CHAPTER: 9

Effects of Co-solutes on Cr (VI) removal – A comparative study Emulsion Liquid Membrane with Micellar Enhanced Ultrafiltration (MEUF) Process

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9.1 Introduction

Chromium compounds are widely used heavy metal in leather processing, textile, wood preserving, chemical and electroplating industries. Wastewater from those industries contains huge quantities of chromium compounds. Among them hexavalent state of chromium is carcinogenic and toxic [1]. They are harmful to both human and aquatic life. If wastewater containing chromium is directly discharged to the water sewerage, it affects the aquatic life and destructs the environmental system. Cr(VI) exists mainly in soluble forms of $\text{HCrO}_4^-$, $\text{Cr}_2\text{O}_7^{2-}$ and $\text{CrO}_4^{2-}$ in the aqueous environment.

Development of cost efficient separation processes is therefore of the utmost importance. Membrane separation systems have nowadays become an important wastewater treatment technology, which facilitate the removal and recovery of pollutants as well as solvent like water [2]. Among various pressure driven membranes, ultrafiltration (UF) is the one which has a higher flux and low energy requirement compared to Nanofiltration (NF) and Reverse Osmosis (RO). Micellar enhanced ultrafiltration (MEUF) is a promising technique to remove lower molecular weight substances. Removal of heavy metals by micelles enhanced ultrafiltration (MEUF) process was extensively investigated in the past decade. It combines the efficiency of RO and the high flux of ultrafiltration (UF). The main feature of this process is to increase the retention coefficient of the contaminants by increasing the surfactant concentration to the critical micelle concentration (CMC) [3]. MEUF involves the addition of a surfactant above the critical micelle concentration (CMC) in order to entrap ionic solutes in an aqueous stream [4]. Upon introduction of surfactants (or any surface active materials) into the system they will initially partition into the interface, reducing the system free energy by (a) lowering the energy of the interface and (b) by removing the hydrophobic parts of the surfactant from contacts with water. Subsequently, when the surface coverage by the surfactants increases then the surface free energy (surface tension) has decreased. Then the surfactants start agglomerating into micelles, which again decreasing the system free energy by decreasing the contact area of hydrophobic parts of the surfactant with water. Above the CMC, the surfactant monomers form a spherical or cylindrical aggregate, called a micelle. In the colloidal-based wastewater treatment process of MEUF, oppositely charged surfactant is added to the aqueous stream containing the target heavy metal ions, at a concentration greater than CMC of the surfactant; so that they can form micelles [5]. Heavy
metal ions bind electrostatically on the surface of opposite-charged micelles. Then it can be retained by an ultra filtration (UF) membrane[6]. But one of the major drawbacks in the surfactant-based ultrafiltration is the leakage problem. The leakage of surfactant to the permeate and discharge to the ecosystem cause secondary pollution instead of the removed metal ions. The leakage of the surfactant is also undesirable from the economic point of view, unless the leaked surfactant is recycled to the feed stream [7].

The addition of salts is known to modify significantly the properties of aqueous solutions, such as solubility, dissociation equilibrium, aggregation numbers, hydration, and solute–solute and solute–solvent interaction parameters. The influence of added salt has also been one of main subjects in the research of surfactant solutions. The critical micelle concentrations are modified significantly upon the addition of salts. Often McDevit and Long’s theory has been used and criticized in discussions concerning the effect of salt on the cmcs of nonionic surfactants. The empirical equation of the salt effect is given as

\[ \ln f = k_s C_s \]  

where \( f \) is the activity coefficient of the nonelectrolyte, \( k_s \) the salt constant, and \( C_s \) the concentration of the salt. For nonionic surfactant solutions, the salt effect on the cmc is given by

\[ \ln (\text{cmc}) = \ln (\text{cmc}_0) - k_s C_s \]  

where \( \text{cmc} \) and \( \text{cmc}_0 \) are the critical micelle concentrations in the presence of salt and in its absence. It was observed in some early investigations that in the presence of salts (electrolyte) the CMC of ionic surfactants decreases. The addition of inorganic or organic salts to an ionic surfactant solution may facilitated the transition of structure of micelles from spherical to cylindrical (or rodlike) structure, which is due to the repulsions between the same charged head groups (hydrophilic head group) or may be due to sterric effect of large size of hydrophilic head group [8].

A review of literature related to MEUF reveals that a number of studies have been carried out to understand the mechanism of separation and solubilization of the solute in the micelles to optimize the operating conditions. Dunn et al. (1985)[9] have studied the performance of MEUF to remove dissolved 4-tert-butylphenol (TBP) from aqueous phase using CPC as a cationic
surfactant. Tucker et al. (1985) [10] studied the effect of added sodium chloride on solubilization of benzene during MEUF using sodium octylsulfate as an anionic surfactant. In this work, solubilization studies of phenol during MEUF have also been studied. Bhat et al. (1987) [11] carried out both solubilization as well as MEUF studies on cresol and CPC micelles in aqueous medium under a wide range of composition and concluded that highly polar solutes tend to solubilize in the vicinity of the micellar surface due to a strong ionic or polar interaction between the organic solutes and the micelles. Huang et al. (1994) [12] indicated that two important criteria, namely surfactant concentrations of greater than its CMC and surfactant to metal molar ratio (S/M ratio) of greater than certain value (denoted by these authors as the critical S/M ratio), have to be met to achieve an efficient metal removal efficiency by MEUF. A surfactant-based membrane process, MEUF, has also been investigated by Hojeong K. et al. (2006) [13] in order to remove heavy metal ions from groundwater or wastewater. The removal of phenol, p-cresol, xylenol and Cr(III) ions in simultaneous micellar-enhanced ultrafiltration process was examined by Anna W. et al. (2006) [14].

As a continuation of research in this direction the present work tries to elucidate the separation of Cr (VI) from aqueous stream (stimulated feed solution) based on MEUF using cross flow module. The process optimization has determined in terms of removal efficiency of chromium at different pH of feed. It was also determined the optimum flux rate at different system pressure and in different surfactant concentration. Effect of salt concentration in terms of chromium removal from aqueous feed solution was investigated in details. The concentration of surfactant in permeate was also measured to monitor extent leakage.

9.2. Experimental Procedure

9.2.1 Instruments for measurement

All the experiments were carried out continuously with constant chromium ion concentration in feed solutions of different concentrations of salt (electrolyte). The spectrophotometer used for measuring Cr (VI) and CPC concentration was a VARIAN UV-visible spectrophotometer (Cary50 Bio, S/N EL07113760)(CARY 50) Australia. The pH was measure with an AELICO make LI 127 pH meter. The determination of Cr(VI) was carried out using the diphenylcarbazide method as per the standard method [15]. The mixing and stirring was done by LABSONICTM
(Sartorius, Germany) sonicator. It generated a longitudinal mechanical vibration with a frequency of 30,000 Hz (in 100% amplitude).

9.2.2 Cross flow membrane module

Figure: 1 shows the schematic diagram of the experimental setup for membrane processing. The cross flow module was Viva-flow200\textsuperscript{TM} (S/N 03VF20028) supplied by VivaScience AG, Germany. The membrane material was polyethersulfone (PES) with a nominal molecular weight cutoff (MWCO) of 10 kDa. Different characteristics of membrane modules are follows: Overall L/H/W of 126/138/38 mm; channel (W/H) of 10mm/0.4mm; active membrane area $200\text{cm}^2$; hold up volume (module) 5.3mL; minimum recirculation volume less than 20mL and non recoverable holdup less than 2mL. The module could be operated up to the maximum pressure of 4 bar (60psi) and maximum temperature of 60 °C, with pump flow rate in the range of 200-400mL/min.

9.2.3 Methodology of cross flow membrane module

First, the fresh membrane of 10 kDa MWCO was rinsed with deionized water to remove glycerin coating. Prior to use in experiments, UF membrane was subjected to compaction for about one hour with DI water at a pressure of 2.75bar, higher than the highest operating pressure used in this study, to prevent any possibility of change of membrane hydraulic resistance during ultrafiltration. Once the water flux becomes steady with no further decrease, it was concluded that full compaction of the membrane has taken place. After compaction, membrane hydraulic resistance ($R_m$) was determined based on water runs at different transmembrane pressures (TMPs) of 1.5, 1.75, 2.0 and 2.25bar, which was found to be $1.43\times10^{13} \text{ m}^{-1}$ for a 10 kDa PES UF membrane used in this study. Membrane was rinsed thoroughly with distilled water after every run so as to remove any deposited fouling layer, which was followed by water runs to determine the extent of fouling.
Fig. 9.1: Single Module Operation of Viva flow Cross-flow module

9.2.4 Chemicals

A potassium dichromate solution (99.99% pure, MERCK made, CAS No. 7778-50-9) was used as a feed solution throughout the experiment. Cetyl Pyridinium Chloride (CPC) from Loba Chemie (purity: 98%) and sodium chloride (99.9% pure) from Merck, India were obtained. The experiment was done with 200 ml of feed solution. The chromium ion concentration in feed was 50 ppm. The surfactant concentration (CPC concentration) was changed from 0.1mM to 30mM. The concentration of electrolyte (Nacl concentration) varied from 0.5 m(M) to 300m(M). The permeate concentrations of CPC and Cr (VI) were calculated from the absorbance of the permeate samples. The absorbance was measured at wavelengths 260 nm and 540 nm for CPC and chromium respectively.

9.2.5 Feed Treatment

To reduce the extent of membrane fouling by any suspended particles, the feed solutions were subjected to microfiltration (MF) using “all glass vacuum filtration unit” (make: Sartorius A.G., Göttingen, Germany), with an oil-free portable vacuum pump (Sartorius, A.G., Göttingen, Germany, model ROC 300 with moisture trap) and polyethersulfone (PES) membrane (47 mm diameter, pore size 0.45mm) being used as filter media.
9.2.6 Steps of experiment

To carry out experiment, polyethersulfone (PES) membrane of 10000 Da (6” x 4” x 1.3”) molecular MWCO of the type VIVA flow 200, that offer a novel tangential flow design resulting in significantly faster concentrate performance with less hold up than other comparable devices was used. In order to study the effect of salt, NaCl concentration was varied from 05 mM to 300 mM. Feed solutions of CPC and chromate were prepared with different concentration of NaCl in double distilled water. The ultra-pure deionised (DI) water, used in this study was obtained from Arium 611DI ultrapure water system (make: Sartorius A.G., Göttingen, Germany). The feed for DI water system was distilled water prepared by reverse osmosis (RO) system (Model: Arium 61315, make: Sartorius AG, Göttingen, Germany). The feed solution was mixed for 10 minutes under sonicator with a 80% amplitude (approximately 24,000 hz). It was allowed to settle for 10 minutes. The compacted membrane, after being rinsed with double distilled water, was connected with pump and the test solution was then passed through the membrane with a constant Δp of 1 bar across the membrane. After 20 minutes, concentrations of Cr (VI) and CPC in permeate were measured spectrophotometrically. Same experiment was also done without any addition of salt. After each run the membrane was washed thoroughly and rinsed with double distilled water. The water flux was measured after each run to check the loss of permeability of the membrane. All experiments have been done under constant temperature of 34°±0.5°C.

9.3 Results and Discussions

9.3.1 Effect of change of system pressure, surfactant and electrolyte concentration on permeate flux

Fig. 2 is described the flux variation with time at different pressure levels in constant surfactant concentration. It was observed that the flux remains constant with time at a particular pressure. The flux was increased with increase in pressure. The change of flux with time in different surfactant concentration is described in Fig. 3. The permeate flux was constant for a particular concentration of surfactant. The permeate flux was decreased with increase the surfactant concentration in feed solution. In Fig 3, there is a marginal decline in permeate flux when the surfactant concentration gradually increases. Results of change of permeate flux with surfactant at different salt (electrolyte) concentration are represented in Fig 4. As shown in Fig. 4, the
permeate flux is decreased with the increase of surfactant concentration in a particular time period. This is may be due to the partial blockage of membrane pores by micelles and/or a formation of an additional resistant layer which may have declined the flux at higher concentration of surfactant.

9.3.2 Optimize pH of feed solution in separation of chromium ion
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 changed from 2.0 to 6.0 with a constant concentration of surfactant and chromium (VI) ions in feed solution. Results in terms of percent rejection of chromium ion with time at different pH were plotted from Figs. 5 - 7. It is observed in figs 5.6 &7 that at moderate pH the separation is better compare to higher pH of feed solution. This particular phenomenon may be explained by the fact that the hexavalent chromium is present in different ionic forms at different pH conditions. It was observed from the literature [16,17] that the hexavalent chromium normally remains in the form of chromic acid \((H_2CrO_4)\) at very acidic pH condition and it changes to acid chromates \((HCrO_4^{-})\) of different concentrations with respect to pH up to 6.5. Further at higher pH values beyond 7, it gets transformed to chromates \((CrO_4^{2-})\) of different concentrations. The dichromate \((Cr_2O_7^{2-})\) ion concentration is also present and it depends on the feed concentration with respect to pH. Normally it is dominant at high chromium concentration and high acidic conditions (pH 1–7). Its concentration is reduced with the presence of an increasing amount of \(CrO_4^{2-}\) ions by further increasing the pH. The most active forms \(HCrO_4^{-}\) and \(CrO_2^{-}\) prevail in the pH range 5.5 to 6.5. Moreover at higher pH, chromate has to compete with \(OH^{-}\) ions to get adsorbed on the CPC micelle. As a result, lower chromate removal was observed at a higher pH. The binding of chromium ion \([Cr(VI)]\) and its maximum rejection are observed at this pH value (pH 5 -6). So the beset separation is observed at pH 5.0 of the system.
Fig. 9.2: Variation of permeate flux with time at different operating pressure at 0.88 m(M) CPC Concentration. MWCO = 10 kD, Temperature = 34°C

Fig. 9.3: Variation of permeate flux with time at different Surfactant concentration (CPC Concentration) at constant operating pressure 1.0 bar. MWCO = 10 kD, Temperature = 34°C
Fig. 9.4 : Variation of permeate flux with different Surfactant concentration (CPC concentration) at Different electrolyte concentration at constant operating pressure 1.0 bar. MWCO = 10 kD, Temperature = 34°C, Salt concentration in mM.

Fig. 9.5 : Effect of electrolyte at different pH in removal of Chromium, Nacl = 0 mM, CPC = 0.88 mM, MWCO = 10 kD, Temperature = 34°C
Fig. 9.6: Effect of electrolyte at different pH in removal of Chromium, NaCl = 5 mM, CPC = 0.88 mM, MWCO = 10 kD, Temperature = 34°C

Fig. 9.7: Effect of electrolyte at different pH in removal of Chromium, NaCl = 10 mM, CPC = 0.88 mM, MWCO = 10 kD, Temperature = 34°C
9.3.3 Effect of surfactant in separation of chromium ion

Here the experiment was carried out with different concentration of surfactant (CPC concentration) in feed solution (50 ppm Cr (VI) concentration) with a fixed concentration of electrolyte (10 mM NaCl) at pH 6.0. The experiment was also carried out without CPC. The average removal efficiency of chromium ion (without surfactant) was 50% after 30 minutes Fig. 8. UF alone cannot remove chromate ions due to the membrane pore size being larger than the ions. The screening action of the membrane was ineffective and the rejection of them was due to the adsorption on the membrane surface and inside the pore walls. Thus, two implications can be made from this result. Firstly, chromate removal was mainly due to the adsorption mechanism, and, secondly, no secondary layer was formed to reduce the flux from the membrane. In the MEUF process the flux decline was mainly due to the accumulation of micelles on the membrane surface. So Cr (VI) removal efficiency, without surfactant, is slightly increased after certain period of time. In presence of surfactant, the micells formation is accelerated. But when CPC concentration is lower than critical micelles concentration, all the surfactant molecules are under the form of free monomers, the size of which is largely smaller than the pore diameter of the membrane. In these conditions, monomers should easily cross the barrier. The surfactant monomer is partly hindered when it passes through the membrane into permeate. This hindrance may be caused by charge or by steric effects of surfactant. But at very high surfactant concentration, the ratio of Cr(VI)/Cl decreases. As a result chloride ions of CPC get preferentially adsorbed on the micelle surface and the chromate concentration in the bulk increases. Hence, at a higher surfactant concentration, percent removal of chromate decreases Fig 9.9.
Fig. 9.8: Removal efficiency of chromium ion through ultra filtration without surfactant in presence of 10 mM of NaCl in feed and at constant operating pressure 1.0 bar and 6 pH of feed. MWCO = 10 kD, Temperature = 34°C

Fig. 9.9: Effect of surfactant in removal of chromium ion through ultra filtration at 10 mM NaCl in feed at constant operating pressure 1.0 bar at 6 pH of feed. MWCO = 10 kD, Temperature = 34°C
**9.3.4 Effect of electrolyte (NaCl concentration) in separation of chromium ion**

In presence of electrolyte the CMC of ionic surfactants decreases and thereby, reduces the loss of surfactant in the monomeric state. In presence of electrolyte the lowering of CMC (critical micelles concentration) can be explained on the basis of micelles structure formation. More micelles are formed in the presence of electrolyte compared to the absence of the electrolyte in feed solution. It should cause the increase of surfactant retention coefficient. But in the presence of chromate anions, addition of salt increases the concentration of free Cl\textsuperscript{−} ions. Additionally cations of salt (Na\textsuperscript{+}) can form the complexes with chromate anions. So even at lower concentration of electrolyte in the solution decreases the CMC of surfactant and enhance the chromium removal efficiency. Moreover the dissociation of CPC in solution is reduced due to the presence of more and more chloride ion at higher concentration of NaCl. Results show in Fig. 9.10 and Fig. 11, that with increasing of concentration of salt in the aqueous stream, the Cr (VI) concentration in permeates also increases i.e. removal efficiency of chromate decreases. We also observed that initially the CPC concentration in permeate slightly increases with increasing salt concentration. Again the surfactant concentration decreases in permeate. Further increase of electrolyte concentration the surfactant concentration in the permeate increases. This has been represented in Fig.11. The experiment was carried out without electrolyte also. When CPC concentration is towards the cmc, micelles are formed in both bulk solution and the vicinity of the membrane. It is clear from the experimental data that addition of salt has an influence on the adsorption of chromate ions on the micelles of CPC, which has a direct effect on the retention of chromium (VI) as well as leakage of CPC in permeate. Presence of electrolyte (NaCl) in the aqueous stream influences the electric environment of the medium. Ionic strength of the medium will increase with gradual addition of NaCl. Now we know according to BrØnsted-Bjerrum equation:-

\[
\log k = \log k_0 + 1.018Z_AZ_B\sqrt{i}
\]  

(3)

The rate constant of a process depends on the ionic strength of the medium as well as on the charges of the reacting ions. Since in this adsorption process chromate ions are negatively charged and CPC micelles are positively charged, accordingly to equation (i), rate of chemisorptions; which follows Langmuir equation, decrease with increasing ionic strength.
Hence, salt concentration increases ionic strength, resulting gradual decrease of rate constant of the process. As a result, less adsorption of chromate ions by micelles is expected. So we have observed higher concentration of Cr (VI) and CPC in permeate stream for higher NaCl concentration.
Fig. 9.10: Removal efficiency of Cr (VI) at different concentration of Nacl (electrolyte) after 20 minutes at 0.88 mM Surfactant concentration (CPC). MWCO = 10 kD, Temperature = 34°C

Fig 9.11 Concentration of Surfactant (CPC concentration) in permeate at different concentration of Nacl. Surfactant concentration 0.88 mM in 200 ml feed solution with 50 ppm Cr (VI) concentration. MWCO = 10 kD,
9.4. Conclusion:

Removal of chromate Cr (VI) ions from aqueous stream by MEUF using cationic surfactant was studied at various system pressure, permeate flux, pH of feed, concentration of surfactant at different electrolyte concentration. The most important point to separate chromium ion is to reach critical micelles concentration (CMC) of surfactant. Below the CMC, the addition of surfactant to an aqueous solution causes an increase in the number of charge carriers and consequently an increase in the conductivity. Above the CMC, further addition of surfactant increases the micelle concentration while the monomer concentration remains approximately constant (at the CMC level). Since a micelle is much larger than a CPC monomer, it diffuses more slowly through solution and so is a less efficient charge carrier. As a result the separation efficiency of chromium ion decreases and concentration of surfactant in permeate increases. It is also concluded that micelles growth enhanced as the electrolyte concentration increases as well as separation efficiency of chromium ion. As the added salt concentration is increased, the CMC of the surfactant decreases. However, the further addition of salt from 10 mM to 20 mM, may not significantly change the micellar size, resulting in only a slight or negligible change in the separation of chromium ion. But further addition of electrolyte from 20 mM to 100 mM, there is an abrupt change in separation of chromium ion. So, it is evident, that, a salt concentration of 10 mM at pH 6 is the optimum salt dozing where removal of Cr (VI) ion, as well as leakage of CPC is economical and permissible according to environmental rules and regulations.

The total results are compared with the results obtained in liquid membrane separation process. It is observed that there is no effect during separation due to addition of salt in ELM process.
9.5 Symbol

\( f \) - activity coefficient
\( k_s \) - salt constant
\( \text{cmc} \) & \( \text{cmc}_0 \) - critical micelle concentrations with salt and without salt
\( C_s \) - concentration of the salt
\( k \) - rate constant,
\( i \) - ionic strength
\( k_0 \) - rate constant at \( i = 0 \);
\( Z_A \) & \( Z_B \) - charges of the corresponding reactants.
9.6 Reference: