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Hexavalent chromium ion removal through micellar enhanced ultrafiltration

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Abstract

Micellar enhanced ultrafiltration (MEUF) experiments were carried out in an unstirred batch cell using cetyl pyridinium chloride (CPC) as the surfactant to analyze the adsorption of chromate ions on the surfaces of the surfactant micelles. The influence of independent variables was studied on the retention of the surfactant and chromate ions as well as on permeating flux. The flux, for a particular pressure, remained constant against constant bulk concentration of CPC, suggesting negligible concentration polarization in the range of feed surfactant concentrations considered herein. There was distinct evidence of adsorption of Cr(VI) ions during MEUF. The *Langmuir* adsorption equilibrium constant (K_{ads}) for chromate ions was found out with the help of MEUF results. It was observed that at high feed concentration, the percent retention of chromate ions increases. However, the flux declined over a varying range of feed concentration (CPC and chromate ions). Further, at a much higher surfactant concentration (60 mM), the retention of chromate ions slightly decreased. The exclusive experimental runs with chromium ion solution showed an initial rapid decline of retention from 10 to 2.3% with increase in pressure.

Keywords: Micellar enhanced ultrafiltration; Hexavalent chromium; Cetyl pyridinium chloride; Flux; Retention

1. Introduction

Environmental pollution control laws are becoming stringent and hence the removal of metal ions from the aqueous streams, generated from industries like electroplating, tanneries, photographic, is becoming increasingly important. Generally, most of the metal ion pollutants are highly toxic and have carcinogenic effect. Conventional processes like electrolytic method, ion exchange method, activated carbon adsorption, and solvent extraction method, etc. are in practice but have disadvantages in processing and recovering such effluents. These are generation of sludge, loss of expensive chemicals to wastewater, strong pH sensitivity, and treatment cost of chemicals. Emergence of membrane based separation processes appear to be promising in overcoming many such disadvantages. Membrane technology appears attractive owing to low space requirement, low labour costs and low energy requirements. A new version of ultrafiltration process, called micellar enhanced ultrafiltration (MEUF) may prove effective in treating such effluents.

In MEUF process, the surfactant having charge opposite to target ions, is added to the effluent stream containing the metal ions at a concentration greater than the critical micellar concentration (CMC), so that they form aggregates of around 50–150 of monomer molecules, called micelles [1]. Therefore, a large fraction of the metal ions get electrostatically attached to the micelle surface. Retention of such metal ions *attached to the micelles* is possible if the resulting solution is passed through an ultrafilter, having pore size smaller than the micelle diameter [2]. The recovery and the reuse of surfactant are of utmost importance from economical point of view. Precipitation of surfactant using mono or multivalent counter ions has been proposed [3]. Juang et al. [4] studied the feasibility of repeated use of surfactant after treating the retentate with 6N NaOH. Purkait et al. [5] reported ∼90% recovery of surfactant molecules from the permeate solution. MEUF is versatile enough to include the separation of hydrocarbons, removal and recovery of organic acids and amines, apart from separation of metal ions.

The application of MEUF for removing heavy metal ions from water is gaining importance [6]. MEUF was found to be extremely effective in separating Cu^{2+} (under dilute concentration) and retention of 99.8% was observed [7]. However, the permeate purity decreased as the metal concentration

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Nomenclature

a	molar extinction coefficient ($\text{mole}^{-1}\ \text{L}^{-1}$)
C	concentration (kg/m^3)
K_{ads}	Langmuir adsorption equilibrium constant
Greek letters	
ν	kinematic viscosity ($\text{m}^2\text{/s}$)
π	osmotic pressure (kPa)

in the feed increased. MEUF of gold(III) from hydrochloric acid media was also studied [8] using poly-oxyethylene nonylphenyl ethers (PONPEs) as a nonionic surfactant. It has been reported that the higher selectivity to gold(III) is provided by the use of MEUF with PONPE rather than those with charged surfactant such as cetyl pyridinium chloride (CPC) and sodium dodecyl sulphate (SDS). Quantitative retention of aluminium present at μg/ml concentration level has been achieved [9] at pH 5.9 with 1×10^{-3} M lumogallion and 2×10^{-2} M cetyl tri-methyl-ammonium bromide. Sodium dodecyl benzene sulphonate (SDBS) was found to be more efficient than sodium dodecyl sulphate (SDS) in separating cadmium ions from aqueous solution [10]. A rejection rate of 97.8% was observed [10]. Ligand modified micellar-enhanced ultrafiltration (LM-MEUF) for the removal of copper has been studied [11,12]. It has been shown that the cationic surfactant CPC is superior over SDS-MEUF in copper removal [11] and the efficiency of the process depends on the ligand to copper ratio as well as on the types of ligands [11]. Rejection of copper over 99% was observed in the presence of calcium when cetyl tri-methyl-ammonium bromide (CTAB) and 1-phenyl-3-isoheptyl-1, 3-propane dione was used as the surfactant and ligand, respectively [12]. Industrial wastewater from metal plating, petroleum refining, chemical and food processing plants may contain toxic substances like heavy metal cations and chemical compounds in the aqueous phase and oil fractions. Feasibility of using MEUF in industrial applications has been investigated by applying this technology to simultaneous removal of metal ion mixtures from solutions [13–16]. The ability of MEUF to simultaneously remove dissolved organics and metal ions from solutions further proves the efficiency of MEUF as a practical method to treat wastewater [17–19]. For simultaneous removal of nitrate and phosphate under MEUF, rejections greater than 86% and 91%, respectively, were obtained [13]. In a tertiary system consisting of nitrate, chromate and ferric cyanide, the removal efficiency is in the following order: nitrate < chromate < ferric cyanide. This was observed to be same as that obtained while treating the pollutants individually [14]. The observed order is same as the order of the valences of the chosen ions. MEUF studies of wastewater containing cyanide and cadmium reported a removal rate of over 90% and 99% for cyanide and cadmium, respectively [15]. Experiments with divalent cadmium, zinc, copper and calcium ions and their mixtures from aqueous streams showed a rejection efficiency of at least 96% [16]. MEUF of a mixture containing phenol, *o*-cresol, zinc and nickel ion (Zn^{2+} and Ni^{2+}) showed that the removal of neither the organic solutes nor the metal ions is affected by the co-presence of the pollutants [17]. However, rejection of copper ion was found to increase in the presence of phenol using MEUF [18]. Mixed surfactants (CPC and Tween 20) were employed to study the feasibility of simultaneous removal of trichloroethylene (TCE) and chromate by MEUF [19]. The removal of neither TCE nor chromate was inhibited by the co-existence of the pollutants [19]. It had been proposed [20] to combine MEUF and algae containing membrane bioreactors (MB) to completely remove the metal ions from metal finishing industry's effluent.

Hexavalent chromium ion is highly toxic and its permissibility in the inland water by Indian Standard is 0.1 g/m^3. The industries like electroplating and leather are heavy users of chromium salts and mostly generate effluents containing hexavalent chromium ions. Hence, it has become almost imperative for these industries to look for attractive alternative methods to treat their effluents. The removal of hexavalent chromium by micellar-enhanced ultrafiltration, using cetyl tri-methyl-ammonium bromide (CTABr) as well as cetyl pyridinium chloride (CPC), was studied [21,22]. Rejection coefficients, higher than 99%, were obtained as long as the feed concentration was less than or equal to 200 times the standard.

In the design of MEUF process, the effect of operating parameters on the efficiency of the process, permeate flux and retention of micelles along with metal ions and quality of permeate concentrations are to be properly understood. Markels et al. [23] carried out MEUF in an unstirred batch cell and had proposed an unsteady state mass transfer model to describe the retention characteristics of the membrane. The model helps to estimate the intrinsic retention for both, the surfactant and organic solute and describes the physics at the membrane surfaces. Markels et al. [24] had also conducted crossflow ultrafiltration of micellar solutions. A steady state fouling resistance and osmotic pressure model was proposed by them to predict flux in crossflow MEUF process. Mathematical model was developed for MEUF process for the removal of phenol and aniline [25].

Vakarelski and Dushkin [26] studied the kinetics of adsorption using anionic sodium dodecyl polyoxyethylene-2 sulphate as the surfactant. They obtained a faster relaxation of the surface tension towards the equilibrium value upon increasing counter ion valance. Gu et al. [27] observed the influence of the type and concentration of ionic surfactants with respect to electric charge on small silicone oil droplets. They used electrical suspension method and observed that with increasing surfactant concentration, the adsorption process may lead to charge reversal. MEUF of chromate anion from aqueous streams was studied in detail by Christian et al. [28]. In an interesting study [29] it was observed that with increasing the length of the surfactant hydrocarbon tail, adsorption gets displayed to lower concentration region due to electrostatic screening of the headgroup charge. Ratkin and Pack [30] estimated the distribution of ions around the micelles by *Monte Carlo* method. They modeled solvent as a structure-less dielectric continuum, combined with a static all atom model of the ionic micelle.

The present work has been undertaken to study the adsorption of chromate ions on the micelle surface. Cetyl pyridinium chlo-

Table 1
Molar extinction coefficients

Wavelength (nm)	Molar extinction coefficient (a)	
	CPC	Cr(VI)
259	3.774	2.884
270	0.895	3.35

ride (CPC), a cationic surfactant, was taken along with potassium chromate (anionic solute) in a medium of 0.01 M sodium chloride solution. Keeping the above-mentioned objectives in mind, experiments were carried out to study the effects of operating conditions, such as pressure and concentration (of both CPC and chromate) on the permeate flux and retentions (of surfactant and chromate).

2. Experimental work

2.1. Materials, physical properties and concentration measurements

CPC (purity: 98%) from Loba Chemie, Mumbai, sodium chloride (99.9% pure) from BDH, Mumbai, and potassium chromate (99%) from Ranbaxy Ltd., India were obtained. The permeate concentrations of CPC and hexavalent chromium were calculated from the absorbance of the permeate samples. The absorbance was measured at wavelengths 259 and 270 nm. The molar extinction coefficients of these compounds are given in Table 1. Further, physical properties of the surfactant are given in Table 2. The osmotic pressure for CPC in a solution of 0.01 M NaCl was obtained [24] as:

$$\pi = 0.00366C + 0.01209C^2 - 8.0 \times 10^{-5}C^3 + 2.592 \times 10^{-7}C^4 \tag{1}$$

where, π is in kPa and C is the total surfactant concentration in kg/m^3. The above equation is valid up to $C = 250$ kg/m^3. Kinematic viscosity of CPC solution was estimated as a function of concentration [25] as:

$$\nu = 9.98 \times 10^{-7} + 5.59 \times 10^{-9}C_2 + 2.50 \times 10^{-11}C_2^2 - 1.43 \times 10^{-13}C_2^3 + 4.46 \times 10^{-16}C_2^4 \tag{2}$$

where, C_2 is in mM and ν is in m^2/s.

Table 2
Physical constants of surfactant

Physical property	Value [References]
Diffusivity of CPC (m^2/s)	1.5×10^{-10} [12]
Critical micelle concentration of CPC in 0.01 M NaCl	8.8×10^{-4} M = 0.3 kg/m^3 [1]
Aggregation number of CPC (N)	136 monomers/micelle [12]
Monomer hydrodynamic radius	0.42 nm [12]

2.2. Ultrafiltration cell and experimental variables

The UF cell was made of stainless steel with a capacity of 300 ml. Effective diameter of the membrane was 68 mm. Experiments were designed to study the influence of applied pressure and feed concentration on permeate flux and retention of chromate. The flux and permeate concentration were measured at varying surfactant concentrations. The surfactant concentration was then held constant and the permeate flux and concentration was measured as a function of time for three different pressures (376, 580 and 716 kPa). The permeate flux and concentration of chromate solution was also measured as a function of time for the above three levels of pressures. For adsorption of counter ions on the micelles, chromate concentration was varied from 0.1 to 1.5 mM at constant surfactant concentration (30 mM). The chromate concentration was then kept constant (0.5 mM) while the surfactant concentration was varied from 1 to 60 mM.

2.3. Experimental procedure

To carry out experiments, membrane of the *type*: GR81PP (Danish Separation Systems, Denmark) with MWCO (of 10,000) was used. Hydraulic membrane resistance ($R_{\mathrm{hm}} = \Delta P/\mu_{\mathrm{w}}J_{\mathrm{w}}$) was found to be 1.85×10^{14} m^{-1}. Solutions of cetyl pyridinium chloride and chromate were prepared with 0.01 M sodium chloride in distilled water. The presence of salt decreases the CMC of ionic surfactants and thereby, reduces the loss of surfactant in the monomeric state. The density and the viscosities of the solutions were measured at ambient temperature. Initially, the membrane was compacted at a pressure of 952 kPa for 6 h. For estimation of the hydraulic membrane resistance (R_{hm}) the pressure was then varied and the flux was recorded as a function of applied pressure. R_{hm} was obtained from the linear relationship of flux versus pressure data. The compacted membrane, after being rinsed with distilled water, was placed on the porous support of the UF cell. The test solution was then poured into the cell. It was pressurized and the permeate flux was measured at regular intervals. Permeate concentrations of the surfactant and chromate was measured from the absorption values using VIS–UV spectrophotometer (Model: UV-1601, Shimadzu Corporation, Japan). The duration of each experiment was about 2 h. After each run, the cell was rinsed with distilled water and the membrane was washed thoroughly and rinsed with distilled water. The water flux was measured after each run to check the loss of permeability of the membrane.

3. Results and discussion

3.1. Selection of operating conditions

A concentration, as high as 180 kg/m^3 of CPC, exerts an osmotic pressure of around 210 kPa [11]. To obtain flux at measurable level, the operating pressure range was kept on the higher side and was varied from 376 to 716 kPa.

The micelles of CPC form at a critical concentration of 0.88 mM. The concentration of CPC was varied from 0.1 to

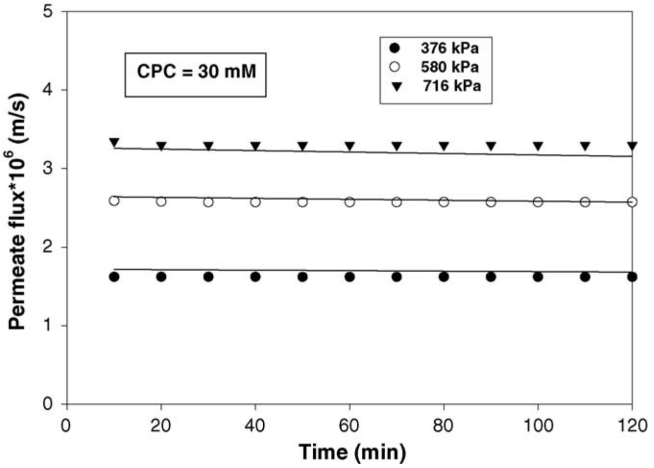

Fig. 1. Variation of permeate flux with time at 30 mM CPC concentration.

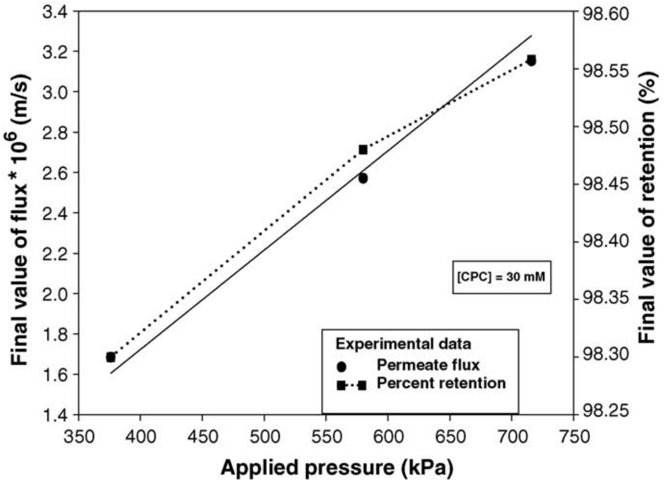

Fig. 2. Variation of permeate flux and CPC retention against applied pressure.

0.5 mM to study the surfactant behaviour below CMC. Whereas, the concentration of feed CPC was varied up-to 60 mM in order to study the effect of concentration beyond CMC. This helped us to study the behaviour of CPC when it falls below CMC during MEUF. The chromate concentration was varied from 0.1 to 1.5 mM. Beyond this limit, the permeate concentration of chromate is way above that of standard wastewater norms which is 0.1 g/m^3 for inland water disposal [21].

Hexavalent chromium remains in solution as $[CrO_4]^{-2}$ and as $[HCrO_4]^{-}$. Hence, anionic surfactant cannot be used in the present case. Hence, it was decided to carry out experiments with cationic surfactants, which in fact give advantages in terms of low Kraft temperature and possibility of the formation of large micelles [2]. Cetyl pyridinium chloride, a cationic surfactant, was used as it has a large hydrophobic group with the Kraft temperature of 10.8 °C. Therefore, it can be used effectively at room temperature. Ong et al. [31] estimated the hydrophilic/lipophilic balance [HLB] of CPC to be 24–29, indicating that CPC has higher affinity towards aqueous phases.

3.2. *Micellisation and ultrafiltration of surfactant solution*

Effects of pressure as well as concentration of the surfactant on permeate flux and retention of surfactant was studied. Permeate flux and its concentrations were measured and analyzed as a function of time. The experiments were conducted and the values were recorded until not much appreciable change was observed. Such values (obtained almost constant) will now be henceforth referred as '*final*' values.

3.2.1. *Effect of pressure on permeate flux and surfactant retention*

Fig. 1 depicts the flux variation with time using 30 mM surfactant solution at three different pressure levels. It was observed that the flux remains constant with time. This shows that the effect of concentration polarization is negligible; otherwise a decline of flux would have been observed. This is being reiterated as the experiments were carried out under unstirred condition, there could have been a possibility of the partial blockage of membrane pores by micelles and/or a formation of an additional resistant layer which may have declined the flux. Further, on plotting final values of flux with applied pressure (Fig. 2), a linear relationship was observed which confirms negligible effect of concentration polarization.

Fig. 3 depicts CPC retention values as a function of time. There is an exponential decay of percent retention of CPC as a function of time. As the time progresses, the retentate side concentration (bulk + micelles) increases. Since the bulk monomer concentration is maintained at CMC level, extra CPC monomers contribute towards the growth of separate small size micelles or increase the size of already existing micelles. These may also allow breakage of micelles into dimmers and trimmers, which may pass through the membrane and reduce retention values as a function of time [1,2,12]. Further, this effect is more pronounced as the pressure is in the lower region. Percent retention increases with increase in pressure. Surfactants under relatively larger concentrations form micelles having tendency to settle at the membrane surface. This eventually forms micellar aggregation

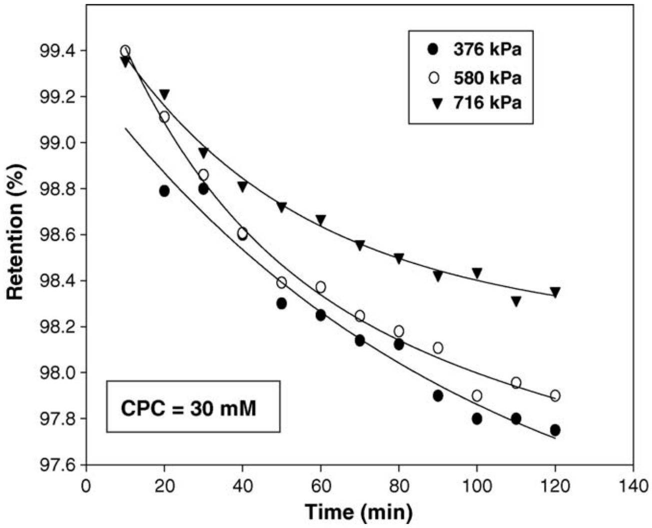

Fig. 3. Percent retention vs. time plot at 30 mM CPC solution under varying pressures.

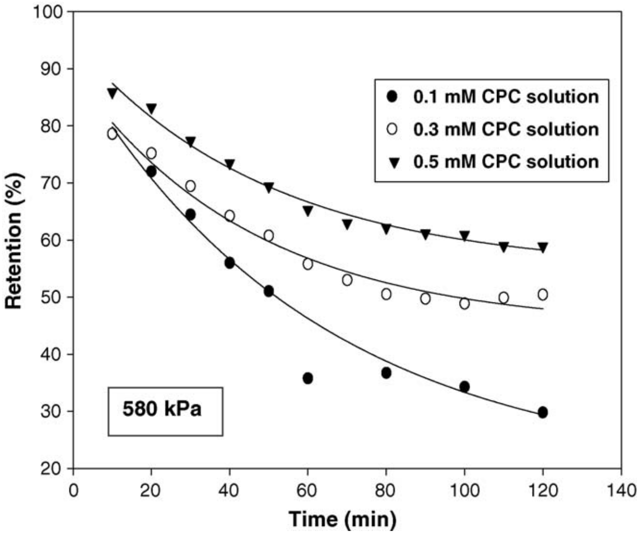

Fig. 4. Percent retention vs. time plot at 580 kPa under varying but below CMC concentration of CPC solutions.

layer (MAL), restricting the passage of smaller sized micelles through the membrane. At higher pressures, resistance of MAL increases due to the compaction that also increases the retention of such broken micelles and hence increases percent retention. However, an observation shown in Fig. 2 also depicts a variation of final values of surfactant retention with pressure. Since the surfactant concentration was much higher than the CMC (up to around 34 times), the retentions were not found to vary much with pressure, even though a trend was observed. The MAL provides an additional resistance and deters the passage of free surfactant through the membrane. This phenomenon is strong at higher pressures due to compaction of such an aggregation layer.

3.2.2. *Effect of feed surfactant concentration on permeate flux and surfactant retention*

To observe the influence of CPC concentration below CMC, a plot was made between percent retention and time and shown in Fig. 4. It may be observed that the trends of curves are similar to that obtained with CPC concentration above CMC. However, the percent retentions were found to be much less, particularly as the duration of ultrafiltration proceeds. This is because all the surfactant molecules are in the form of free monomers, the size of which is much smaller than the pore diameter of the membrane used (MWCO-10000). Other authors have reported similar trends [9]. Higher retention during the initial stages of ultrafiltration may be due to temporary blockage of pores by surfactant molecules.

A relationship is shown in Fig. 5 between the final values of permeate flux as a function of feed surfactant concentration. With the increase in surfactant feed concentrations, larger fractions of micelles are formed. Hence, the MAL thickness increases; as a result of which the resistance offered by MAL increases and consequently permeate flux declines [32]. However, it may be stated that at this juncture that a higher permeate flux would have been observed under stirred condition. Because of stirring, instead of settling down the micelles tend to remain in random motion [33]. Accordingly, MAL thickness would have decreased, which in-turn would have resulted in an increased flux.

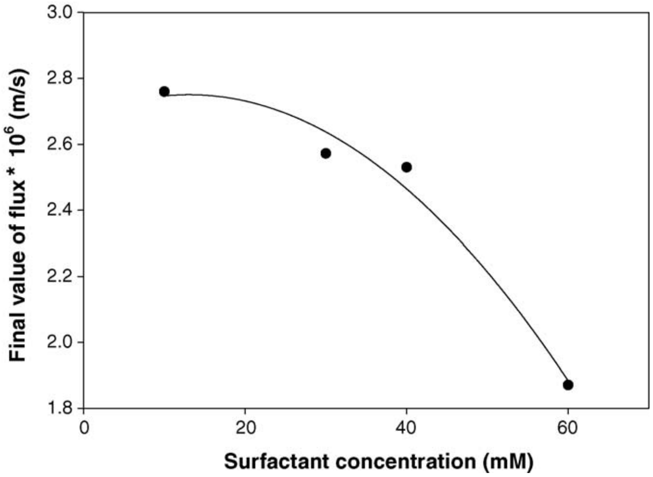

Fig. 5. Permeate flux vs. feed CPC concentration at 580 kPa.

In an attempt to observe the range of feed CPC concentration for MEUF, a plot was made between permeate CPC and feed CPC concentration, which is shown in Fig. 6. It is evident from the figure that beyond a feed concentration of 43 mM (critical feed concentration, CFC), the permeate concentration increases beyond CMC value. The rapid rise in permeate concentrations sets the limit for the maximum operational feed concentrations (known as CFC). This may be explained due to the permeation of smaller sized micelles through the membrane. Therefore, it may be concluded that the feed CPC concentration should be well below CFC. However, Fig. 7 depicts an immediate rise in retention with the increase in feed CPC concentration, which later on attains a plateau at higher CPC concentration. Increase in feed CPC concentration leads to the formation of increased number of micelles in the retentate side. This is being reiterated as the

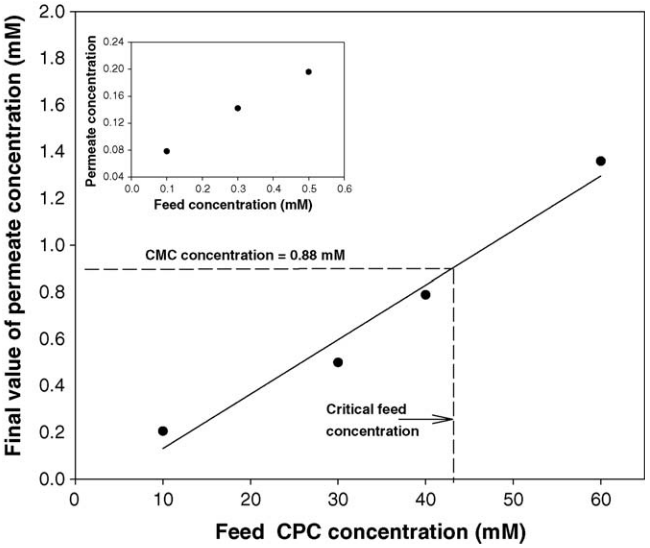

Fig. 6. Final value of permeate concentrations vs. feed concentrations at 580 kPa and definition of critical feed concentration (CFC).

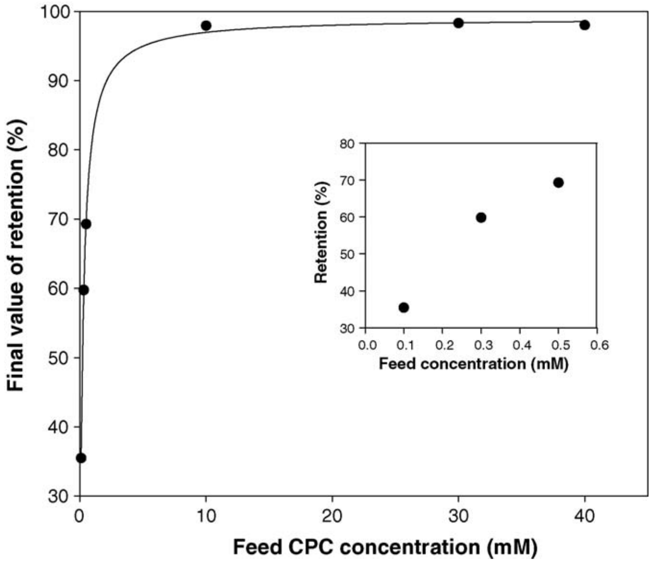

Fig. 7. Percent retention vs. feed concentration at 580 kPa.

experiments were carried out under unstirred condition; there is an overwhelming tendency of these micelles to settle down. As a result of more settling of micelles, MAL thickness increases with increase in feed CPC concentration. This in-turn leads to an increased resistance to the passage of smaller micelles.

Consequently, the percent retention increases with increase in feed CPC concentration. Comparing Figs. 6 and 7, it seems that to retain CPC at highest possible level, the feed CPC concentration should be in the range of 10–30 mM.

3.3. Ultrafiltration: chromate in absence of surfactant

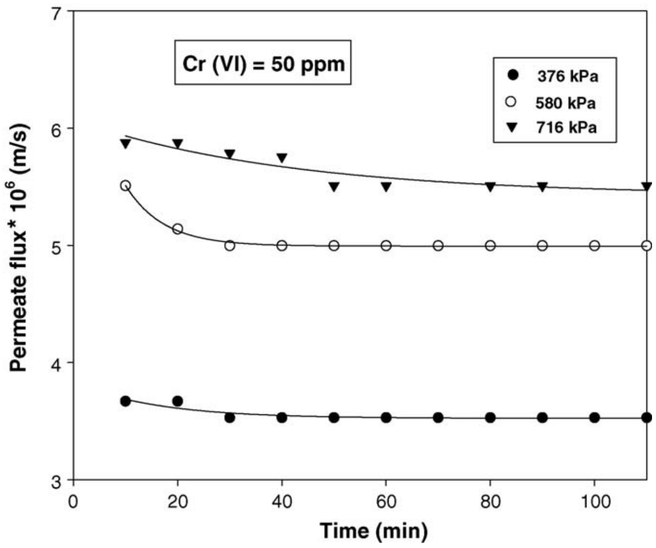

Fig. 8. Plot of permeate flux vs. time at 50 ppm chromate solution under varying pressures (blank runs with chromium solution).

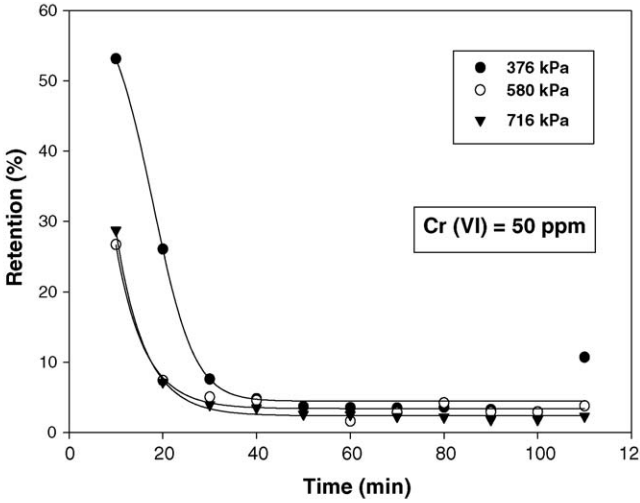

Fig. 9. Plot of percent retention vs. time at 50 ppm chromate solution under varying pressures (blank runs with chromium solution).

It was thought appropriate to observe the behaviour of percent retention as well as permeate flux using exclusively chromate solution as feed. Figs. 8 and 9 show permeate flux and percent retention of Cr(VI) ions, respectively, as a function of time, at three different pressures. Although negligible, there is a clear evidence of effect of concentration polarization, during the initial period of ultrafiltration with respect to increase in pressure, as observed in Fig. 8. It is evident from Fig. 9 that there is a distinct drop in percent retention during the initial period. This may be due to the initial adsorption of chromate with the polymeric membrane.

A plot was made (Fig. 10) to show the variation between chromium ion retention and permeate flux as a function of applied pressure for an initial chromate concentration of 50 ppm. The plot shows that the retention of chromate anions in water decreases from 10.5 to 2.3% with the increase in pressure from 376 to 716 kPa. Such low retention values suggest that there may be little adsorption of chromium ions on the membrane surface and most of it permeate through the membrane. The permeate flux is found to vary linearly with pressure which indicates there is practically no development of resistance against flow at such a low value of chromate concentration in feed.

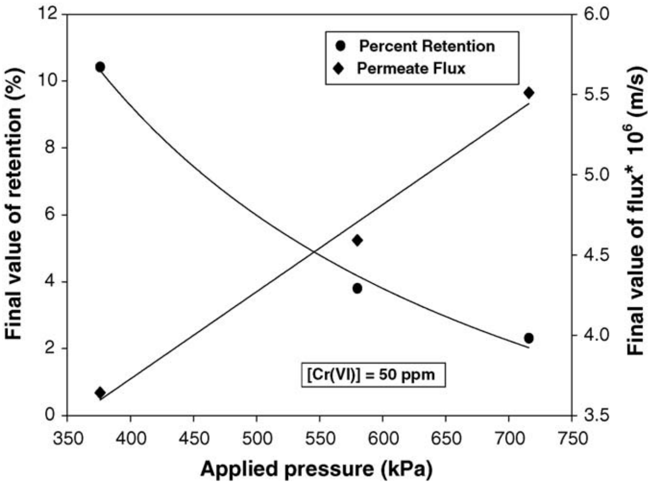

Fig. 10. Final value of percent retention and permeate flux as a function of applied pressure (blank runs with chromium solution).

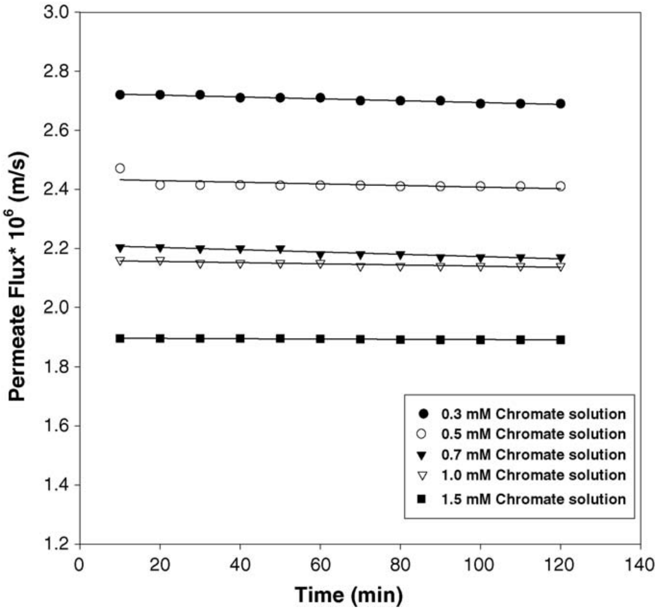

Fig. 11. Permeate flux as a function of time at CPC = 30 mM under varying concentration of chromate solutions.

3.4. MEUF of chromate ion using CPC

In this part of the work, the experiments were carried out with CPC as surfactant and potassium dichromate for release of Cr(VI) metal ions. The pH of the solutions was found to be around 6.5 for all the concentration of chromate ions in CPC solution. It is known that at this condition of pH, the chromate ion exists in the form of $[CrO_4]^{-2}$ as well as $[HCrO_4]^-$ in the solution. The effects of feed surfactant concentration, metal ion concentration as well as the effect of pressure on the permeate flux and chromate adsorption on the micelles (measured in terms of retention during UF) were studied.

3.4.1. Effect of chromate concentration

A plot in Fig. 11 of permeate flux at varying concentration of chromate ions as a function of time is made, keeping the feed surfactant concentration (30 mM) constant. These curves depict constant (more or less) permeate flux over the time range, indicating concentration polarization to be negligible. However, on close observation, there is an evidence of marginal decline in flux. Further, with the increase in chromate concentration there is clear evidence of decrease in permeate flux. Fig. 12 shows the influence of chromate concentration on flux. It is clearly evident that at higher chromate concentration the decline in flux is comparatively less. This may be due to the large structure formed by the surfactant micelles after adsorption of the chromate ions offering more resistance against the solvent flux. Fig. 13 shows average percent retention of chromate ions as a function of feed Cr(VI) concentration. Retention values were observed to vary with time at fixed Cr(VI) concentration and did not show much of a trend. Therefore, average retentions are reported against varying Cr(VI) concentrations in Fig. 13. Overall, there is little effect on percent retention with increase in feed Cr(VI) concentration, as these values are observed higher than 98%. However, on expanded scale there is decline of retention with increase in feed Cr(VI) concentration. This may be explained through the control of adsorption capacity of micelles, as the surfactant concentration remains constant.

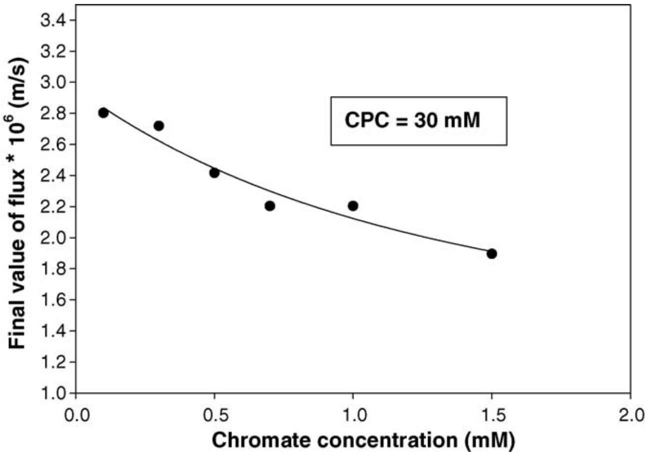

Fig. 12. Final value of permeate flux as a function of chromate concentration at CPC = 30 mM.

3.4.2. Effect of surfactant concentration

Fig. 14 shows negligible influence of concentration polarization, as the permeate flux was observed to be invariant with time in presence of chromate ions for all concentration values of CPC; the explanation of which has been given earlier for runs with only CPC. Further, Fig. 15 shows final values of permeate flux with increase in feed CPC concentration. This decline is marginal in the lower concentration range and increases at the higher concentration range. Obviously, this is due to the increased resistance of MAL against flow. Similarly, Fig. 16 depicts a significant increase in the final values of retentions against increase in feed CPC concentration; which then start declining steadily at higher range of concentrations. However, the decline is little. The initial significant chromium retentions are due to the formation of more micelles. The two opposite effects come into play at this situation which leads to a nearly constant permeate concentration even with increase in surfactant concentration [21]. However, on

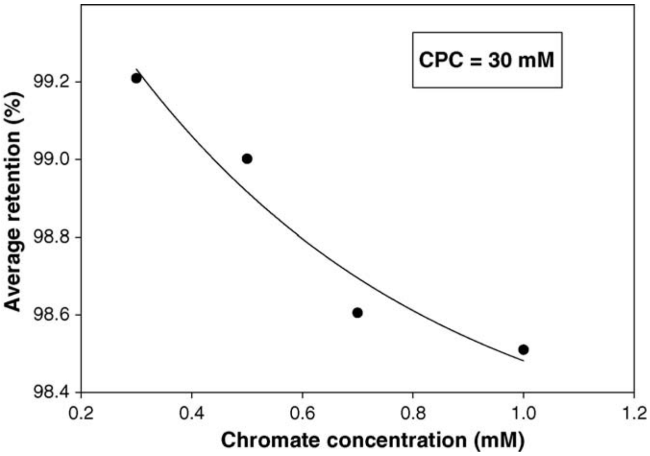

Fig. 13. Average retention against chromate concentration at CPC = 30 mM.

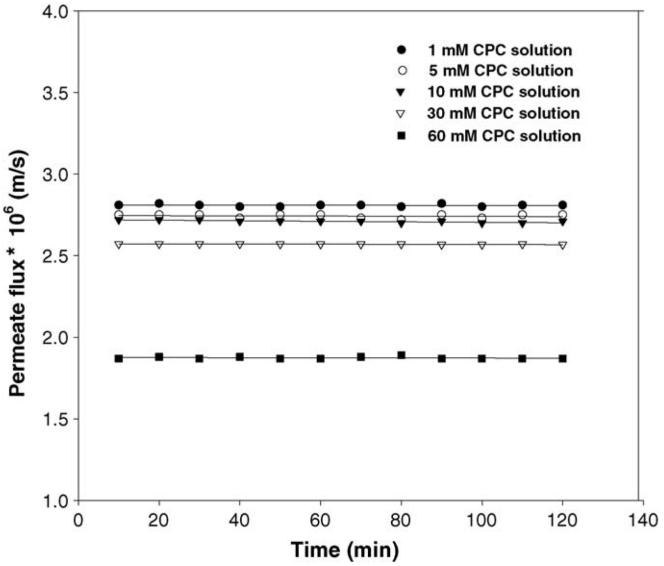

Fig. 14. Permeate flux as a function of time at [Cr(VI)] = 0.5 mM under varying CPC concentration.

increasing the surfactant concentration, micelle mole fraction increases and more chromate ions get entrapped. But at very high surfactant concentration, the ratio Cr(VI)/Cl decreases. As a result chloride ions get preferentially adsorbed on the micelle surface and the chromate concentration in the bulk increases. Hence, at a higher surfactant concentration, percent retention slightly decreases [21].

3.4.3. *Effect of pressure*

The final values of the permeate flux and chromium retention with the pressure are shown in Fig. 17. The linear flux–pressure relationship indicates negligible concentration polarization in the range of feed surfactant concentration. On the other hand, reduction in the retention with pressure is expected, as more solutes (chromium) may pass through the membrane at higher pressure.

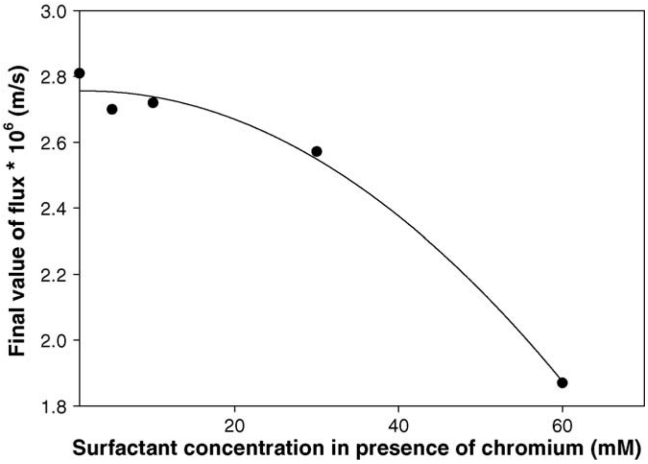

Fig. 15. Permeate flux as a function of surfactant concentration in presence of fixed Cr(VI) concentration of 0.5 mM.

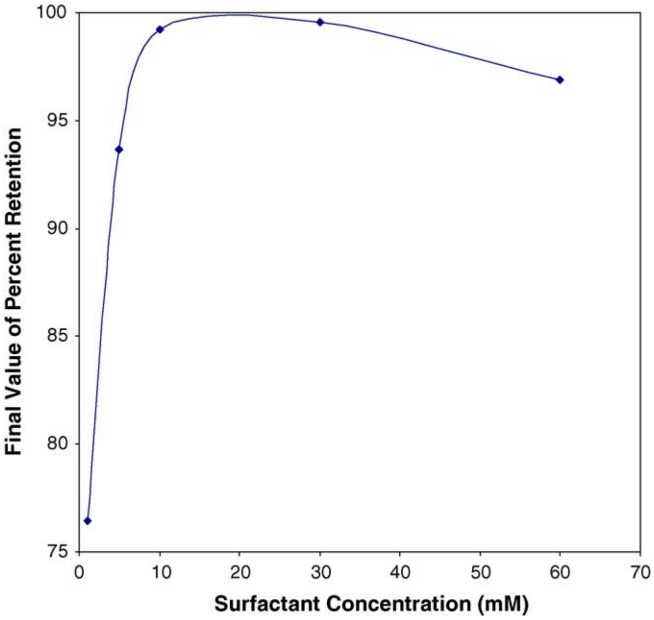

Fig. 16. Influence of surfactant concentration on percent retention of Cr(VI).

3.5. *Analysis of results*

3.5.1. *Chromate adsorption on micelles*

In MEUF, it is now assumed that the permeate concentration of chromate is equal to the unadsorbed (in the bulk) chromate concentration in the retentate. However, such equality may be possible with negligible adsorption of chromate on the membrane surface. On the micelle phase boundary, the metal ion concentration is in equilibrium with the unadsorbed free ion concentration in the bulk phase [33]. Accordingly, the value of adsorbed chromium concentration and consequently the adsorption equilibrium constant, K_{ads}, was estimated. The adsorption equilibrium values were estimated according to the Langmuir

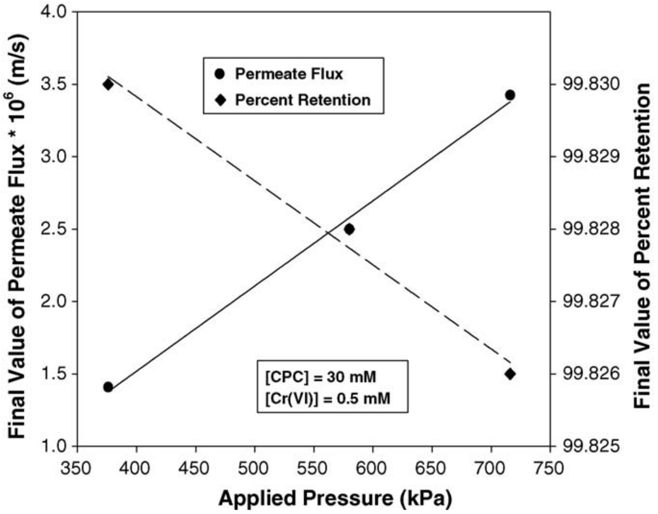

Fig. 17. Variation of permeate flux and percent retention as a function of applied pressure.

Table 3
Variation of K_{ads} with surfactant concentration

CPC concentration (mM)	K_{ads} (dimensionless)	Regression coefficient
5	212.2	1.0000
10	115.2	0.9993
30	30.0	0.9998

equation and the relationship is expressed as:

$$C_{ads} = \left[\frac{K_{ads}C_{eq}}{K_{ads}C_{eq}+1}\right] \quad (3)$$

Further, C_{ads} was evaluated from mass balance using the experimental data [34]. Adsorption equilibrium constants were estimated with MEUF data and the obtained values are reported in Table 3.

4. Conclusions

The permeate flux was found to be constant under constant applied pressure indicating negligible presence of concentration polarization in the range of feed surfactant concentrations considered herein. The increase in pressure leads to increased retention of CPC. This is due to the compaction of the micellar aggregation layer (MAL). Further, the increased resistance offered by MAL to the flow may be the reasons for decline of permeate flux with the increase in feed CPC concentration. The permeate concentration was found to increase with increase in feed surfactant concentration (under its exclusive runs) and was experienced to go beyond CMC above critical feed concentration (43 mM). Permeate flux was found to decrease with the increase in chromate concentration. The existing micelles along with metal ions become further bigger in size to cause greater resistance to flow. The increase in surfactant concentration provides increased percent retention of chromate ions. Pressure was found to have no significant effect on the percent retention of chromate. However, the permeate flux was found to increase linearly with increase in pressure, indicating negligible presence of concentration polarization; again, in the range of feed surfactant concentrations considered herein.

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