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Simultaneous Separation of Two Oxyanions from Their Mixture Using Micellar Enhanced Ultrafiltration

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Abstract: Surfactant-based separation of two oxyanions ($Cr_2O_7^{=}$ and MnO_4^{-}) from their mixture is studied to assess the potential of micellar enhanced ultrafiltration (MEUF). Cetyl(hexadecyl) pyridinium chloride (CPC) has been taken as the cationic surfactant. An organic polyamide membrane of a molecular weight cut off of 1000 is used. About 99% retention of the solutes is observed under unstirred batch mode. In order to improve the permeate flux and the retention of the solutes, cross-flow studies are also conducted. The retention of solutes without using surfactant varies from 6 to 15% only, at a typical feed mixture concentration of $0.05\,kg/m^3$ for each of the two solutes. Under the same operating conditions, the solute retention increases up to 99% using surfactant micelle. The effects of various operating conditions, e.g., concentrations of surfactant and solutes, transmembrane pressure drop and cross-flow rate (for cross-flow experiments), etc., on the permeate flux and observed retention are studied in detail in the batch as well as in the cross-flow mode. Surfactants present in the permeate and retentate are then recovered by a two-step chemical treatment process. In the first step, the surfactant is precipitated by potassium iodide and in the second step, it is recovered from the precipitate by the addition of cupric chloride. Optimum amounts of potassium iodide and cupric chloride are also experimentally obtained.

Keywords: Oxyanions, cationic surfactant, micellar enhanced ultrafiltration, permeate flux, observed retention, precipitation

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INTRODUCTION

Traditional methods for separation, purification, and concentration of metal ions include sorption and chemical precipitation (1, 2). However these techniques are incapable of reducing metal ion concentrations to the levels required by law or are prohibitively expensive. Therefore, it is desirable to develop a low-energy intensive separation process. Rate-governed separation process, like reverse osmosis (RO), is already recognized as one of the best available techniques for the separation of several inorganic and organic compounds. Compared to nanofiltration (NF), ultrafiltration (UF), and microfiltration (MF), relatively dense membranes are used in the RO process. Permeability of RO membranes is quite low, and to get the desired throughput (permeate flux), higher operating pressures are required. Therefore, a modified membrane separation process can prove to be a competitive alternative where the operating pressure requirement is low compared to RO, and a membrane of higher permeability can be used.

Micellar enhanced ultrafiltration (MEUF) is one such promising technology that employs surfactant micelles to solubilize inorganic and organic contaminants from the aqueous stream (3). In MEUF, the solute-containing stream is treated with a surfactant at a concentration well above the critical micellar concentration (CMC). Most of the solute molecules are solubilized in the micelles. Micelles being larger in size can be removed along with the solubilized organic contaminants using a relatively porous membrane at lower operating pressure. The permeate stream contains unsolubilized solutes and free surfactants. Therefore, MEUF may be an alternative to overcome the inherent limitations of the RO process.

So far, MEUF is used to separate different organic (4–7), inorganic compound (8), and dye (9, 10), using various surfactants. A number of studies have been carried out to remove multivalent metal ions from aqueous medium (1, 11–13). However, most of these studies are focused on the MEUF of single compound rather than MEUF of a multi-solute system (14–16). Competition due to the difference in binding power of various solutes plays an important role during the MEUF of mixture of solutes.

In the present work, simultaneous separation of potassium dichromate, $K_2Cr_2O_7$ (PD) and potassium permanganate, $KMnO_4$ (PP) from aqueous stream is studied. The MEUF experiments are first conducted in unstirred batch mode. The effects of important factors, like ionic character of the solute, concentration of surfactant and solutes, transmembrane pressure drop, etc., on the solubilizing capacity of CPC micelles and the concentration polarization over the membrane surface in terms of retention and flux have been investigated in detail. It is well known that the filtration performance is poor in batch mode as the permeate flux and the solute retention decrease substantially with time, especially for a system with low operating volume (as is used in this work). Therefore, to improve the permeate flux as well as the quality of the permeate, the separation studies are conducted in a steady-state cross-flow mode as well. The effects of various operating conditions (concentration of surfactant and solutes, transmembrane pressure drop and cross-flow rate) on the permeate flux and observed retention of the solute are similarly studied in cross-flow modes.

To improve the economics of the MEUF system it is necessary to recycle the surfactant molecules present in the retentate as well as in the permeate stream before disposal. Several authors have studied precipitation method for the recycling of sodium dodecyl sulphate (SDS) using multivalent counter ions (1). Air stripping method for the separation of surfactant and reuse of the surfactant have also been reported (17). Many researchers used MEUF with CPC as the cationic surfactant (16), but literature regarding the recovery of CPC is still scant. The present work also involves the recovery of CPC by the precipitation method. A two-step chemical treatment process has been adopted to recover the surfactant from the permeate stream. In the first step, monovalent iodide (I^-) is used to precipitate the cetyl pyridinium ion. In the second step, concentrated CPC is regenerated using cupric chloride solution and is recycled to the feed stream. The optimum consumption of potassium iodide and cupric chloride is also experimentally obtained. The same procedure is used to recover the surfactant from the retentate stream. A schematic of the MEUF and surfactant recovery is shown in Fig. 1.

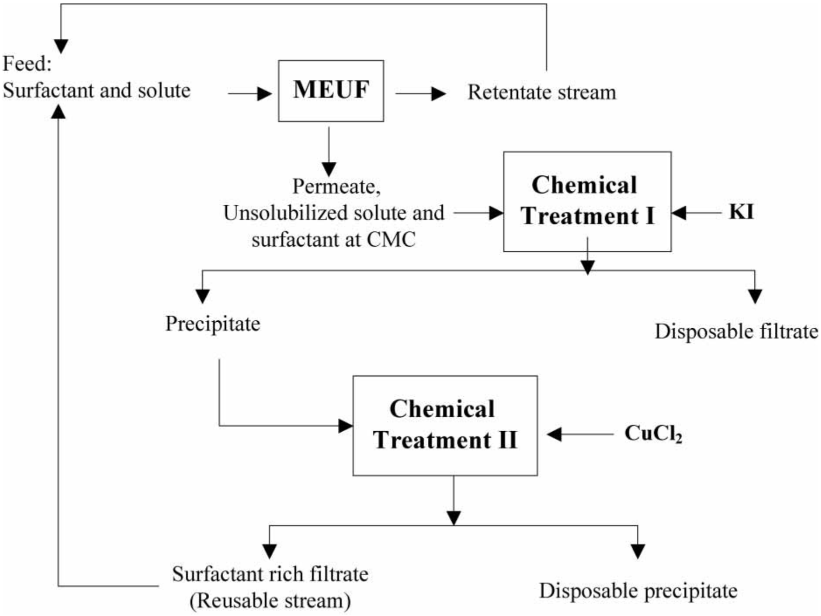

Figure 1. Schematic of the MEUF and recovery of the surfactant.

EXPERIMENTAL

Materials

The surfactant CPC (MW 358) is procured from SISCO Research Laboratories, Mumbai, India. Potassium dichromate ($K_2Cr_2O_7$, MW 294.19), potassium permanganate ($KMnO_4$, MW 157.94), potassium iodide (KI, MW 166), and cupric chloride ($CuCl_2 \cdot 2H_2O$, MW 170.48) are obtained from Merck, Mumbai, India.

Membranes

The membrane used is of 1000 molecular weight cut-off (MWCO), and is obtained from Genesis Sepratech Pvt. Ltd, Mumbai, India. The permeability of the membrane is experimentally evaluated as $3.35 \times 10^{-11}\,\mathrm{m/Pa \cdot s}$.

Experimental Setup

Batch Cell

The unstirred batch experiments are conducted in a 50 mL capacity filtration cell (MILLIPORE, model 8050, USA). Inside the cell, a circular membrane is placed over a base support. The effective membrane area is $13.4 \times 10^{-4}\,\mathrm{m^2}$. The maximum allowable pressure is 518 kPa. The permeate is collected from the outlet of the cell at the bottom. The cell is pressurized by nitrogen. The schematic of the experimental set up is shown elsewhere (10).

Cross-Flow Cell

A rectangular cross-flow cell, made of stainless steel, is designed and fabricated. A schematic of the experimental setup is shown in Fig. 2. The cell consists of two matching flanges. The inner surface of the top flange is mirror polished. The bottom flange is grooved forming the channel for the permeate flow. A porous stainless steel plate is placed on the lower plate to provide mechanical support to the membrane. A teflon gasket is placed over the membrane. The effective length of the membrane is $37.3 \times 10^{-2}\,\mathrm{m}$ and width is $5.2 \times 10^{-2}\,\mathrm{m}$. The channel height after the tightening of the flanges is found to be $3.44 \times 10^{-3}\,\mathrm{m}$. The micellar solution with solutes is placed in a stainless steel feed tank of 10 L capacity. A reciprocating pump is used to feed the solution in the cell. The retentate stream is recycled to the feed tank. The permeate stream is also recycled to maintain a constant concentration in the feed tank. A bypass from the pump delivery to the feed

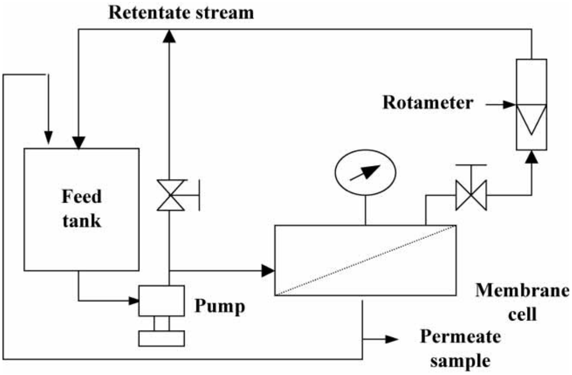

Figure 2. Schematic of the cross-flow experimental set up.

tank is provided. The two valves in the bypass and the retentate lines are used to vary the pressure and the flow rate through the cell, independently.

EXPERIMENTS

Micellar Enhanced Ultrafiltration

Batch Cell

Filtration experiments are carried out with (i) the mixture of surfactant and solutes with different concentrations and (ii) individual solutes in aqueous solution in an unstirred batch cell. The experiments are conducted for about 30 min for the solution of solutes only and about 60 min for the solute and surfactant mixture. Experiments are designed to observe the effects of the variation in solute concentration and the transmembrane pressure drop on the permeate flux and the retention of both the solute and the surfactant. Various operating conditions used during the batch experiments are given in Table 1.

Table 1. Operating conditions for the experiments in batch cell

CPC (kg/m^3)	PD (kg/m^3)	PP (kg/m^3)	Pressure (kPa)
—	0.05	0.05	345, 414, and 483
10	0.05, 0.10, 0.15, 0.20	—	345
10	—	0.05, 0.10, 0.15, 0.20	345
10	0.05, 0.10, 0.15, 0.20	0.05, 0.10, 0.15, 0.20	345, 414, and 483

Cross-Flow Cell

MEUF experiments of PD and PP have been conducted using CPC in a cross-flow cell to observe the effect of concentrations of both the surfactant and solute, cross-flow rate, transmembrane pressure drop, and the ionic characteristic of solute. Operating conditions for the cross-flow experiments are given in Table 2.

Chemical Treatment for Recovery of the Surfactant

Experiments for the recovery of surfactant, both from the permeate and the retentate stream, are carried out by two successive chemical treatments. The main reactions of chemical treatment I and II for the precipitation of CPC and the redissolution of CPI are discussed elsewhere for the recovery of CPC from the permeate during MEUF of dye solution (9). A series of experiments have been carried out to obtain the optimum ratio of KI to CPC for maximum precipitation of the surfactant in chemical treatment I and the ratio of $CuCl_2$ to CPI (cetyl pyridinium iodide) in chemical treatment II for the maximum recovery of CPC. Recovery studies of CPC from the retentate stream are performed for a typical PD-CPC mixture.

PROCEDURE

MEUF Run

Fresh membrane is compacted at a pressure of 500 kPa for 3 h using distilled water. The feed solution of each batch is prepared by weighing measured

Table 2. Operating conditions for the experiments in cross-flow cell

CPC (kg/m^3)	PD (kg/m^3)	PP (kg/m^3)	Pressure (kPa)	Flow rate (l/h)
10	0.05	0.05	345	30
10	0.10	0.10	345	30
10	0.15	0.15	345	30
10	0.20	0.20	345	30
10	0.25	0.25	345	30
10	0.10	0.10	414	30
10	0.10	0.10	483	30
10	0.10	0.10	345	45
10	0.10	0.10	345	75
8	0.10	0.10	345	30
9	0.10	0.10	345	30
11	0.10	0.10	345	30

amounts of solute and surfactant and using distilled water. The batch cell is pressurized by nitrogen. Permeate from the bottom of the cell is collected and its cumulative weight is measured with the help of an electronic balance. The density of the permeate stream is measured and the cumulative weights are converted to cumulative volumes. From the slope of the cumulative volume vs. time curve, the permeate flux is obtained as a function of operating time. The permeate concentrations of the collected samples are determined spectrophotometrically.

In cross-flow experiments, the pure water flux at various operating pressures are measured and the membrane permeability is determined from the slope of the flux vs. pressure plot. The magnitude of the permeate flux at different points of time are calculated from the slopes of the cumulative volume vs. time plot. Permeate samples are analyzed using a spectrophotometer. The duration of a cross-flow experiment is 1 h.

After each experiment, the membrane is thoroughly washed, in situ, by distilled water for 15 min at a pressure of 500 kPa. The cross-flow channel is dismantled thereafter, and the membrane is dipped in distilled water for about 30 min and washed carefully with distilled water to remove traces of the surfactant. The cross-flow cell is reassembled and the membrane permeability is measured again. It is observed that the membrane permeability remains almost constant between successive runs. All the experiments have been conducted at a room temperature of $32 \pm 2°C$. The observed retention of each solute is defined as $R_0 = 1 - C_p/C_0$, where, C_p and C_0 are the solute concentrations in the permeate and feed, respectively.

Chemical Treatment

Typical permeate and retentate streams of a MEUF experiment with a mixture of PD and PP in cross-flow, corresponding to the optimum solute-to-surfactant ratio (for maximum solute retention), has been selected for the chemical treatment. The experimental procedure for both chemical treatments I and II are discussed elsewhere (9).

ANALYSIS

Feed and permeate concentrations of surfactant and solute are measured by a UV spectrophotometer (make: Thermo Spectronic, USA; model: GENESYS 2). The wavelengths at which maximum absorption occurs and molar extinction coefficients of the different species are obtained from the measurements of the pure components and are shown in Table 3. A standard method is used to calculate the concentrations of different solute and surfactant in the mixture (18).

Table 3. Molar extinction coefficients for different solutes at different wave lengths

Compound	Wave length (nm)	Molar extinction coefficients (m^3/kg cm)		
		PD	CPC	PP
PD	355	2,950	4,016	9.2
CPC	259	10.7	3,880	5.8
PP	526	1,026	501	2,128

RESULTS AND DISCUSSIONS

This section is divided into three parts. The first part explains the effects of transmembrane pressure drop and different combinations of surfactant and solutes on the permeate flux and the retention characteristic of the solutes in the batch cell. Variations of flux and retention in the cross-flow cell at different operating conditions are discussed in the second part. The third part deals with the recovery of the surfactant from the retentate and permeate stream using chemical treatments (I and II).

MICELLAR ENHANCED ULTRAFILTRATION IN BATCH CELL

Variation of the Solute Retention and Permeate Flux During UF in Absence and in Presence of Surfactant

The variation of solute retention with and without surfactant is presented in Fig. 3 for a mixture of PD and PP at concentrations of 0.05 kg/m^3 each and at a transmembrane pressure of 345 kPa using 10 kg/m^3 of surfactant. For the solutes-only case, it is observed that the retention decreases slightly as more solution permeated out (with increase in operating time). In this case, about 90% of the feed volume has been permeated within half an hour. It may be observed that the retention of the solutes by the membrane is very low. The retention of PD decreases from about 12 to 6%, whereas that for PP is from about 15 to 8%. This trend shows that without surfactant, both PD and PP permeate through the membrane almost freely. The slight decrease in retention of these solutes may be explained due to the concentration polarization effects. As more filtrate permeates, the retentate gets concentrated in the solute and more solutes deposit over the membrane surface, leading to concentration polarization. This results in an increase in the convective transport of the solutes to the permeate side, thereby increasing the permeate concentration and subsequently decreasing the observed retention. In the presence of surfactant, the retention of both PD and PP is

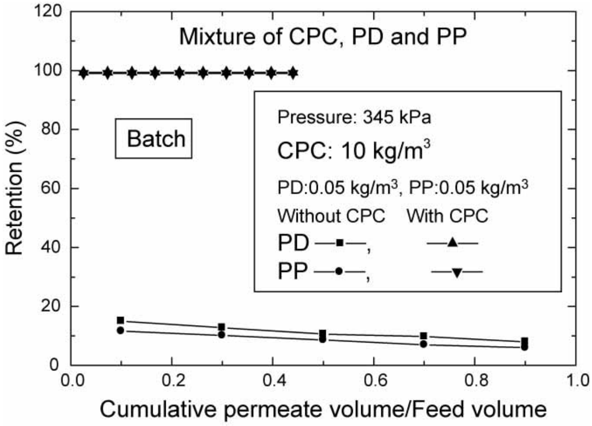

Figure 3. Variations of solute retention during MEUF of mixture of PD and PP in the presence and absence of surfactant using batch cell. Feed: CPC: 10 kg/m^3, PD: 0.05 kg/m^3, and PP: 0.05 kg/m^3.

almost constant at about 99%. In this case, about 44% of feed volume has been permeated within an hour of operation. This clearly shows that almost all the solutes are solubilized within the surfactant micelles, and the concentration of the free solutes is very low. Hence, the effect of concentration polarization due to the solutes on their retention is negligible. This results in almost constant retention of solutes as more filtrate permeated through the membrane (i.e., with the time of operation). This clearly indicates that the solutes are solubilized on the surfactant micelles (10), which are subsequently retained by the ultrafiltration membrane.

The variation of the permeate flux with and without surfactants is shown in Fig. 4 for the MEUF of the mixture of PD and PP at a concentration of 0.05 kg/m^3 each and at a transmembrane pressure of 345 kPa using 10 kg/m^3 of surfactant. Lower flux is observed during UF of solutes with surfactant micelles than that of without surfactant. For example, the permeate flux is about $4.7 \times 10^{-6}\,\mathrm{m^3/m^2 \cdot s}$, when about 44% of feed volume permeate (at the end of 1 h) for the mixture of PD, PP, and surfactant. In cases without surfactant, the flux is about $9.8 \times 10^{-6}\,\mathrm{m^3/m^2 \cdot s}$ at the same retentate volume reduction. The decrease in flux due to addition of surfactant is about 52%. By the addition of surfactants above the critical micellar concentration (CMC of CPC is 0.322 kg/m^3 (19)), the surfactant micelles form large aggregates resulting in a deposited layer over the membrane surface (3, 4) and consequently, increasing the resistance against the solvent flux through the membrane. This results in a sharp decrease in the permeate flux, compared to that of cases without surfactant.

A marginal decrease of flux is observed as more filtrate permeate out (with the progress of operating time), in both cases. As discussed earlier,

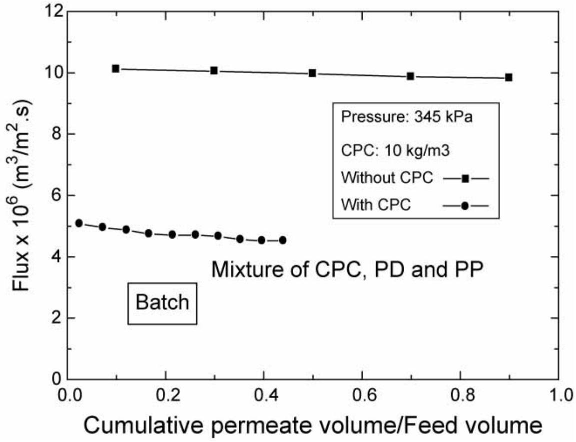

Figure 4. Variation of permeate flux during MEUF of a mixture of PD and PP in presence and absence of surfactant using batch cell. Feed: CPC: $10\,\mathrm{kg/m^3}$, PD: $0.05\,\mathrm{kg/m^3}$, and PP: $0.05\,\mathrm{kg/m^3}$.

for the case of filtration of solutes only, the permeate flux declines with the time of operation due to concentration polarization. For example, in the case of filtration of the mixture of PD and PP only, the permeate flux decreases from about $10.1 \times 10^{-6}\,\mathrm{m^3/m^2 \cdot s}$ (when 10% of feed volume has been permeated) to $9.8 \times 10^{-6}\,\mathrm{m^3/m^2 \cdot s}$ (when 90% of feed volume has been permeated) at 345 kPa. This indicates that a drop in flux of about 3% occurred during half an hour of operation. For the case of MEUF of PD, PP, and CPC mixture, the permeate flux drops from about $5.0 \times 10^{-6}\,\mathrm{m^3/m^2 \cdot s}$ (when 2.5% of feed volume has been permeated) to $4.5 \times 10^{-6}\,\mathrm{m^3/m^2 \cdot s}$ (when 44% of feed volume has been permeated) at 345 kPa. Moreover, due to volume reduction of the retentate, the micellar concentration also increases. For example, at the end of one hour, about 44% of filtrate volume has been permeated leading to about 1.8 times increase in feed concentration of surfactant. Hence, with the progress of filtration, the micelles form a more concentrated layer on the membrane surface, leading to a decline in flux. Therefore, the flux of the micelle containing mixture drops about 7% during 1 h of operation.

Effect of Feed Solute Concentration, Pressure Drop, and the Ionic Character of the Solute on the Observed Retention

The effects of the solute concentration in the feed on observed retention at fixed CPC concentration ($10\,\mathrm{kg/m^3}$) are shown in Fig. 5 at three different pressures. The solute concentration is gradually increased (from 0.05 to $0.20\,\mathrm{kg/m^3}$), keeping PD and PP concentration in the ratio of 1 : 1. The figure shows that the retention of PD and PP decreases with feed

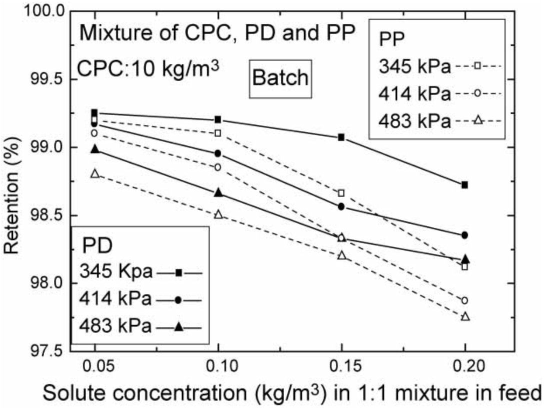

Figure 5. Effect of initial solute concentration on the retention of solute at three different pressures during MEUF of PD and PP mixture in presence of 10 kg/m^3 of CPC at the end of batch experiment.

concentration. Since the concentration of micelle is nearly constant (as feed CPC concentration is fixed), the solubilization capacity of the micelles is almost constant. Further increase in solute concentration results in an increase of the concentration of unsolubilized solute. This, in turn, increases the permeate concentration and reduces the observed retention of the solutes.

The effect of operating pressure on the observed retention at different feed solute concentration at the end of the experiment is also shown in Fig. 5. The retention of solute increases with decrease in the operating pressure. For example, at a feed concentration of 0.1 kg/m^3, the retention of PD increases from 98.6% to 99.2% when the pressure is decreased from 483 to 345 kPa. At higher operating pressure, micelles become compact and therefore solubilization capability of the micelles decreases (6, 9) resulting in more concentration of free PD in the solution. Similar trend is observed for the retention of PP.

From Fig. 5 it may also be observed that the extent of retention of PD and PP are slightly different (more for PD and less for PP at the same operating condition). PD and PP exist as divalent and monovalent oxyanions, respectively, in aqueous medium and hence readily get solubilized on the outer periphery of the positively charged micelles (19). The slight difference in the extent of the solubilization for PD and PP is due to their ionic characteristics. Attachment of divalent oxyanion (PD) to the exterior of the micelles is more compared to that of the monovalent oxyanion (PP). Therefore, the permeate (containing unsolubilized solute) concentration of PD is lower and hence it shows more observed retention (about 98.8% for PD and 98.1% for PP at 345 kPa pressure and a feed concentration of 0.2 kg/m^3 in Fig. 5).

The retention characteristic of PD and PP in their individual micellar solution is also shown in Fig. 6 with feed solute concentration at 345 kPa

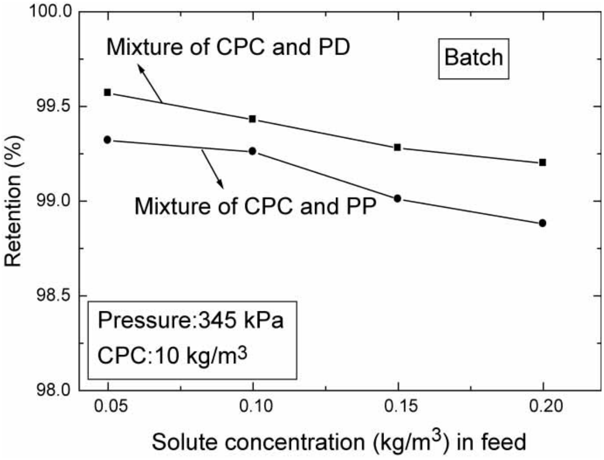

Figure 6. Effect of initial solute concentration on the retention of solute at 345 kPa pressure during MEUF of PD and PP separately, in presence of $10\,kg/m^3$ of CPC at the end of batch experiment.

pressure. In this case, MEUF experiments are performed using different concentrations of PD and PP separately with $10\,kg/m^3$ of CPC. The variation of solute retention with feed solute concentration is consistent with the results discussed in Fig. 5.

In the mixture of CPC, PD, and PP, there is competitive solubilization of the counter ions on the micellar surface. The solubilized dichromate and free monovalent permanganate also cause mutual repulsion and thus adversely affect their solubilization. This effect is absent in the single solute system in the micellar solution. Thus it may be observed from Fig. 6 that at a solute concentration of $0.2\,kg/m^3$ and 345 kPa pressure, the retention of PD and PP are about 99.2% and 98.8%. Whereas, at the same condition, in the mixture of PD and PP, the values of the retention are about 98.8% and 98.1% (Fig. 5).

Variation of Permeate Flux with Pressure at the End of Batch Experiment

The effects of the operating pressure on the permeate flux are presented in Fig. 7 for different concentrations of the mixture of PD and PP using $10\,kg/m^3$ of CPC at the end of batch experiments. The figure shows that for all the solute concentrations, the flux linearly increases with pressure due to an increase in the effective driving force. From Fig. 7 it may also be observed that the flux is more for lower solute concentration at the same pressure. For example, flux decreases from about 4.5 to $1.9 \times 10^{-6}\,m^3/m^2 \cdot s$ when the solute concentration increases from 0.05 to $0.20\,kg/m^3$. The CMC of ionic surfactant decreases with an increase of concentrations of

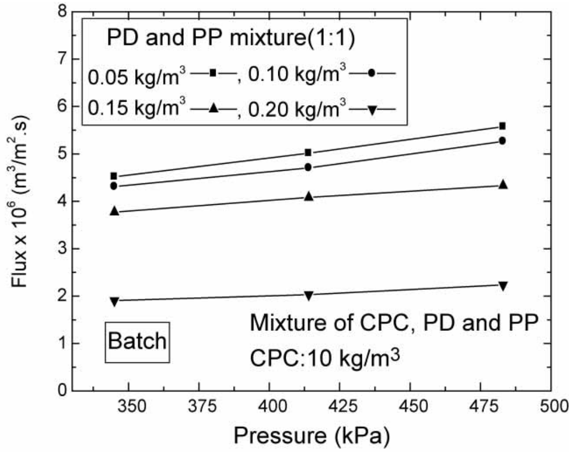

Figure 7. Variation of permeate flux with pressure during MEUF of PD and PP mixture in presence of $10\,\mathrm{kg/m^3}$ of CPC at the end of batch experiment.

counter ions in aqueous medium (19). The extent of binding of counter ions depends on the degree of ionic character of the solute (20). Being highly ionic in nature, PD and PP decrease the CMC of CPC substantially. This increases concentration of micelles and hence, more solutes are solubilized, resulting in an increase in the size of micellar aggregates (19, 20). These larger aggregates deposit over the membrane surface and results in a decrease in the permeate flux with feed concentration.

MICELLAR ENHANCED ULTRAFILTRATION IN CROSS-FLOW CELL

Once concept of the separation of the mixture of oxyanions in an unstirred batch cell using MEUF is successfully validated, the mixture is then subjected to a steady-state cross-flow ultrafiltration as this should substantially improve flux and retention. A detailed parametric study is also conducted to observe the effects of the operating conditions on the permeate flux and observed retention.

Effect of the Feed Surfactant Concentration on the Retention of Solute and the Permeate Flux

The effect of feed surfactant concentration on the retention and the permeate flux of a 1 : 1 (each concentration is $0.1\,\mathrm{kg/m^3}$) solute mixture is presented in Fig. 8. The results are obtained at an operating pressure difference of 345 kPa and cross-flow rate of 30 l/h. It may be noted from Fig. 8 that the permeate

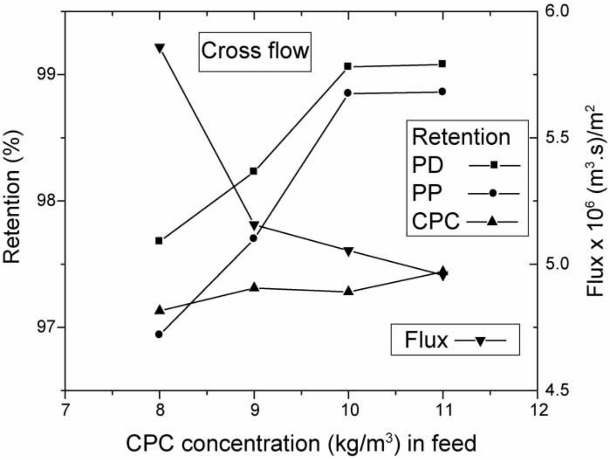

Figure 8. Effect of feed surfactant concentration on the retention of solute and permeate flux. Operating pressure: 345 kPa; cross-flow rate: 30 l/h; Concentrations: PD: 0.1 kg/m^3; PP: 0.1 kg/m^3.

flux decreases with the feed CPC concentration due to more concentration polarization over the membrane surface. The permeate flux at a CPC concentration of 10 kg/m^3 and pressure of 345 kPa is about 5.1×10^{-6} m^3/m$^2 \cdot$ s. It may also be observed that the retention of both PD and PP increases with CPC concentration and remains almost constant beyond a surfactant concentration of 10 kg/m^3. Therefore, 10 kg/m^3 may be considered as the optimum surfactant concentration for the separation of PD and PP in their mixture at a concentration of 0.1 kg/m^3 each. The retention of PP increases from about 96.7% to 98.7% when feed CPC concentration increases from 8 to 11 kg/m^3. In the same range, the observed retention of PD increases from about 97.6% to 99%. The retention of PD is more than that of PP because of the reasons discussed earlier. The retention of the CPC is also presented in the same figure and it is in the range of about 97% to 97.4%.

Effects of Solute Concentration on the Observed Retention and Permeate Flux

Effects of solute concentration on the observed retention and the permeate flux are shown in Fig. 9. In this figure, the operating pressure is 345 kPa and cross-flow rate is kept constant at 30 l/h. The feed CPC concentration is kept constant at 10 kg/m^3 and the solute mixture composition is varied as 0.05 : 0.05, 0.1 : 0.1, 0.15 : 0.15, 0.2 : 0.2, and 0.25 : 0.25 (all concentrations are in kg/m^3). It may be observed from Fig. 9 that the permeate flux decreases with increase in solute concentration due to concentration polarization. The micelles will also contain more amounts of solutes, and these

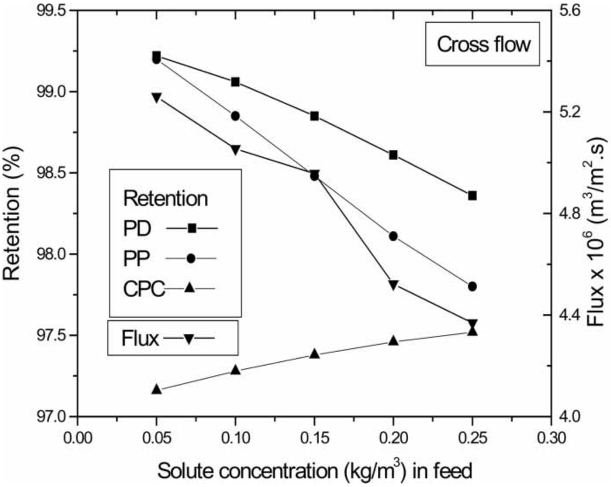

Figure 9. Effect of initial solute concentration on the observed retention and permeate flux. Operating pressure: 345 kPa; cross-flow rate: 30 l/h; Feed CPC concentration: 10 kg/m^3.

can be increased deposition on the membrane. The observed retention of PD and PP decreases with solute concentration for reasons already discussed in Section 3.1.2. The retention of PD is more than that of PP due to its ionic charge as discussed earlier. Interestingly, it may be observed from the figure that the observed retention of CPC increases slightly from about 97.1% to 97.5% with solute concentration in the mixture. As mentioned earlier, higher solute concentration increases the concentration of solutes in the micelles. Since ionic PD and PP get attached on the outer surface of the micelles, solubilized solute slightly enhances the size of the micellar aggregates. Hence, at higher concentration of solute mixture, only the smaller-sized micelles permeate through the membrane leading to a slight increase in the observed retention of the surfactant.

Effects of Pressure on the Observed Retention and the Permeate Flux

Effects of pressure on the observed retention and the permeate flux are shown in Fig. 10 for a flow rate of 30 l/h, solute concentration in a mixture of 0.1 : 0.1 (kg/m^3) and CPC concentration of 10 kg/m^3. The permeate flux increases with pressure as expected, due to an increase in the driving force. The observed retention of both the solutes shows a very slow decline with pressure for reasons discussed before. The retention of PD decreases from 99% to 98.6% and that for PP decreases from about 98.7% to 98.3% as pressure increases from 345 to 483 kPa. The retention of CPC decreases

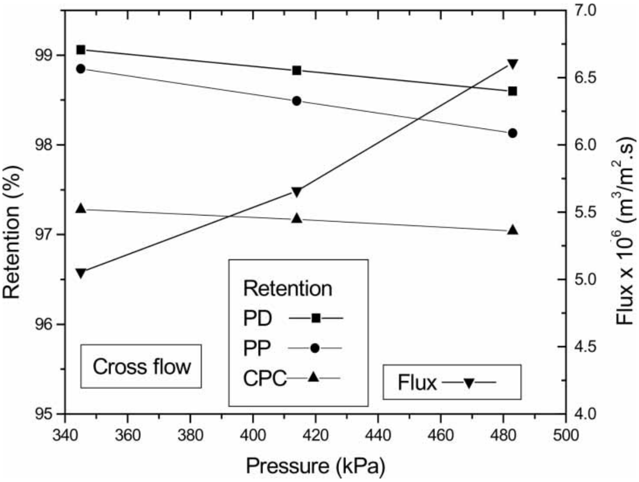

Figure 10. Effect of pressure on the observed retention and permeate flux. Cross-flow rate: 30 l/h; Feed concentrations, CPC: 10 kg/m^3; PD: 0.1 kg/m^3; PP: 0.1 kg/m^3.

marginally from 97.3% to about 97% in the pressure range. This may be due to smaller sized micelles permeating through the membrane at higher pressure.

Effect of Cross-Flow Rate on the Observed Retention and the Permeate Flux

Effect of the cross-flow rate on the observed retention and the permeate flux at a fixed pressure (345 kPa), surfactant concentration (10 kg/m^3) and solute concentration (0.1 kg/m^3 each) in the mixture is shown in Fig. 11. It may be observed from the figure that the permeate flux increases with cross-flow rate almost linearly. This is due to the reduction of the thickness of the micellar layer over the membrane surface by the forced convection imposed by cross flow. The flux enhancement is about 6% when the cross-flow rate is increased from 30 to 75 l/h. It is also evident that the variations of the observed retention of the solutes and CPC remain almost constant. Therefore, cross-flow velocity improves the permeate flux without alternating the retention values significantly.

CHEMICAL TREATMENTS FOR RECOVERY OF SURFACTANT FROM THE PERMEATE STREAM

Chemical Treatment I

A typical MEUF permeate stream (as shown in Table 4) is selected to test the efficacy of the two-step chemical treatment process for the recovery of the

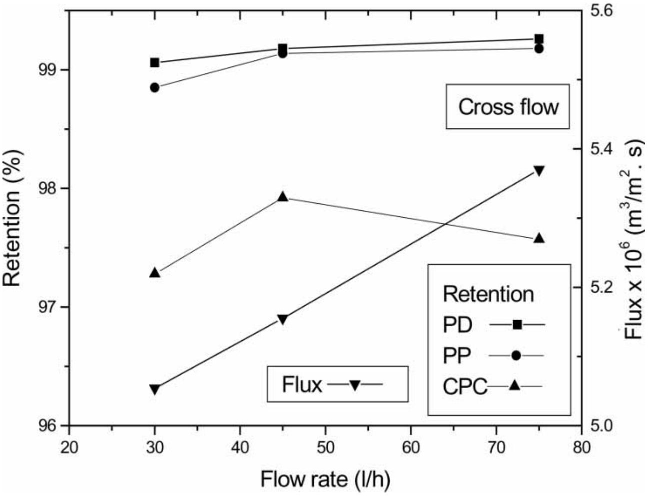

Figure 11. Effect of cross-flow rate on the observed retention and permeate flux. Operating pressure: 345 kPa; Feed concentrations, CPC: 10 kg/m^3; PD: 0.1 kg/m^3; PP: 0.1 kg/m^3.

surfactant. In the first treatment process, potassium iodide is added to the permeate stream resulting in the precipitation of cetyl pyridinium iodide. The extent of precipitation is highly dependent on (i) pH of the medium (ii) degree of dissociation of precipitating agent, and (iii) temperature. The solubility of cetyl pyridinium ions in the presence of Cl$^-$, Br$^-$, S^{-2}, CO_3^{-2}, or SO_4^{-2} is high and it cannot be precipitated even at neutral pH. On the other hand, in presence of iodide ion (I$^-$), cetyl pyridinium ions produce cetyl

Table 4. Performance of MEUF for a typical feed condition using cross-flow cell

	Solute	
	PD	PP
ΔP (kPa)	345	
Feed solute (kg/m^3) (1 : 1)	0.20	
Feed CPC (kg/m^3)	10	
Flow rate (1/h)	30	
Permeate solute (kg/m^3) × 10^2	1.60	2.23
Permeate CPC (kg/m^3)	0.30	
Retention of CPC (%)	97.0	
Retention of solute (%)	99.20	98.88
Flux (m^3/m^2 · s) × 10^6	4.522	

pyridinium iodide (CPI), which has a very low solubility at room temperature and neutral pH (21). Some amount of PD and PP are also trapped in the precipitate of CPI. Fig. 12 shows the variations of % CPC precipitation from the permeate obtained after MEUF of PD and PP mixture for different KI to CPC ratio. With the addition of KI, in the permeate, simultaneous production of CPI and KCl will start. The extent of precipitation reaction depends on the degree of dissociation of KI which, in turn, depends on the concentration of KCl produced by the precipitation reaction and PD and PP present in the solution. Since KCl is more ionic than KI, dissociation of KI is restricted due to common ion effect. It is clear from Fig. 12 that at KI to CPC ratio of 1.5, the percentage of CPC precipitation is maximum, and above that ratio, the percentage of CPC precipitation gradually decreases due to common ion effects. The results of chemical treatment I are summarized in Table 5.

Chemical Treatment II

The CPI 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, precipitated CPI should be transformed to a water-soluble chloride or bromide salt. In this case, cupric chloride ($CuCl_2$) is added to the precipitate obtained from chemical treatment I. The relevant reactions are presented elsewhere (9). The effects of concentrations of $CuCl_2$ on the percentage redissolution of CPI have been studied as a function of $CuCl_2$ to CPI ratio, and the results are shown in Fig. 13. With increase in $CuCl_2$ to CPI ratio, the percentage dissolution of CPC increases for both the cases and beyond a ratio of 3.75, the change in the percentage dissolution of CPC becomes gradual. The results of chemical treatment II are summarized in Table 6.

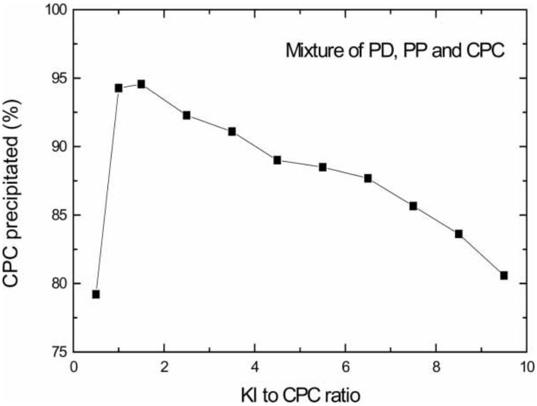

Figure 12. Variation of CPC precipitation with KI to CPC ratio.

Table 5. Performance of chemical treatment I

	Solute	
	PD	PP
Permeate CPC (kg/m^3)	0.30	
Permeate solute (kg/m^3) × 10^3	1.60	2.23
KI/CPC (wt/wt)	1.5	
CPC precipitated (%)	93.62	
Solute present in precipitate (%)	28.62	22.36
CPC in filtrate (kg/m^3) × 10^2	1.914	
Solute in filtrate (kg/m^3) × 10^3	1.142	1.731
% Removal, by combination of MEUF and precipitation.1*		
CPC	99.80	
Solute	99.43	99.13

1*: With respect to MEUF feed.

CHEMICAL TREATMENTS FOR THE RECOVERY OF SURFACTANT FROM THE RETENTATE STREAM

The two-step treatment process, as described in Section 3.3, is adopted to recover CPC from the retentate stream. A typical retentate of MEUF experiments (PD-CPC mixture) is considered for this study, using the optimum quantities of KI and $CuCl_2$ as described above. The results are presented in

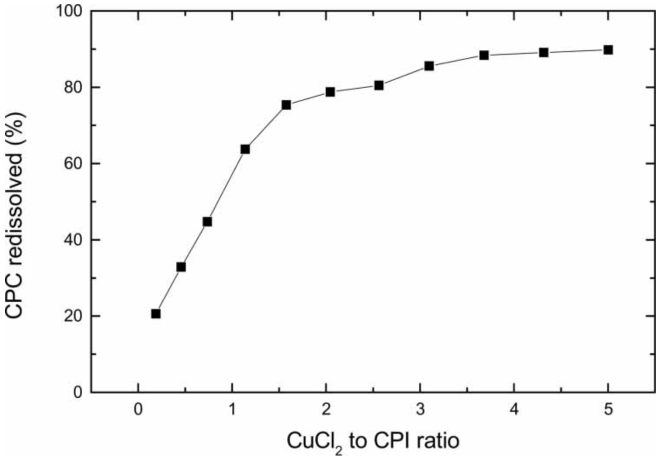

Figure 13. Variation CPC redissolved from CPI precipitate with $CuCl_2$ to CPI ratio.

Table 6. Performance of chemical treatment II

Solute	$CuCl_2$/CPI (wt/wt)	CPC redissolve (%)	Solute redissolve (%)	% Recovered by chemical treatment I & II.2*	
				CPC	Solute
PD	3.75	87.16	7.52	83.69	27.91
PP			94.28		4.42

2*: With respect to MEUF permeate.

Table 7. It can be observed from Table 7 that about 94% CPC can be recovered from the retentate stream and be reused.

CONCLUSION

MEUF studies for the separation of two inorganic salts (PD and PP) are investigated. Batch experiments result into a retention of both the salts from their mixture in the range of 96% to 99.3% but are associated with substantial decline in the flux over time. Slight improvement of the retention is achieved in cross flow. Significant flux enhancement in the range of 13% to 18% is achieved in cross-flow experiments. The flux increases by 6% when the cross-flow rate increases from 30 to 75 l/h. Retention of PD is more than that of PP due to its divalent ionic character. To improve the economics of the MEUF process, the surfactants from the permeate and retentate stream are recovered by a precipitation method followed by separation and redissolution of the precipitate to obtain surfactant rich stream. In chemical treatment I,

Table 7. Performance of chemical treatment I and II for a typical retentate

	Solute (PD)
Retentate CPC concentration (kg/m^3)	10
Retentate PD concentration (kg/m^3)	0.20
KI/CPC (wt/wt)	1.5
CPC precipitated (%)	97.7
PD in filtrate (%)	99.3
$CuCl_2$/CPI	3.75
Recovered with respect to retentate (%)	
CPC	94.08
PD	<1.0

KI to CPC ratio of 1.5 is found to be the optimum whereas, the optimum ratio of $CuCl_2$ to CPI for chemical treatment II is 3.75. From the experimental results, it can be concluded that the MEUF process can effectively be used for the separation of PD and PP from aqueous medium.

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REFERENCES

1. Sh, L.H. and Juang, R.S. (2002) Heavy metal removal from water by sorption using surfactant modified montmorillonite. *J. Hazard. Materials*, B92: 315–326.
2. Brower, J.B, Ryan, R.L., and Pazirandeh, M. (1997) Comparison of ion-exchange resign and biosorbents for the removal of heavy metals from plating factory waste water. *Environ. Sci. Technol.*, 31: 2910–2914.
3. Scamehorn, J.F. and Harwell, J.H. (1989) *Surfactant Based Separation Processes*; Scamehorn, J.F. and Harwell, J.H., eds.; Surfactant Science Series,, Marcel Dekker, Inc.: New York.
4. Dunn, R.O., Jr., Scamehorn, J.F., and Christian, S.D. (1985) Use of micellar-enhanced ultrafiltration to remove dissolved organics from aqueous stream. *Sep. Sci. Technol.*, 20: 257–284.
5. Sabate, J., Pujola, M., and Llorens, J. (2002) Comparison of polysulfone and ceramic membranes for the separation of phenol in micellar-enhanced ultrafiltration. *J. Colloid. Interf. Sci.*, 246: 157–163.
6. Syamal, M., De, S., and Bhattacharya, P.K. (1995) Phenol solubilization by cetylpyridinium chloride micelles in micellar enhanced ultrafiltration. *J. Membr. Sci.*, 137: 99–107.
7. Adamczak, H., Materna, K., Urbanski, R., and Szymanowski, J. (1999) Ultrafiltration of micellar solution containing phenols. *J. Colloid. Interf. Sci.*, 218: 359–368.
8. Gzara, L. and Dhahbi, M. (2001) Removal of chromate anions by micellar enhanced ultrafiltration using cationic surfactants. *Desalination*, 137: 241–250.
9. Purkait, M.K., DasGupta, S., and De, S. (2004) Removal of dye from wastewater using micellar enhanced ultrafiltration and recovery of surfactant. *Sep. and Purif. Technol.*, 37: 81–92.
10. Purkait, M.K., DasGupta, S., and De, S. (2004) Resistance in series model for micellar enhanced ultrafiltration of eosin dye. *J. Colloid. Interf. Sci.*, 270: 496–506.
11. Juang, R.S., Xu, Y.Y., and Chen, C.L. (2003) Separation and removal of metal ions from dilute solutions using micellar enhanced ultrafiltration. *J. Membr. Sci.*, 218: 257–267.

12. Akita, S., Sastillo, L.P., Nii, S., Takahashi, K., and Takeuchi, H. (1999) Separation of Co(II)/Ni(II) via micellar enhanced ultrafiltration using organo phosphorous acid extractant solubilized by nonionic surfactant. *J. Membr. Sci.*, 162: 111–117.
13. Tung, C.C., Yang, Y.M., Chang, C.H., and Maa, J.R. (2002) Removal of copper ions and dissolved phenol from water using micellar-enhanced ultrafiltration with mixed surfactants. *Waste Management*, 22: 695–701.
14. Baek, K., Kim, B.K., and Yang, J.W. (2003) Application of micellar-enhanced ultrafiltration for nutrients removal. *Desalination*, 156: 137–144.
15. Baek, K., Lee, H.H., and Yang, J.W. (2003) Micellar-enhanced ultrafiltration for simultaneous removal of ferricyanide and nitrate. *Desalination*, 158: 157–166.
16. Jadhav, S.R., Verma, N., Sharma, A., and Bhattacharya, P.K. (2001) Flux and retention analysis during micellar enhanced ultrafiltration for the removal of phenol and aniline. *Sep. and Purif. Technol.*, 24: 541–557.
17. Lipe, K.M., Sabatini, D.A., Hasegawa, M.A., and Harwell, J.H. (1996) Micellar-enhanced ultrafiltration and air stripping for surfactant contaminant separation and surfactant reuse. *Ground Water Monit. Rem.*, 16: 85–92.
18. Jeffery, G.H., Basseh, J., Mendham, J., and Denney, R.C. (1989) *Vogel's Textbook Of Quantitative Chemical Analysis*, 5th Ed.; Longman: London.
19. Rosen, M.J. (1978) *Surfactants and Interfacial Phenomena*; A Wiley-Interscience Publication, John Wiley & Sons: New York.
20. Clint, J.H. (1992) *Surfactant Aggregation*; Blackie: Glasgow.
21. Vanjara, A.K. and Dixit, S.G. (1996) Recovery of cationic surfactant using precipitation method. *Separations Technol.*, 6: 91–93.