.05–0.25 kg/m^3, in the single solute system. Five combinations of composition of the binary mixture were selected, to observe the effect of solute (copper, PP) concentration in the feed. The concentrations (in kg/m^3) of solutes were Cu^{2+}:PP = 0.05:0.25; 2:0.2; 3:0.15; 3.5:0.1; 4:0.05. To observe the effects of transmembrane pressure drop and cross-flow rate, three pressures in the range of 345–483 kPa and three flow rates

Table 1
Operating conditions for single solute system

SDS (kg/m^3)	25
CPC (kg/m^3)	10
Cu^{2+} only (kg/m^3)	0.05, 1, 2, 2.5, 3, 3.5 and 4
PP only (kg/m^3)	0.05, 0.1, 0.15, 0.2 and 0.25
Pressure (kPa)	345
Cross-flow rate ($\times 10^5$ m^3/s)	0.835

Table 2
Operating conditions for mixture

SDS (kg/m^3)	CPC (kg/m^3)	(Cu^{2+} + PP) in mix. ($kg/m^3 + kg/m^3$)	Pressure (kPa)	Cross-flow rate ($\times 10^5\ m^3/s$)
25	10	0.05 + 0.25, 2 + 0.2, 3 + 0.15, 3.5 + 0.1 and 4 + 0.05	345	0.835, 1.25 and 1.67
25	10	0.05 + 0.25, 2 + 0.2, 3 + 0.15, 3.5 + 0.1 and 4 + 0.05	345, 414 and 483	0.835

in the range of 0.835×10^{-5} to $1.67 \times 10^{-5}\ m^3/s$ were selected. Overall 37 MEUF experiments were conducted. The experimental conditions are given in Tables 1 and 2 for single solute system and for binary mixture, respectively.

2.4.3. Chemical treatment for recovery of the surfactants

Recovery of surfactants from the permeate stream before final disposal was carried out by four successive processes, chemical treatment I (SDS precipitation), chemical treatment II (dissolution of calcium dodecyl sulfate), chemical treatment III (CPC precipitation) and chemical treatment IV (dissolution of CPI). The reactions involved in all the steps are presented in Appendix A. Optimum ratio of calcium chloride to SDS for maximum precipitation of the SDS in chemical treatment I and the ratio of sodium carbonate to calcium dodecyl sulfate in chemical treatment II for maximum regeneration of SDS were obtained from literature [21]. Optimum ratio of KI to CPC in chemical treatment III and the optimum ratio of $CuCl_2$ to CPI were also available [13].

2.5. Procedure

2.5.1. 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 flux versus 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 30 min. 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 temperature of $32 \pm 2\,°C$. 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.

2.5.2. Chemical treatment

A typical permeate sample of MEUF experiment was selected for the chemical treatment I. Measured amount of $CaCl_2$ (from optimum $CaCl_2$ to SDS ratio) was taken in 100 ml volumetric flask. The experiment was conducted at 30 °C and then cooled to freezing temperature to force precipitation as surfactant solutions stay supersaturated for long period. The solution was then kept in a constant temperature bath at 30 °C for 4 days and was shaken periodically. After complete precipitation, the solution was 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 optimum amount of Na_2CO_3 in chemical treatment II. Percent redissolution of calcium dodecyl sulfate was calculated in the same way as in chemical treatment I. The filtrate of chemical treatment I was subjected to chemical treatment III with optimum KI to CPC ratio. The solution was filtered after complete precipitation. The equilibrium concentration of CPC in the filtrate was measured using UV-spectrophotometer and the amount of CPC precipitated had been calculated by material balance. In chemical treatment IV, the precipitated CPI was treated with optimum amount of $CuCl_2$ solution. Percent redissolution of CPC was calculated in the same way as in chemical treatment III.

2.6. Analysis

2.6.1. Measurement of copper concentration

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

2.6.2. Measurement of potassium permanganate and CPC

Feed and permeate concentrations of CPC and PP were measured by a UV-spectrophotometer (make: Thermo Spectronic, USA; model: GENESYS 2). The wavelengths at which maximum absorption occurred and molar extinction coefficients of the different species were obtained from the measurements of the pure components and were shown elsewhere [13]. A standard method was used to calculate the concentrations of PP and CPC in the mixture [22].

2.6.3. Measurement of SDS concentration

SDS concentration was determined by a two-phase titration according to Epton [23]. The titrant was benzothonium chloride (often called hyamine 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. SDS concentration was

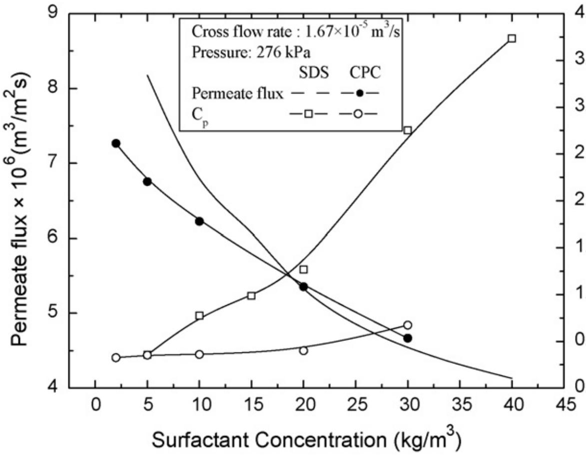


Fig. 2. Selection of feed surfactant concentrations.

determined using the following equation:

$$\text{SDS concentration} = \frac{a \times \text{molar concentration of hyamine} \times 288.38}{5\,\text{ml of sample}} \quad (1)$$

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

3. Results and discussions

3.1. Micellar-enhanced ultrafiltration

3.1.1. Selection of surfactant concentrations

Variations of permeate flux and permeate concentration for each of the surfactants are shown in Fig. 2. It is observed from the figure that the permeate flux decreases and permeate concentration increases with surfactant concentration in the feed. During filtration, surfactant micelles form a gel layer over the membrane surface. Thickness of this gel layer increases with surfactant concentration resulting in further decrease in permeate flux. Permeate concentration of surfactant increases with feed concentration. As surfactant concentration increases, permeate concentration may even go beyond the CMC level due to the leakage of smaller sized micelles. Therefore, feed surfactant concentration is selected such that permeate concentration is around the level of CMC. Based on these criteria and from the results presented in Fig. 2, feed surfactant concentrations are selected as 25 kg/m^3 for SDS (CMC = 2.33 kg/m^3) and 10 kg/m^3 for CPC (CMC = 0.322 kg/m^3). On mixing the two surfactants at these concentrations (SDS = 25 kg/m^3 and CPC = 10 kg/m^3), no precipitation is observed. However, it may be noted here that when SDS and CPC solutions are mixed in the concentration (in kg/m^3) range of 0.3:3.3 to 2.6:0.4 (corresponding molar concentration ratio 1:9 to 9:1), which are substantially lower than that used herein, immediate precipitation occurs. Therefore, it is clear that precipitate forms in a certain concentration range. Similar observations were made in a related study by Stellner and Scamehorn [24] where they presented a precipitation phase boundary plot, clearly showing the existence of a “precipitation zone” flanked by “clear solution zones” at lower and higher concentrations.

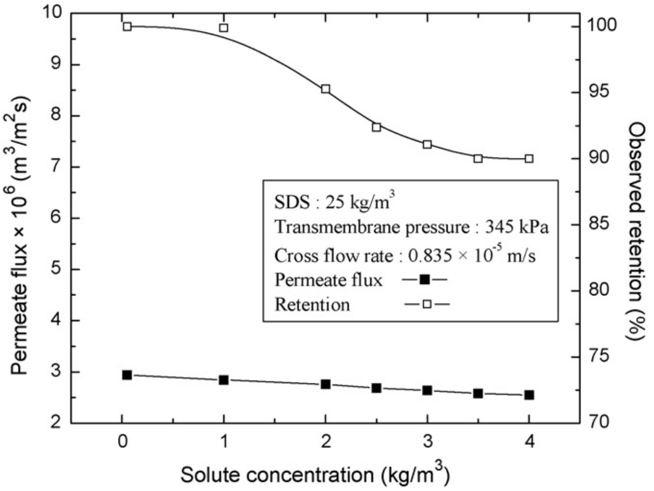


Fig. 3. Effect of feed concentration on permeate flux and solute retention for copper in the single component system.

3.2. MEUF of single component system

3.2.1. Effect of feed concentration on permeate flux and retention of copper and PP

Effects of feed concentration of solute on the permeate flux and retention of copper and potassium permanganate (PP) in single solute system are shown in Figs. 3 and 4, respectively. It is observed from these figures that permeate flux decreases with feed concentration of solute. It may be observed that permeate flux of 25 kg/m^3 SDS solution is about 4.8×10^{-6} m^3/m^2 s (refer Fig. 2), whereas addition of 1 kg/m^3 solute brings down the flux by almost 40% (Fig. 3). It may be noted that the flux of surfactant-copper system reported in Fig. 3 is at a transmembrane pressure of 345 kPa while that of the surfactant only system is at 276 kPa (Fig. 2). Therefore, if the flux of the surfactant-copper system at 345 kPa is compared with pure surfactant flux at an even higher

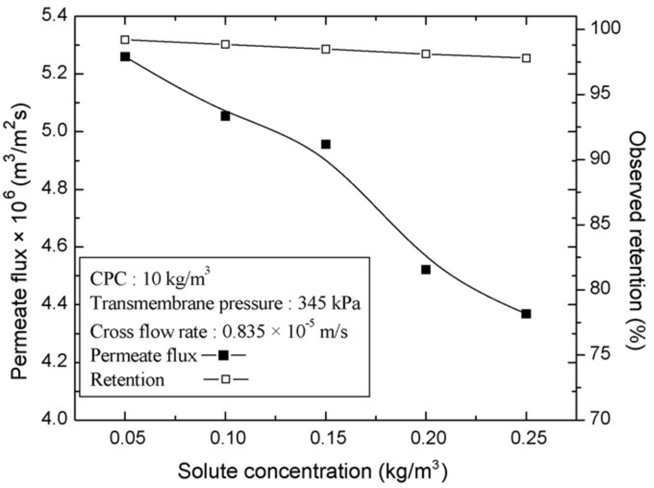


Fig. 4. Effect of feed concentration on permeate flux and solute retention for PP in the single component system.

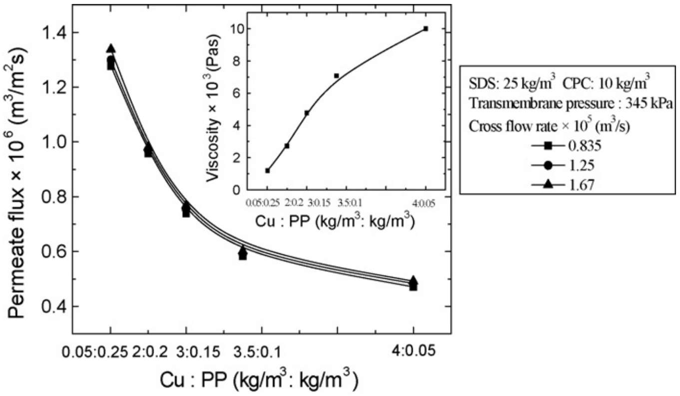


Fig. 5. Variation of permeate flux with cross-flow rate in the mixture.

pressure of 345 kPa (resulting in higher flux), this percentage decrease would be even higher. This signifies that the gel layer concentration of SDS is reduced on addition of counter ions. Copper being positively charged can act as bridge between negatively charged micelles, leading to larger micelles and earlier onset of the gel-layer over the membrane surface at lower surfactant concentration. In case of CPC, addition of 0.25 kg/m^3 PP reduces the flux by about 30%, compared to pure CPC solution (refer Figs. 2 and 4). It may be noted that the flux of surfactant-PP system reported in Fig. 4 is at a transmembrane pressure of 345 kPa while that of the surfactant only system is at 276 kPa (Fig. 2). Therefore, if the flux of the surfactant-PP system at 345 kPa is compared with pure surfactant flux at an even higher pressure of 345 kPa (resulting in higher flux), this percentage decrease would be even higher. When PP is added to CPC solution, attachment of bulkier permanganate group (MnO_4^-) to CPC micelles increases the size of the micelles leading to enhancement of gel layer resistance over the membrane surface causing a flux decline. This effect is more pronounced as the solute concentration increases. Since, surfactant concentration remains constant, the solubilization capacity of the micelles remains constant. Hence, an increase in solute concentration, leads to permeation of unsolubilized solutes in the permeate side, resulting in decrease in the observed retention. The observed retention decreases from about 100% to about 90% for copper and about 99 to 96% for potassium permanganate.

3.3. MEUF of binary mixture of copper and PP

Variation of permeate flux for five composition of mixture with the cross-flow rate is shown in Fig. 5. It is observed from the figure that the permeate flux is reduced significantly in the mixed micellar system. The flux is in the range of 2.7 to about 3×10^{-6} m^3/m^2 s for SDS and it varies from 4.4 to 5.2×10^{-6} m^3/m^2 s for CPC at various concentrations of counter ions in single solute system. In the mixed micellar system, the flux varies from about 0.5 to 1.4×10^{-6} m^3/m^2 s. Therefore, in mixed micellar system, inter micellar interaction of the oppositely charged micelles (negative for SDS and positive for CPC micelles) is quite strong in the gel type layer deposited over the membrane surface. Apart from that, presence of both type micelles leads to formation of more compact gel layer with larger thickness. For example, at 345 kPa pressure and 1.67×10^{-5} m^3/s flow rate but without the presence of copper or PP, flux is 2.97×10^{-6} m^3/m^2 s for a 25 kg/m^3 SDS and 10 kg/m^3 CPC mixture. Hence, the flux of mixed micellar system is much less compared to single component system (Fig. 2). It is also observed from Fig. 5 that flux decreases by about 3.5 times as copper concentration increases from 0.05 to 4 kg/m^3. Viscosity of the feed mixtures increases drastically from 1.2 to 10×10^{-3} (Pa s) as copper concentration in feed increases (Fig. 5 inset), resulting in sharp flux decline with copper concentration. Effect of cross-flow rate is negligible on this system. As observed from this figure, flux improvement is marginal for 100% increase in cross-flow rate. This also suggests viscosity being one of the causes of this decline which should remain unaffected with flow rate.

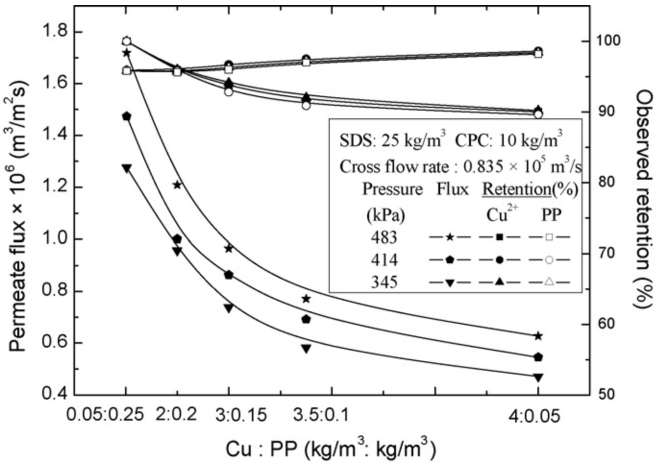


Fig. 6. Variation of permeate flux and solute retention with transmembrane pressure in the mixture.

Effect of transmembrane pressure on the mixed micellar system is shown in Fig. 6 for various feed composition of copper and potassium permanganate. It is observed that the flux increases almost linearly with pressure at fixed concentrations of copper and PP due to enhanced driving force. For example,

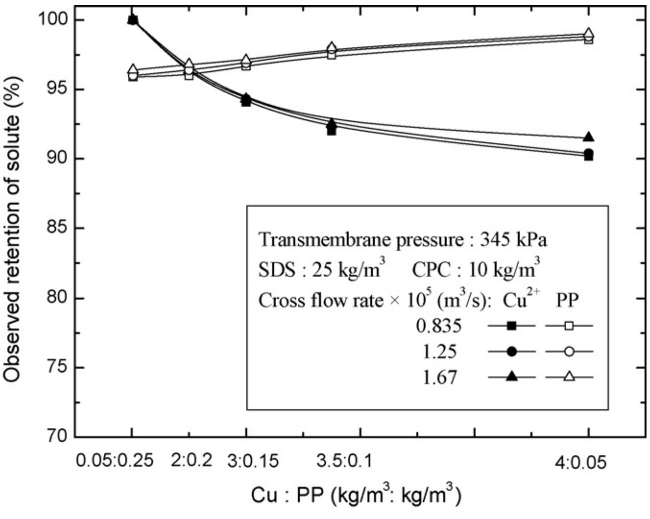


Fig. 7. Variation of solute retention with cross-flow rate in the mixture.

Table 3
Performance of MEUF for a typical feed condition at the end of experiment

Substrate	ΔP (kPa)	Cross-flow rate ($\times 10^5$ m^3/s)	Feed concentration (kg/m^3)	Permeate concentration (kg/m^3)	Retention (%)	Flux ($\times 10^6$ m^3/m^2 s)
SDS	345	0.835	25	2	92	0.7
CPC			10	0.36	96.5	
Cu^{2+}			3.5	0.302	91	
PP			0.1	0.003	97	

at copper and potassium permanganate composition of 4:0.05, flux is 0.47×10^{-6} m^3/m^2 s for pressure 345 kPa. At 414 kPa, flux is 0.55×10^{-6} m^3/m^2 s (17% increase). At 483 kPa, flux is 0.63×10^{-6} m^3/m^2 s (34% increase with respect to flux at 345 kPa). From Fig. 6, it is clear that effect of operating pressure is also insignificant on solute retention, in the mixed micellar system. Therefore, the operating conditions, namely, cross-flow rate and operating pressure do not affect the solute retention. It is governed solely by solubilization of counter ions on the micellar surface. Variation of solute retentions with cross-flow rate is presented in Fig. 7. The figure shows that observed retention varies from 90 to 100% for copper and 96 to 99% for potassium permanganate in the mixed micellar system. Theses values are quantitatively same with the single solute system. Hence, the solubilization capacity of mixed micellar system remains same. It is evident from the figure that cross-flow rate does not affect the observed retention of the solutes.

Observed retention of SDS varies in a range of 92–93.5% and that of CPC is in the range of 96–97.5% for a cross-flow range of 0.835–1.67 × 10^{-5} m^3/s and for a pressure range of 345–483 kPa. Hence, retention of surfactants is independent of operating conditions.

3.4. Chemical treatment for the recovery of surfactant from the permeate stream

3.4.1. Chemical treatment I

A typical MEUF permeate stream, as shown in Table 3, is 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. The relevant reaction is presented in Appendix A. The optimum $CaCl_2$ to SDS ratio is found out to be 0.384 [22]. With this optimum value, SDS precipitation is 91%.

Table 4
Performance of chemical treatment I to IV for a typical permeate concentration

Mixture	Copper PP
Copper (kg/m^3)	3.5
PP (kg/m^3)	0.1
Permeate SDS concentration (kg/m^3)	2.0
Permeate CPC concentration (kg/m^3)	0.36
$CaCl_2$/SDS (w/w)	0.384
SDS precipitated (%)	91
Na_2CO_3/calcium dodecyl sulfate (w/w)	0.71
KI/CPC (wt/wt)	1.5
CPC precipitated (%)	86.1
PP in filtrate (kg/m^3)	0.0023
$CuCl_2$/CPI	3.75
Recovered with respect to permeate (%)	
SDS	86.75
CPC	80.6

3.4.2. Chemical treatment II

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 aqueous medium. So, calcium dodecyl sulfate should be transformed to a 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 A. The optimum Na_2CO_3 to calcium dodecyl sulfate concentration is taken as 0.71 [22]. The percent redissolution of SDS for this optimum Na_2CO_3 to calcium dodecyl sulfate concentration ratio is 95.3 and SDS recovery is about 86.8% with respect to the permeate stream.

3.4.3. Chemical treatment III

Potassium iodide is added to the filtrate of chemical treatment I resulting in the precipitation of cetylpyridinium iodide. The optimum KI to CPC, obtained from literature is 1.5 [13]. CPC precipitation is 86.1% for this optimum KI to CPC ratio.

3.4.4. Chemical treatment IV

CPI obtained from chemical treatment III, cannot be recycled directly to the main feed of MEUF. So, CPI is treated with $CuCl_2$ to get back CPC. The optimum $CuCl_2$ to CPI ratio is taken from literature and is 3.75 [13]. The relevant reactions are presented in Appendix A. The redissolution of CPC is 93.6% and about 80.6% CPC is recovered from permeate stream. The results of chemical treatment I to IV are summarized in Table 4.

4. Conclusions

Simultaneous separation of cation (copper) and anion (PP) from their aqueous binary mixture was studied using MEUF with mixed micellar system comprising of SDS and CPC. The feed anionic surfactant (SDS) and cationic surfactant (CPC) concentrations were selected as 25 and 10 kg/m^3, respectively to be used with a 5 kDa membrane. A wide range of concentration of both solutes was studied (0.054–4.0 kg/m^3 for copper; 0.05–0.25 kg/m^3 for PP). Retention of copper and PP was in the range of 90–100% and 96–99%, respectively. For copper–PP system, retention of copper and PP was found to be quantitatively same with single solute system. Hence, the solubilization capacity of mixed micellar system remained same. Retention values were found to be independent of MEUF operating conditions, e.g., cross-flow rate and transmembrane pressure drop. The permeate flux of the mixed micellar system was found to be quite less than that of the single surfactant-solute system. A four step chemical treatment process was used for surfactant recovery. In the first step, for the optimum weight ratio of 0.38 of $CaCl_2$ to SDS, the SDS precipitation was found to be 91% and with second step, percent redissolution of SDS was about 95.3 for the optimum Na_2CO_3 to $Ca(DS)_2$ ratio of 0.71. About 87% SDS was recovered from permeate stream. In the third step, 86% CPC was precipitated for optimum KI to CPC ratio of 1.5 and with the fourth step, redissolution of CPC was about 94% for the optimum $CuCl_2$ to CPI ratio of 3.75.

Acknowledgements

This work is partially supported by a grant from the Department of Science and Technology, New Delhi, Government of India under the scheme no. SR/FTP/CS-11/2001 and from the Ministry of Human Resource Development under scheme no. F 27-1/2004/T. S. V., New Delhi, Government of India

Appendix A

Reaction occurring during chemical treatment I:

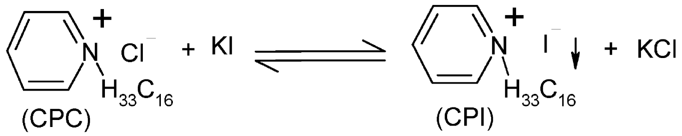
$$2C_{12}H_{25}SO_4^-Na^+(aq) + CaCl_2(aq) \rightleftharpoons Ca^{2+}(C_{12}H_{25}SO_4^-)_2(s)\downarrow + 2NaCl(aq)$$

Reaction occurring during chemical treatment II:

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

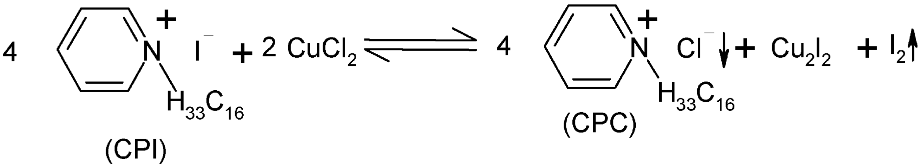
Reaction occurring during chemical treatment III:

$$KI \rightleftharpoons K^+ + I^-$$



Reactions occurring during chemical treatment IV:

$$CuCl_2 \rightleftharpoons Cu^{2+} + 2Cl^-$$



References

[1] A. Verma, S. Chakraborty, J.K. Basu, Sep. Purif. Technol. 50 (2006) 336.
[2] J.A.S. Tenório, D.C.R. Espinosa, Waste Manage. 21 (2001) 637.
[3] J.G. Dean, F.L. Bosqui, K.H. Lanouette, Environ. Sci. Technol. 6 (1972) 518.
[4] T.K. Rout, D.K. Sengupta, G. Kaur, S. Kumar, Int. J. Miner. Process. 80 (2–4) (2006) 215.
[5] R.E. Treybal, Mass-transfer Operations, 2nd ed., McGraw Hill, New York, 1968.
[6] C.K. Liu, C.W. Li, Sep. Purif. Technol. 43 (2005) 25.
[7] L. Gzara, A. Hafiane, M. Dhahbi, Rev. Sci. Eau 13 (3) (2000) 289 (article in French).
[8] L. Yurlova, A. Kryvoruchko, B. Kornilovich, Desalination 144 (2002) 255.
[9] N. Hankins, N. Hilal, O.O. Ogunbiyi, B. Azzopardi, Desalination 185 (2005) 185.
[10] R.S. Juang, Y.Y. Xu, C.L. Chen, J. Membr. Sci. 218 (2003) 257.
[11] S. Akita, L.P. Castillo, S. Nii, K. Takahashi, H. Takeuchi, J. Membr. Sci. 162 (1999) 111.
[12] H. Kim, K. Baek, J. Lee, J. Iqbal, J.W. Yang, Desalination 191 (2006) 186.
[13] M.K. Purkait, S. DasGupta, S. De, Sep. Sci. Technol. 40 (2005) 1439.
[14] K. Baek, J.W. Yang, J. Hazard. Mater. B108 (2004) 119.
[15] K. Baek, B.K. Kim, J.W. Yang, Desalination 156 (2003) 137.
[16] B.R. Fillipi, L.W. Brant, J.F. Scamehorn, S.D. Christian, J. Colloid Interface Sci. 213 (1999) 68.
[17] M. Aoudia, N. Allal, A. Djennet, L. Toumi, J. Membr. Sci. 217 (2003) 181–192.
[18] C.W. Li, C.K. Liu, W.-S. Yen, Chemosphere 63 (2006) 353.
[19] J.F. Rathman, J.F. Scamehorn, J. Phys. Chem. 88 (1984) 5807.
[20] M.K. Purkait, S. DasGupta, S. De, J. Membr. Sci. 250 (2005) 47.
[21] C. Das, S. DasGupta, S. De, Sep. Sci. Technol. 43 (2008) 71.
[22] G.H. Jeffery, J. Basseh, J. Mendham, R.C. Denney, Vogel's Textbook of Quantitative Chemical Analysis, 5th ed., Longman, London, 1989.
[23] S.R. Epton, Trans. Faraday Soc. 44 (1948) 226.
[24] K.L. Stellner, J.F. Scamehorn, Langmuir 5 (1989) 70.