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Membrane Characteristics and Fouling Study in MEUF for the Removal of Chromate Anions from Aqueous Streams

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Abstract: Micellar-Enhanced Ultrafiltration (MEUF) of the chromate anions from aqueous solutions has been studied at room temperature (28 ± 2°C) using cationic surfactants, cetyltrimethylammonium bromide (CTAB), and cetylpyridinium chloride (CPC), micelles of which adsorb the chromate ions by electrostatic interactions. The solution is processed by ultrafiltration, using a membrane with a pore size small enough to block the passage of the micelles and the adsorbed ions. The process is highly efficient in removing the chromate ions. In the absence of other electrolytes, chromate ion rejections up to 99% were observed at optimal conditions of pH, pressure, temperature, feed chromate, and surfactant concentrations. The presence of added NaCl reduces the chromate rejection, but it was still considerable (up to 82%), even in the presence of 100 mM NaCl. The rejection rate of chromate was found to be highly dependent on the pH of the feed solution. The influence of membrane characteristics on the chromate ion removal was also studied. Various resistances like fouling resistance, concentration polarization resistance, and membrane resistance were also estimated to quantify their effects on the removal efficiency and on the flux behavior.

Keywords: Chromate ions removal, surfactant, cetyltrimethylammonium bromide, cetylpyridinium chloride, micelles, membrane process, wastewater treatment, micellar-enhanced ultrafiltration, resistances, fouling, concentration polarization

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INTRODUCTION

Chromium, particularly hexavalent chromium or chromate, is very mobile in the environment and is a chronic hazard. Hexavalent chromium compounds are considered to be carcinogenic and corrosive to tissue. When accumulated in the human body, skin sensitization and kidney damage may occur (1, 2). Chromium exists in the industrial waste streams generally as hexavalent [Cr(VI)] and trivalent [Cr(III)] ions, of which its hexavalent form is much more toxic. According to the Water Prevention and Control of Pollution Act 1974, the maximum tolerance limit as put forth by Indian Standards for hexavalent chromium (as chromium) is 0.1 ppm and total chromium is 2 ppm (3). However, considering the stringent specifications in the years to come, it is anticipated that the total chromium would be restricted to levels lower than 0.05 ppm and hexavalent chromium less than 0.01 ppm.

The use of membranes in treating wastewater containing toxic metal ions and/or organics is an attractive and suitable technique, and it can be easily included in the entire manufacturing process (4–7).

Micellar-Enhanced Ultrafiltration (MEUF) is a relatively less energy intensive and safer process than traditional separation techniques such as distillation, evaporation, or distillation followed by extraction (8). MEUF is a pressure driven, membrane-based separation process that makes use of the micellar properties of a surfactant to remove dissolved metal ions and/or organics from aqueous streams (9). Based on the ion exchange properties of ionic surfactant micelles, MEUF can be an efficient technique for removal of multivalent metal ions and/or organics from aqueous effluent streams (10, 11).

The present report primarily deals with studies for removing hexavalent chromium or chromate [Cr(VI)] from aqueous streams. Hexavalent chromium or chromate [Cr(VI)] exists as a stable anionic species throughout a relatively wide pH range, 1.5 to 6.5 (12). On addition of a cationic surfactant to the solutions, positively charged micelles of the surfactant are formed which complex with the chromate anions. Above 25°C (Krafft point temperature of CTAB) and beyond 0.92 mM concentration [critical micellar concentration (cmc)], cetyltrimethylammonium bromide (CTAB) is present in the micellar form in the aqueous solutions (13). Micelles of pure CTAB, with a mean size of about 31,500 Da in water at 30°C, are suitably retained by 20 KD ultrafiltration membrane (14). Various resistances like fouling resistance, concentration polarization resistance, and membrane resistance were also estimated to quantify their effects on the removal efficiency and on the flux behavior.

EXPERIMENTAL

Materials and Reagent

The metallic salt, potassium dichromate ($K_2Cr_2O_7$), the cationic surfactants, cetyltrimethylammonium bromide (CTAB) and cetylpyridinium chloride

(CPC), and sodium chloride, were provided by s.d. fine-chem. Ltd., Mumbai, India. All the chemicals were over 99% pure and of analytical grade. They were used as received without further purification. Pure distilled water was used throughout to prepare the solutions of desired concentrations.

Experimental Set up

The ultrafiltration experiments were carried out in an Osmonics 300 cm^3 batch, stirred, dead-end cell unit. The process was carried out at room temperature (28 ± 2°C) and at pressure 4×10^5 Pa, unless otherwise stated. High-pressure nitrogen was used to maintain the upstream pressure. A 49 mm diameter, Permionics Polysulfone flat sheet membrane with a MWCO -20 KD was used, with an effective membrane area of 855 mm^2. The viscosity of retentate solution was measured by an Ostwald glass viscometer.

EXPERIMENTAL PROCEDURE

In each experimental run, a fresh membrane was used. In each experiment, 250 cm^3 of pure distilled water was charged into the cell to measure the pure water flux. A 30 cm^3 of feed solution was then charged into the cell. The run was continued until approximately 10 cm^3 (1/3rd of feed volume) of retentate sample remained in the cell. Permeate samples were collected during the run and average permeate flux were measured. After removing the retentate solution from the cell, pure water flux was again measured to determine the fouling characteristic of the membrane. The chromate concentrations of the permeate were analyzed as chromium by using a UV-Visible attachment of JASCO spectroflurometer (Model, FP-6200) at $\lambda_{MAX} =$ 532 nm (15). Chromate concentration in the retentate was calculated by material balance. The viscosity of final retentate solution was measured by using an Ostwald glass viscometer. The rejection (R) of chromate [Cr(VI)] was calculated as given below.

$$R = \left(1 - \frac{[Cr(VI)]_P}{[Cr(VI)]_R}\right) \times 100 \qquad (1)$$

The subscripts ‘P’ and ‘R’ indicate the chromate ion concentration in the permeate, and in the retentate solutions respectively. Polysulfone membrane being asymmetric, the membrane pores are randomly placed and the distribution of pore sizes on the membrane surface could be nonuniform. Therefore, a normalized flux or relative flux was considered for the comparison of permeate flux.

$$\text{Normalized flux} = \left(\frac{J_P}{J_W}\right) = \left(\frac{\text{Permeate flux}}{\text{Pure water flux}}\right) \qquad (2)$$

To study the influence of membrane characteristics on the removal efficiency and on the flux behavior, the various resistances offered during the process were calculated as given below.

Membrane Resistance (R_M)

$$R_M = \left(\frac{\Delta P}{\mu_W \times J_W}\right) \quad [m^{-1}] \tag{3}$$

Adsorbed layer resistance or Fouling resistance (R_A)

$$R_A = \left(\frac{\Delta P}{\mu_W \times J_F}\right) - R_M \quad [m^{-1}] \tag{4}$$

Concentration polarization resistance (R_P)

$$R_P = \left(\frac{\Delta P}{\mu_W \times J_P}\right) - (R_M + R_A) \quad [m^{-1}] \tag{5}$$

where, ΔP is the pressure drop in the UF system, μ_W is the viscosity of water (solvent), J_W is the pure water flux, J_P is the permeate flux and J_F is the water flux of fouled membrane.

RESULTS AND DISCUSSION

Effect of Feed Chromate Concentration

Figure 1 shows the effect of feed chromate concentration on adsorbed layer (R_A) and concentration polarization (R_P) resistance and rejection of chromate in the absence of surfactant (membrane effect). Potassium dichromate dissociates in the aqueous solution and gives chromate $[Cr(VI)^-]$ anions and potassium $[K^+]$ cations. There is no significant effect on the normalized flux and on the R_P resistance, because of the absence of surfactant. As the concentration of Cr(VI) in the feed was increased from 0.1 to 1 mM, the number of free ions in the solution, after dissociation of $K_2Cr_2O_7$, also increased and passed through the membrane to the permeate side. Some of them were either adsorbed in/on to the membrane pores or trapped physically within them due to membrane-solute interaction. The membrane is highly hydrophobic and asymmetric in nature. As the feed chromate concentration was increased from 0.1 to 1 mM, the rejection of Cr(VI) in water increased from 16.8 to 29%. The observed rejection may be attributed to the presence of the membrane charge, asymmetricity or hydrophobicity of the membrane. Due to the asymmetric nature of the membrane, the distribution of pore sizes is nonuniform and very small pores may provide resistance to chromate permeation. Increase in R_A resistance supports this mechanism. With no surfactant and with no significant chromate adsorption on the

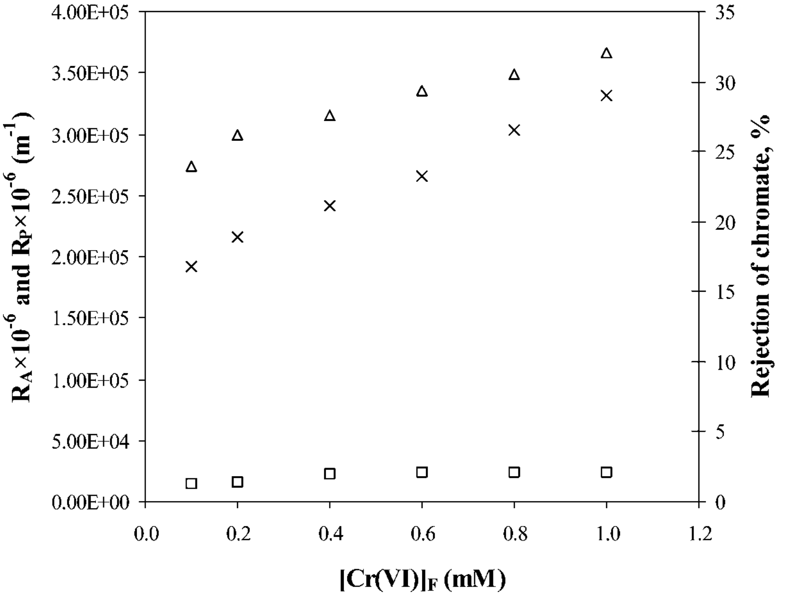

Figure 1. Effect of feed chromate concentration on adsorbed layer (R_A) and concentration polarization (R_P) resistance and rejection of chromate in the absence of surfactant (membrane effect). $[CTAB]_F = 0$, $[NaCl]_F = 0$, $P = 4 \times 10^5$ Pa, T = 27°C, pH = 5.5; △: R_A (m^{-1}), □: R_P (m^{-1}), × : Rejection of chromate, %.

membrane, no rejection of Cr(VI) was expected. Since the polysulfone membranes carry a negative charge, the "membrane charge" effect is probably responsible for this separation under these conditions.

Figure 2 shows the effect of feed chromate concentration on normalized flux and permeate chromate concentration in the presence of CTAB. The increase in chromate concentration from 0.1 to 1 mM results in slight decrease in the normalized flux. When CTAB is present, micellar-complex $CTA^+[Cr(VI)^-]$ is formed and ion exchange takes place between $Cr(VI)^-$ of $K_2Cr_2O_7$ and Br^- of CTAB in the neighborhood of the polar heads. The increase of Cr(VI) concentration leads to an increase in the $CTA^+[Cr(VI)^-]$ micellar-complex formation. The mean size of this complex is smaller than the pure CTAB micelles, they may enter the membrane pores, thus causing a plugging and a corresponding decrease of the flux (16). With the increase in the feed chromate concentration, the permeate chromate concentration also increased proportionally, but the rejection of chromate was still excellent (above 99%). The recovery of metal ions via MEUF is basically due to the electrostatic attraction between the metal ions and oppositely charged micellar surface. Although the initial surfactant concentration was maintained constant (10 mM), the number of positively charged micelles, on which the chromate anions are adsorbed due to electrostatic attraction, can

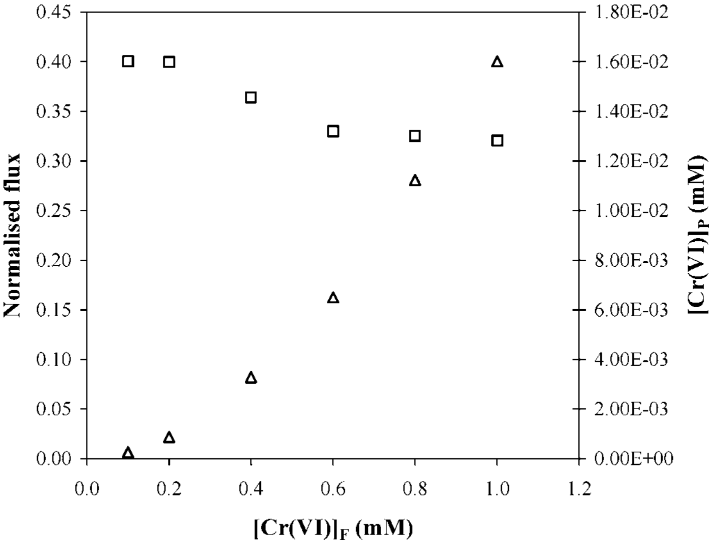

Figure 2. Effect of feed chromate concentration on normalised flux and permeate chromate concentration in the presence of surfactant. $[CTAB]_F = 10\,mM$, $[NaCl]_F = 0$, $P = 4 \times 10^5\,Pa$, $T = 27°C$, $pH = 5.5$; □: Normalised flux, △: $[Cr(VI)]_P$ (mM).

increase over time because of increased concentration. Some surfactant monomers (CTA^+) present in the solution, which do not contribute to the separation, can easily pass through the membrane towards the permeate side. As the feed metal concentration increases, the number of free metal ions in the solution also increases proportionally because of equilibrium between the adsorbed ions and free metal ions in the bulk, thus the chromate concentration in the retentate also increases.

For an aqueous solution containing only CTAB and potassium dichromate, the conditions of charge balance (electroneutrality) are,

$$2[CrO_4^{2-}]_{Ret} + [Br^-]_{Ret} = [CTA^+]_{Ret} + [K^+]_{Ret} \qquad (6)$$

$$2[CrO_4^{2-}]_{Per} + [Br^-]_{Per} = [CTA^+]_{Per} + [K^+]_{Per} \qquad (7)$$

Where subscripts '*Ret*' and '*Per*' denote the retentate and permeate solutions. In the absence of an added electrolyte, the ionic strength is quite low on both sides of the membrane. Therefore, it may be reasonable to assume that activity coefficients are equal in permeate and retentate and thus neglect the activity coefficient effects.

As the feed metal concentration is increased, a point is reached where almost all of the micellar bound counterions are $Cr(VI)^-$ instead of Br^- and no incremental separation capacity will be available. Therefore, the free metal ions which are not able to bound to the micellar surface easily pass through the membrane towards the permeate side causing the increase in the permeate metal concentration. Thus there is no significant effect on the rejection of chromate (99.9 to 99.5%), because both the permeate and retentate chromate concentration increase proportionally. Also the feed surfactant concentration (10 mM) is very high as compared to the feed chromate concentration (0.1 to 1 mM). The results of rejection of chromate indicate that the MEUF has the potential to greatly reduce the concentration of multivalent metal ions.

Figure 3 shows the effect of feed chromate concentration on adsorbed layer (R_A) and concentration polarization (R_P) resistance in the presence of CTAB. The unassociated surfactant monomers [CTA^+] and free ions [Br^-, $Cr(VI)^-$, K^+], which did not contribute to the separation, passes through the membrane towards the permeate side, which may be adsorbed in the membrane pores due to membrane-solute interaction and causing fully or partially plugging of membrane pores. Also, the $CTA^+[Cr(VI)^-]$ micellar-complex, which has a mean size smaller than the pure CTAB micellar size may enter the membrane pores, causing plugging of the membrane pores, which results in increased in R_A resistance. The concentration near the membrane surface increases as feed chromate concentration increases and is high as compared to the bulk retentate concentration, which results in increase in R_P resistance. Increase in R_A and/or R_P resistance is also a cause of decrease in normalized flux, because both the resistances are the

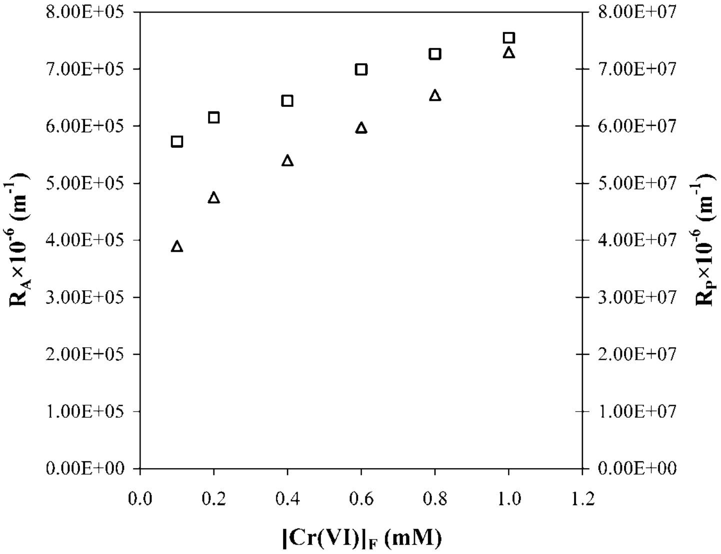

Figure 3. Effect of feed chromate concentration on adsorbed layer (R_A) and concentration polarization (R_P) resistance in the presence of surfactant. $[CTAB]_F = 10$ mM, $[NaCl]_F = 0$, $P = 4 \times 10^5$ Pa, $T = 27°C$, pH = 5.5; △: R_A (m^{-1}), □: R_P (m^{-1}).

additional resistance towards the permeate flow in addition with membrane resistance.

Effect of Feed Surfactant Concentration

Figure 4 shows the effect of feed CTAB concentration on the normalised flux through the membrane and rejection of chromate. Increasing surfactant concentration from 0 to 20 mM results in a decrease in normalised flux indicating that concentration polarization is most severe at higher surfactant concentration. No gel layer or gel concentration (C_g) was observed in the range of concentration studied. Gel concentration is the extreme case of concentration polarization, at which the retentate concentration reaches a maximum value, values close to 500 mM in case of cationic surfactants and 600 mM in the case of anionic surfactants, and permeate fluxes become zero (17). The chromate rejection varied between 16.8 to 61% when the surfactant concentration was moderately below its cmc value, where micelles are initially absent, but would form as soon as the retentate surfactant concentration increased beyond the cmc value. There may be higher surfactant concentration in the layer adjacent to the membrane surface, and also due to the additional effect of membrane (membrane charge, asymmetricity or hydrophobicity etc.) (9). Surfactant monomers also can be rejected to some extent and may accumulate near the membrane surface. The concentration of

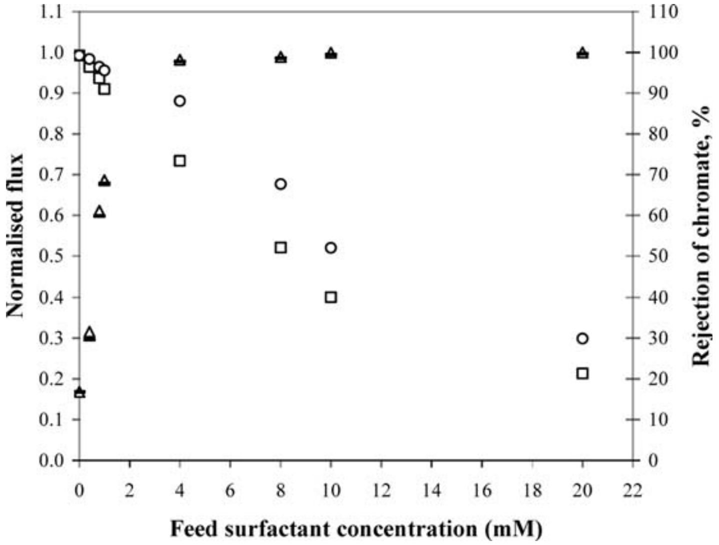

Figure 4. Effect of feed surfactant [CTAB and CPC] concentration on normalised flux and rejection of chromate. $[Cr(VI)]_F = 0.1$ mM, $[NaCl]_F = 0$, $P = 4 \times 10^5$ Pa, T = 27°C, pH = 5.5; □: Normalised flux with CTAB, △: Rejection of chromate with CTAB, %; ○: Normalised flux with CPC, −: Rejection of chromate with CPC, %.

surfactant in this layer can exceed the cmc and micelles can be present in this region, even when in the bulk retentate has no micelles present. When feed surfactant concentration is increased, the number of positively charged micelles and the corresponding surface charge on which the chromate anions get adsorbed, increases. On the other hand, the ratio of $[Cr(VI)^-]/[Br^-]$ in the retentate decreases, by increasing the amount of surfactant. Hence, the ionic competition between the two counterions in the bulk is enhanced and more advantageous to Br^-, which should increase its concentration in the permeate, while $Cr(VI)^-$ is released in the bulk (6). Further increase in the feed surfactant concentration from 4 to 20 mM, resulted in only a marginal increase in rejection (98.1 to 99.9%). Micelles continuously form and break (deformed) at any concentration of the solution. At higher surfactant concentrations, either smaller surfactant aggregates of micelles (n-mers) are formed and/or the spherical micellar shape changes into cylindrical shape (6, 14, 17). The smaller aggregates may bind to the metal ions and transport them through the membrane to the permeate side. This may also be the cause of the decrease in the normalised flux. This means higher surfactant concentrations in the feed do not lead to significant improvement in the metal separation (18).

Figure 5 shows the effect of feed CTAB concentration on adsorbed layer (R_A) and concentration polarization (R_P) resistance. As the feed surfactant

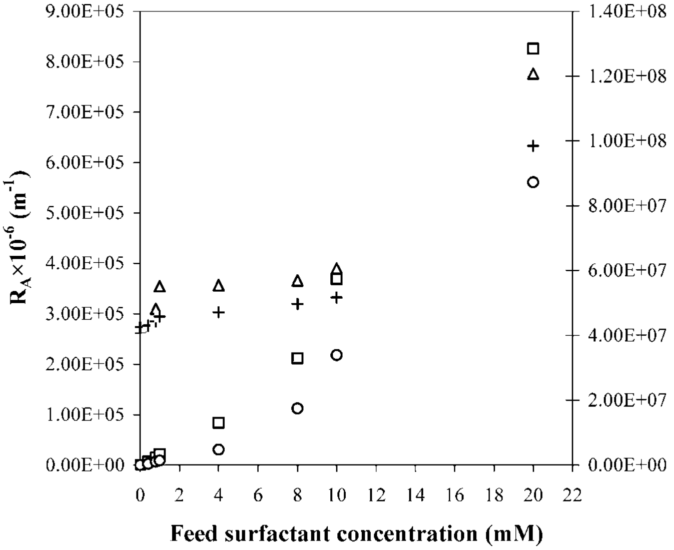

Figure 5. Effect of feed surfactant [CTAB and CPC] concentration on adsorbed layer (R_A) and concentration polarization (R_P) resistance. $[Cr(VI)]_F = 0.1$ mM, $[NaCl]_F = 0$, $P = 4 \times 10^5$ Pa, T = 27°C, pH = 5.5; △: R_A with CTAB (m^{-1}), □: R_P with CTAB (m^{-1}); +: R_A with CPC (m^{-1}), ○: R_P with CPC (m^{-1}).

concentration increases, the concentration of micelles in the solution also increases. The concentration of micelles near the membrane surface is always higher than the bulk retentate concentration. This high concentration of micelles leads to an increase of the organic phase near the membrane surface, which results in increase in R_P resistance. When the feed surfactant concentration (up to 0.8 mM) was less than cmc, R_A resistance increases initially because most of the surfactant molecules are in the form of free monomers (CTA^+). The size of which is much smaller than the pore diameter. These positively charged surfactant monomers are attracted towards the negatively charged membrane due to membrane-solute interaction when it is passing through the membrane. These monomers either get adsorbed in/on to the membrane pores/surface or neutralize the negative sites of the membrane and lie on to the membrane surface. Also, other free ions, which do not contribute to the separation because of the lack of micelles, interact towards the membrane due to hydrophobicity and asymmetricity of the membrane. This leads to increase in R_A resistance at surfactant concentration below its cmc value. When the surfactant concentration increases (1 to 10 mM) above its cmc value, most of the surfactant molecules present in the form of micelles having size larger than the pore size of the membrane and rejected above the membrane, results in marginal increase in R_A resistance or almost constant. When the surfactant concentration in the feed solution is very high (20 mM) as compared with its cmc value, the small surfactant aggregates are formed instead of micelles. These smaller aggregates may bind metal ions and transport them through the membrane into the permeate stream and may get adsorbed in the membrane pores, causing plugging of the pores. This results in significant increase in R_A resistance.

A similar effect was observed when CPC was used as surfactant. Both cationic surfactants have cmc of approximately 1 mM and the same Krafft point temperature (25°C). Hence, both have displayed analogous behavior (19). However rejection was slightly better in the case of CTAB than that with CPC, while the fluxes were slightly better and various resistances (R_A and R_P) were slightly lower in the case of CPC than that with CTAB.

Effect of Salt Concentration

Figure 6 shows the effect of feed NaCl concentration on the normalised flux through the membrane and rejection of chromate. NaCl dissociates in water to give Na^+ and Cl^- ions. With the increased NaCl concentration in the feed, the normalized flux initially increases and then slightly decreases. As the feed NaCl concentration increased from 0 to 40 mM, R_P resistance decreased considerably (Fig. 7). Hence, the corresponding increase in the normalized flux was observed. With increase in NaCl concentration further

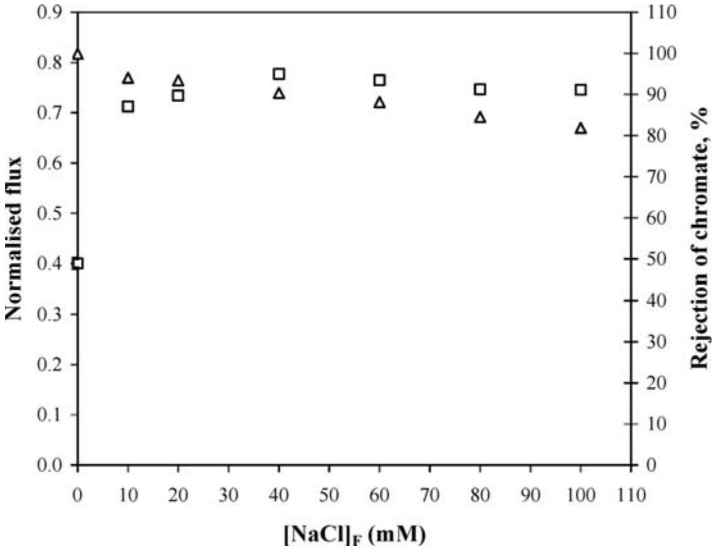

Figure 6. Effect of feed NaCl concentration on normalised flux and rejection of chromate. $[Cr(VI)]_F = 0.1$ mM, $[CTAB]_F = 10$ mM, $P = 4 \times 10^5$ Pa, $T = 27°C$, $pH = 5.5$; □: Normalised flux, △: Rejection of chromate, %.

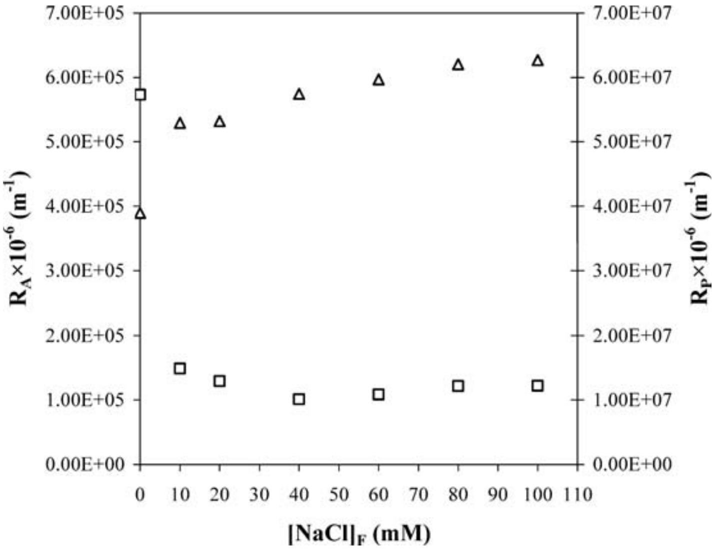

Figure 7. Effect of feed NaCl concentration on adsorbed layer (R_A) and concentration polarization (R_P) resistance. $[Cr(VI)]_F = 0.1$ mM, $[CTAB]_F = 10$ mM, $P = 4 \times 10^5$ Pa, $T = 27°C$, $pH = 5.5$; △: R_A (m^{-1}), □: R_P (m^{-1}).

from 40 to 100 mM, the R_A resistance increased considerably, while R_P resistance was almost constant (Fig. 7). This considerable increase in R_A resistance affects the permeate flow and hence the normalized flux slightly decreased. When NaCl concentration increased from 0 to 100 mM, the rejection of chromate decreased from 99.9 to 81.9%. Similar results were observed by Gzara et al. (16), while using CPC. Increasing NaCl concentration in the feed solution leads to competition for positively charged binding sites on the micellar surface between the chloride and the chromate anions, resulting in a decrease in chromate binding per charged group on the micelle and a decrease in chromate rejection. On the other hand, as the monovalent counterion concentration i.e. Na^+ Cl^- concentration in solution increases, the electrical double layer surrounding the micelles also get compressed. As a result, absolute magnitude of electrical potential of the charged micelle at any given distance from the micellar surface is reduced. This results in a reduced driving force for adsorption of the metal ions on micellar surface due to the electrostatic attraction. This effect may be attributed to the increased ionic strength of solution. Hence, added monovalent salt (NaCl) should tend to decrease adsorption of the multivalent metal ion (chromate in this case) and therefore decreases the rejection of chromate. Using MEUF to remove heavy metals thus would not be nearly as effective when high concentrations of dissolved salts are present. In contrast, added salt has a substantial negative effect on heavy metal removal using MEUF. Still the chromate rejection rate higher than 81% was obtained, indicating that effective separation of metal ions can be attained by MEUF in the presence of the salt.

pH Effect

Polysulfone membrane can be operated in a wide pH range of 1–13. Figure 8 shows the pH effect of the feed solution on the permeate chromate concentration and rejection of chromate. No significant effect was observed on the normalized flux and on the R_A and R_P resistances if the pH of the feed solution was varied from 4 to 6.5. However, the pH of the feed solution when changed from 4 to 5.5, the permeate chromate concentration decreased considerably while the rejection of chromate increased from 95.4 to 99.7%. Further increase in pH of the feed solution from 5.5 to 6.5, did not have any significant effect on the permeate chromate concentration and on the rejection of chromate. Anions commonly form species of different valancies in water and the concentration of each ion depends on pH. Chromate anion is present in different forms depending on pH. For Cr(VI) ions, the predominant species between pH 1.5 and 4 is $HCrO_4^-$. At pH 6.5, $HCrO_4^-$ and CrO_4^{2-} exist in equal amounts and at higher pH, CrO_4^{2-} predominates (16, 20, 21). Its most active form, $HCrO_4^-$ and CrO_4^{2-} prevails in the pH

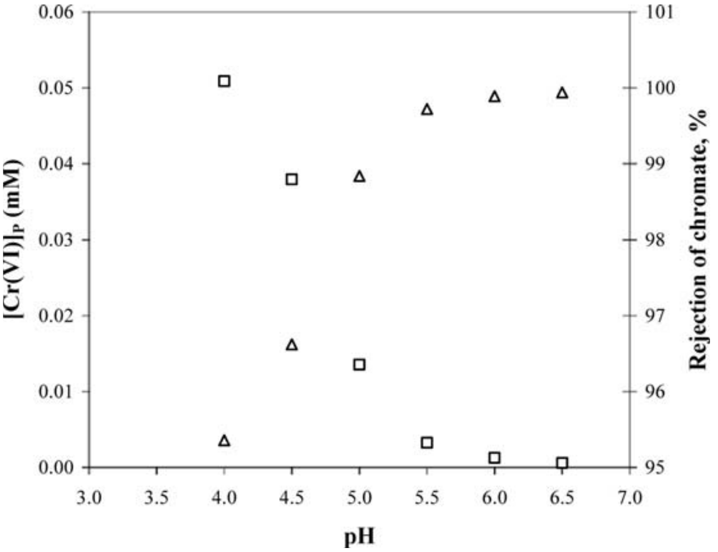

Figure 8. pH effect of feed solution on permeate chromate concentration and rejection of chromate. $[Cr(VI)]_F = 0.4\,mM$, $[CTAB]_F = 10\,mM$, $[NaCl]_F = 0$, $P = 4 \times 10^5\,Pa$, $T = 27°C$; □: $[Cr(VI)]_P$ (mM), △: Rejection of chromate, %.

range of 5.5 to 6.5. As a result, the maximum binding of chromate [Cr(VI)] and its maximum rejection are observed at this pH range.

Pressure Effect

Figure 9 shows the effect of applied pressure on adsorbed layer (R_A) and concentration polarization (R_P) resistance and rejection of chromate in the absence of surfactant (membrane effect). The pressure was varied from 2×10^5 to $6 \times 10^5\,Pa$, because the maximum operating pressure limit in case of flat sheet polysulfone membrane is 7 bar i.e. $7.14 \times 10^5\,Pa$, above this pressure limit the membrane was damaged. No significant effect was observed on the normalized flux, while the permeate and pure water fluxes vary linearly with the applied pressure. Due to absence of surfactant, no significant effect was observed on the R_P resistance. In the absence of surfactant, the ionic solutes are forced through the membrane towards the permeate side as the pressure increased, resulting in decrease in R_A resistance. With the increase in pressure from 2×10^5 to $6 \times 10^5\,Pa$, the rejection of chromate decreased from 29.4 to 4.7% due to decrease in adsorption of chromate ions in the membrane pores, which shows the rejection of ionic solutes to be dependent on the membrane characteristics. Decrease in R_A resistance also supports this mechanism (Fig. 9). The observed rejections may be attributed

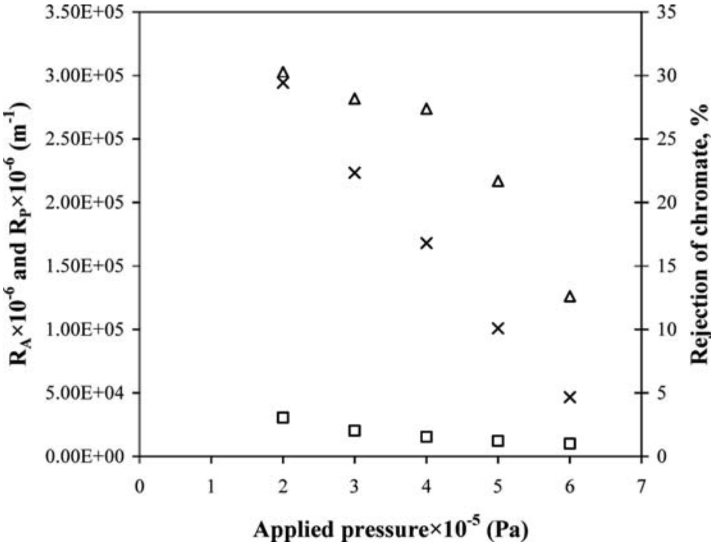

Figure 9. Effect of applied pressure on adsorbed layer (R_A) and concentration polarization (R_P) resistance and rejection of chromate in the absence of surfactant (membrane effect). $[Cr(VI)]_F = 0.1$ mM, $[CTAB]_F = 0$, $[NaCl]_F = 0$, $T = 27°C$; pH = 5.5; △: R_A (m^{-1}), □: R_P (m^{-1}), × : Rejection of chromate, %.

to the presence of the membrane charge, asymmetricity or hydrophobicity of the membrane i.e. the additional effect of membrane.

Figure 10 shows the effect of applied pressure on pure water flux and the permeate flux and permeate chromate concentration in the presence of a surfactant. Both the fluxes vary linearly with the applied pressure, but the permeate flux rate is lower in the presence of surfactant. The flux obeys the Darcy's law (16), i.e. Flux $= L_P \times \Delta P$, where the Membrane Permeability, $L_P = 1/(\mu_S \times R_M)$. No significant effect was observed on the normalized flux if the pressure was increased from 2×10^5 to 6×10^5 Pa, but the permeate chromate concentration decreased slightly and the rejection of chromate slightly increased from 99.5 to 99.9%. Increase in the applied pressure, increases the surfactant concentration polarization layer, which tends to increase in R_P resistance (Fig. 11) near the membrane surface, and consequently results in increasing concentration of micelles in this layer on which the metal ions are adsorbed. The flow of the solution of charged species across the membrane, under the effect of a pressure gradient, also results in an unbalanced distribution of the electrical charges at the upstream and downstream interfaces of the membrane. This distribution generates streaming potential depending upon the pressure gradient, and an increase of the transmembrane pressure may lead to a better rejection of the metal ions (18).

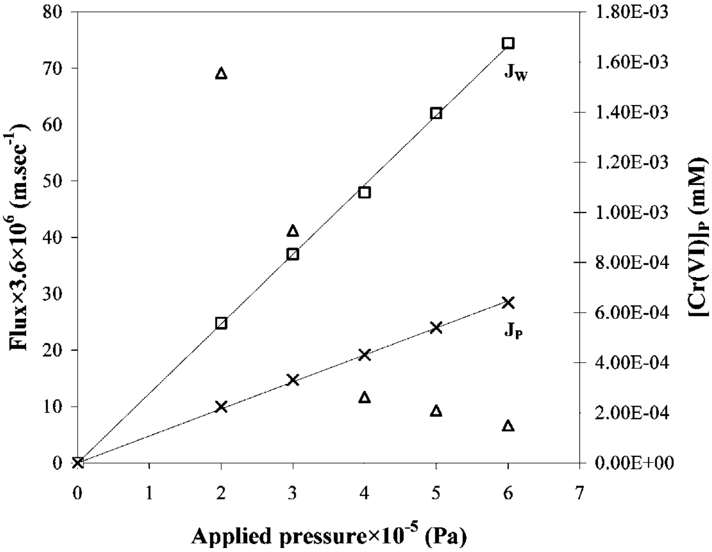

Figure 10. Effect of applied pressure on pure water flux (J_W), permeate flux (J_P) and permeate chromate concentration in the presence of surfactant. $[Cr(VI)]_F = 0.1$ mM, $[CTAB]_F = 10$ mM, $[NaCl]_F = 0$, T = 27°C, pH = 5.5; □: Pure water flux ($m \cdot sec^{-1}$), × : Permeate flux ($m \cdot sec^{-1}$), △: $[Cr(VI)]_P$ (mM).

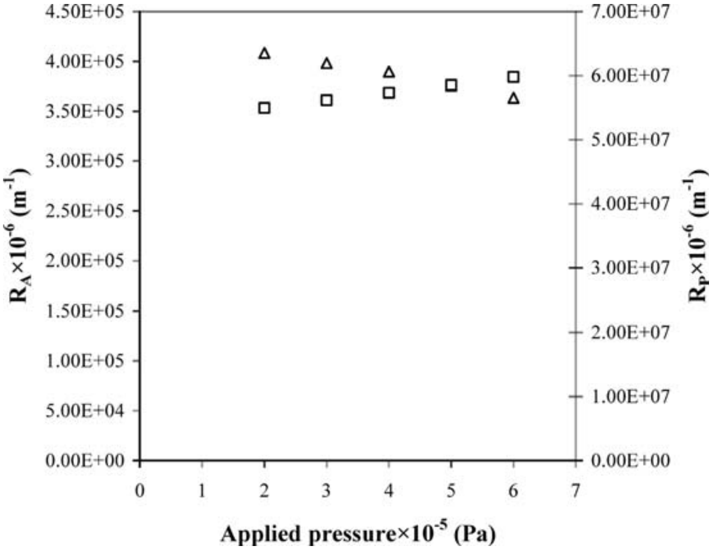

Figure 11. Effect of applied pressure on adsorbed layer (R_A) and concentration polarization (R_P) resistance in the presence of surfactant. $[Cr(VI)]_F = 0.1$ mM, $[CTAB]_F = 10$ mM, $[NaCl]_F = 0$, T = 27°C, pH = 5.5; △: R_A (m^{-1}), □: R_P (m^{-1}).

Temperature Effect

The maximum operating temperature in case of polysulfone membrane is 75°C. In the present studies, the temperature was varied from 27°C to 50°C. Figure 12 shows that pure water flux and the permeate flux vary linearly with the temperature, but the permeate flux is lower than the water flux. The temperature has a marked and a positive influence on both the fluxes. Within the framework of resistance theory, the flux is inversely proportional to the viscosity of solvent. It is well known that, as the temperature increases, the viscosity of solvent (water) decreases, which also results in decrease in R_P resistance (Fig. 13). Figure 14 shows the effect of temperature on the normalised flux and permeate chromate concentration. At higher temperatures, normalised flux increases due to decrease in viscosity of solution. The permeate chromate concentration, however increased, which can be related to the cmc variations with temperature. CTAB cmc is reported to increase with temperature (14). In this case, the free surfactant ion concentration increases with the temperature. The counterion concentrations always obey the electrical charge balance, hence there are more and more free anions in CTAB solution as temperature increases. This should induce a leak of chromate in the permeate. In addition, the size of CTAB micelles depends on temperature (14). Both cmc and CTAB micellar size variation explain the chromate concentration in the permeate and R_A resistance.

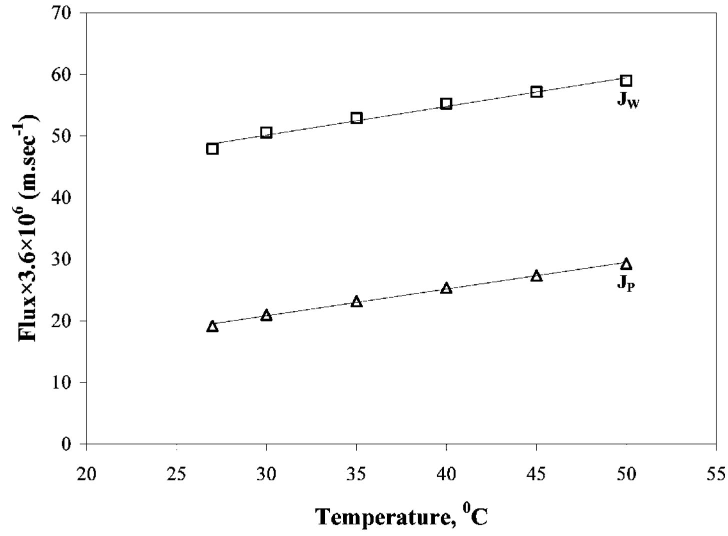

Figure 12. Effect of temperature on pure water flux (J_W) and permeate flux (J_P). $[Cr(VI)]_F = 0.1\,mM$, $[CTAB]_F = 10\,mM$, $[NaCl]_F = 0$, $P = 4 \times 10^5\,Pa$, $pH = 5.5$; □: Pure water flux ($m \cdot sec^{-1}$), △: Permeate flux ($m \cdot sec^{-1}$).

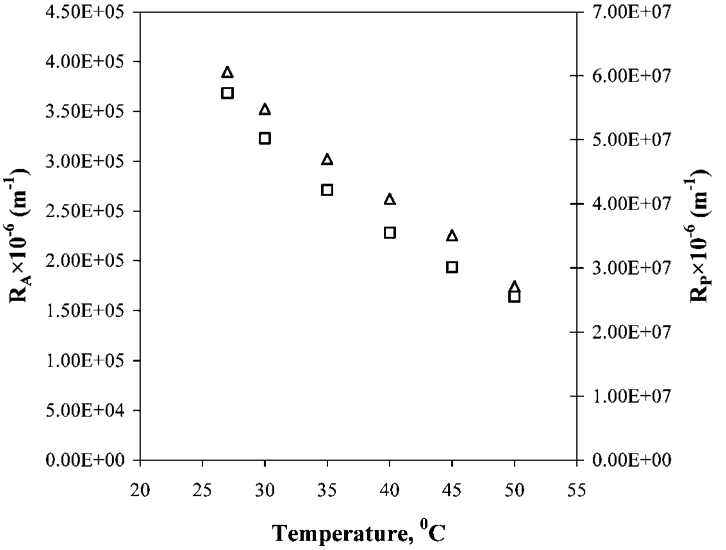

Figure 13. Effect of temperature on adsorbed layer (R_A) and concentration polarization (R_P) resistance. $[Cr(VI)]_F = 0.1$ mM, $[CTAB]_F = 10$ mM, $[NaCl]_F = 0$, $P = 4 \times 10^5$ Pa, pH = 5.5; △: R_A (m^{-1}), □: R_P (m^{-1}).

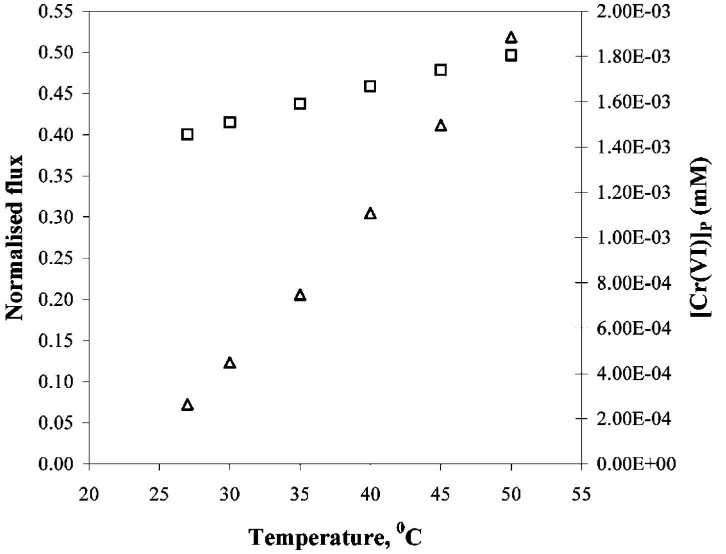

Figure 14. Effect of temperature on normalised flux and permeate chromate concentration. $[Cr(VI)]_F = 0.1$ mM, $[CTAB]_F = 10$ mM, $[NaCl]_F = 0$, $P = 4 \times 10^5$ Pa, pH = 5.5; □: Normalised flux, △: $[Cr(VI)]_P$ (mM).

CONCLUSION

MEUF to remove chromate [Cr(VI)] ions from aqueous streams using cationic surfactants; cetyltrimethylammonium bromide and cetylpyridinium chloride was investigated with 20 KD polysulfone membrane. The following features were observed.

In the absence of the surfactant, the chromate rejection varied from 29.4 to 4.7% with increase in applied pressure and 16.8 to 29% with increase in feed chromate concentration. Therefore, the observed rejection of chromate may be attributed to the presence of membrane charge, asymmetricity, or hydrophobicity of the membrane.

In the presence of the surfactant, permeate chromate concentration increased with increase in feed chromate concentration, feed NaCl concentration, and temperature, while it was decreased with increase in feed surfactant concentration and applied pressure. Chromate rejection was found to be highly dependent on pH condition of the feed solution and approaches maximum at pH of 5.5. Chromate rejection increased with increase in feed surfactant concentration, but found to be almost constant at 4 to 20 mM feed surfactant concentration and also slightly better in the case of CTAB than that with CPC. This means higher surfactant concentration in the feed does not lead to significant improvement in the metal separation. Chromate rejection decreased with increase in feed NaCl concentration, but it was still considerable (up to 82%) even in the presence of up to 100 mM feed NaCl concentration.

The permeate flux depends linearly on the applied pressure and temperature. The normalized flux was found to be decreased with increase in feed chromate concentration and feed surfactant concentration, while it was increased with increase in temperature.

The membrane fouling during ultrafiltration is influenced by the chemical nature of membrane materials. Polysulfone, which is hydrophobic in nature, shows a stronger tendency to adsorb metallic chromate ions and to fouling. The presence of electrolytes in feed solution enhances fouling with a consequent reduction in the flux while the increase in temperature and pressure reduces fouling.

Concentration polarization is most severe at higher surfactant concentration and it is increased with increase in feed surfactant concentration with a consequent reduction in the flux while the increase in temperature reduces concentration polarization resistance.

MEUF can be effectively used to remove chromate ions from aqueous steams even in the presence of up to 100 mM NaCl.

NOMENCLATURE

R	Rejection of chromate, %
J_F	Water flux of fouled membrane ($m \cdot sec^{-1}$)

J_P	Permeate flux ($m \cdot sec^{-1}$)
J_W	Pure water flux ($m \cdot sec^{-1}$)
J_P/J_W	Normalised flux or Relative flux
P	Applied pressure in UF system (Pa)
pH	pH of the feed solution
R_A	Adsorbed layer or Fouling resistance (m^{-1})
R_M	Membrane resistance (m^{-1})
R_P	Concentration polarization resistance (m^{-1})
T	Temperature (°C)
ΔP	Pressure drop (Pa)
λ_{MAX}	Wavelength (nm)
μ_S	Viscosity of solvent ($kg \cdot m^{-1} \cdot sec^{-1}$)
μ_W	Viscosity of water (1E-03 $kg \cdot m^{-1} \cdot sec^{-1}$)
$[CPC]_F$	Concentration of CPC in the feed (mM)
$[NaCl]_F$	Concentration of NaCl in the feed (mM)
$[CTAB]_F$	Concentration of CTAB in the feed (mM)
$[Cr(VI)]_F$	Concentration of Cr(VI) i.e. $K_2Cr_2O_7$ in the feed (mM)
$[Cr(VI)]_P$	Concentration of Cr(VI) in the Permeate (mM)
$[Cr(VI)]_R$	Concentration of Cr(VI) in the Retentate (mM)

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