

# Simultaneous removal of nickel and cobalt from aqueous stream by cross flow micellar enhanced ultrafiltration

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## Abstract

Nickel and cobalt were simultaneously removed from aqueous feed using cross flow micellar enhanced ultrafiltration. Twenty kiloDalton polysulfone membrane was used and the rejection more than 99% was obtained. The effect of operating variables like inlet flow rate, inlet pressure, feed metal ions concentration, surfactant to metal ion (S/M) ratio and pH on the rejection of metal ions was investigated. Gel layer formation and concentration polarization was insignificant under the present experimental condition. Presence of salt in the aqueous feed results in drop in rejection from 99% to 88%. The distribution coefficient of solutes in the micellar phase and aqueous phase was estimated from ultrafiltration data. The loading of micelles was also estimated for both the nickel and cobalt ions which confirmed the reproducibility of the micellar enhanced ultrafiltration (MEUF) experiments.

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**Keywords:** MEUF; Nickel; Cobalt; Cross flow; Ultrafiltration

## 1. Introduction

Removal of heavy metal ions such as nickel, cobalt, zinc, chromium, copper, etc. and/or organic contaminants from aqueous solutions is a problem frequently encountered in the treatment of industrial wastewaters. Among these metals most of the metals are suspected carcinogens. More over these metals will contaminate the soil, potable water source and crops. Another advantage of removing these contaminants is reuse and recycle of water. Because of this fact many government agencies like U.S. EPA had put legislative compliance on released concentration of these metals. An extensive report published by the United States Environmental Protection Agency (U.S. EPA) provides an excellent review of various forms of metals and typical concentrations present in industrial effluents, guidelines for effluent limitations, and currently used treatment methods.

Nickel and cobalt are the toxic metals found in the waste streams of oil refining, metal finishing industry, ferrous foundries, textile industry and dyes operations etc. Food &

Agricultural Organization of the United Nation recommended maximum level in irrigation water for nickel is 200  $\mu\text{g/L}$  (0.0034 mM) and for cobalt is 100  $\mu\text{g/L}$  (0.0017 mM). The use of ultrafiltration 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 whole manufacturing process.

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 [1]. 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 [2]. 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 [3,4]. In MEUF surfactant micelles of ionic surfactant, carrying charge opposite to that of metal ion are introduced in solution to enhance rejection efficiency of metal ion. The bound micelles being larger in size than pore size of UF membrane can be easily retained in UF; the metal ions that are associated to micelles get rejected effectively. Permeate obtained has very low concentration of both surfactant and metal ion. The retentate solution which now

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has high concentrations of both surfactant and metal ions is much less in volume (approximately 10–30% of feed volume); therefore further treatment is much more cost effective as compared to the direct treatment of feed solution. The objective of present work is to study the MEUF of a multicomponent system using synthetic feed containing nickel and cobalt as the pollutants.

## 2. Materials and methods

### 2.1. Materials

The surfactant sodium dodecyl Sulfate (SDS) received from Merck Ltd., Mumbai, India was used as received without further purification, cobalt (II) sulfate heptahydrate ( $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ ) and nickel (II) sulfate ( $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ ) were used as source of metal ions and were used as received from Merck Ltd., Mumbai, India. pH adjustment was done using 0.5 N NaOH and 0.5 N  $\text{H}_2\text{SO}_4$ . NaOH,  $\text{H}_2\text{SO}_4$ , cetyltrimethylammonium bromide (CTAB), chloroform and methylene blue were procured from the company s.d. fine chemicals Ltd., Mumbai, India. Deionized water was used in all the experimental runs. Analysis reagent 4-(2-Pyridylazo) resorcinol monosodium salt indicator (PAR) was used as received from s.d. fine chemicals Ltd., Mumbai, India. Oxalic Acid was used as eluent for analysis was received from Merck Ltd., Mumbai, India. All the chemicals were of analytical grade and had an assay of  $\geq 98.5\%$ .

The membrane for ultrafiltration cell, procured from Sartorius (Germany) was polysulfone (PS) membrane with 20 kDa MWCO and 200  $\text{cm}^2$  effective membrane area.

### 2.2. Ultrafiltration setup

Ultrafiltration experiments were carried out in a cross flow continuous mode system, from Sartorius, Germany (Fig. 1). The micellar solution with solutes was placed in a feed tank of 500 mL capacity. Two hundred and fifty milliliters feed solution was taken for each run. The feed was continuously stirred by magnetic stirrer. A peristaltic pump was used to feed the solu-

tion to the ultrafiltration cell. The retentate stream was recycled to the feed tank. All the tubings are made of pharmed which is a contamination and sorption free material. The volumes of permeate and time for filtration was continuously recorded on a computer. For analysis the permeate samples were collected at different volume fractions, e.g.  $V_p/V_f$  of 0.2, 0.4, 0.6 and 0.8. There are three pressure sensors for measuring the inlet pressure, retentate pressure and permeate pressure.

### 2.3. Method

$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  were added to deionized water to produce the synthetic wastewater. The stock solutions of  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$  of 100 mM each were prepared and all the solutions of desired concentrations were made by diluting the stock solution with deionized water. For each experimental run 250 mL of feed was taken. Before each experimental run 250 mL of deionized water was fed and water flux was measured to check the membrane permeability. The water flux was almost constant. 250 mL of feed solution was taken and its pH was adjusted by using 0.5 N NaOH and 0.5 N  $\text{H}_2\text{SO}_4$ . After each experimental run the membrane was washed thoroughly with deionized water by using back flushing for half an hour then again deionized water was passed through the membrane for 15 min to ensure uniform and constant water flux. All the experiments were carried out at room temperature of  $29 \pm 2^\circ\text{C}$ . Samples were collected dynamically on permeate volume basis and permeate flux was calculated.

### 2.4. Sample analysis

The concentration of  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  in permeate samples were found out by “High Pressure Ion Chromatograph” (HPIC), Dionex, USA at 530 nm wavelength. The column used for the analysis study is “ION Pac CS5A”. Analysis reagent 4-(2-pyridylazo) resorcinol monosodium salt indicator was used. Oxalic acid was used as eluent (mobile phase)

The concentration of retentate was calculated by using material balance. The retentate concentration was calculated by

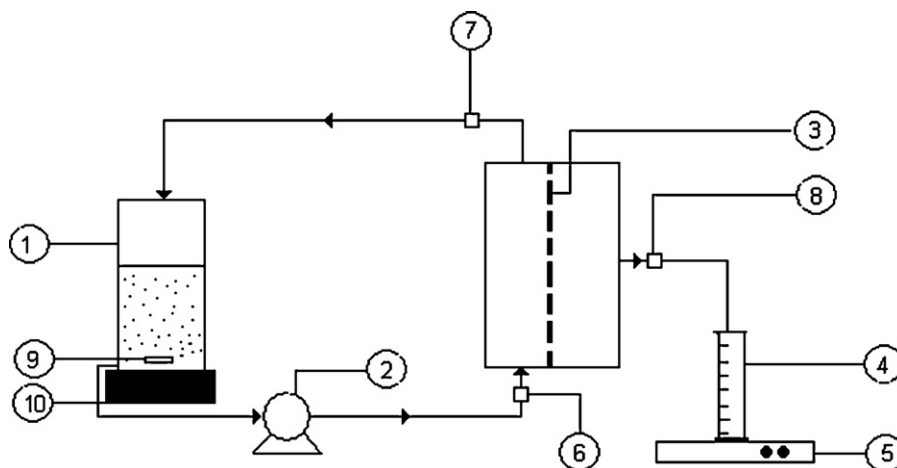


Fig. 1. Schematic of cross flow Ultrafiltration apparatus. 1, Feed tank; 2, peristaltic pump; 3, polysulfone membrane; 4, measuring cylinder; 5, weigh balance; 6, feed inlet pressure sensor; 7, retentate pressure sensor; 8, permeate pressure sensor; 9, magnetic stirrer; 10, magnetic motor.

following equation

$$C_R = \frac{(V_F C_F - V_P C_P)}{V_R} \quad (1)$$

where  $C_R$ ,  $C_F$ , and  $C_P$  represent the metal ion concentration in the retentate, in the feed initially, and in the permeate, respectively.  $V_F$ ,  $V_P$ , and  $V_R$  are the initial feed, the permeate, and the retentate volume, respectively. Thus,  $C_F V_F = C_P V_P + C_R V_R$ . As the retentate is recycled and permeate is collected continuously, there is a change in feed volume and feed concentration with respect to permeate volume collected. Hence, for the next volume compression  $C_F$  is replaced by  $C_R V_R$  of the initial volume compression.

Rejection % for nickel and cobalt are calculated by using following formula.

$$\% \text{Rejection for Ni} = \% R \text{ for Ni} = 1 - \frac{[\text{Ni}^{+2}]_P}{[\text{Ni}^{+2}]_R} \quad (2)$$

$$\% \text{Rejection for Co} = \% R \text{ for Co} = 1 - \frac{[\text{Co}^{+2}]_P}{[\text{Co}^{+2}]_R} \quad (3)$$

The subscripts P and R indicate corresponding quantity as measured in permeate and retentate solutions, respectively. The membrane being non-uniform in its pore distribution all the flux data were reported in terms of normalized flux calculated as [4].

$$\text{Normalized flux} = \frac{J_P}{J_W} = \frac{\text{permeate flux}}{\text{pure water flux}} \quad (4)$$

In presence of  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  the analysis of SDS was carried out by two-phase titration method using cationic surfactant CTAB.

### 3. Results and discussion

#### 3.1. Ultrafiltration of $\text{Ni}^{2+}$ and $\text{Co}^{2+}$ in absence of SDS

The ultrafiltration was carried out in absence of surfactant to study the membrane effect. Two hundred and fifty milliliters of feed solution with 1 mM  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  each was introduced in the feed tank. As expected there is practically no rejection of  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  ions as the membrane pore size is very large compared to the ionic size of  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$ . From Fig. 2, permeate metal ion concentration for nickel and cobalt is also same as that of the initial feed concentration. Thus, there is no adsorption of metal ions on the membrane surface and the membrane resistance is almost zero. In the dead end system 15% rejection of metal ion was obtained without surfactant [5,6] attributing to hydrophobic membrane and hydrophilic solute interaction offering some membrane resistance. But in the present work the hydrophobic membrane and hydrophilic solute interaction is not observed which may be because of the cross flow in the feed solution overcoming the membrane–solute interaction.

#### 3.2. Optimization of flow rate

At standard set of condition such as feed solution 250 mL,  $[\text{Ni}]_F$  and  $[\text{Co}]_F$  1 mM each, pH 8, surfactant to metal ion

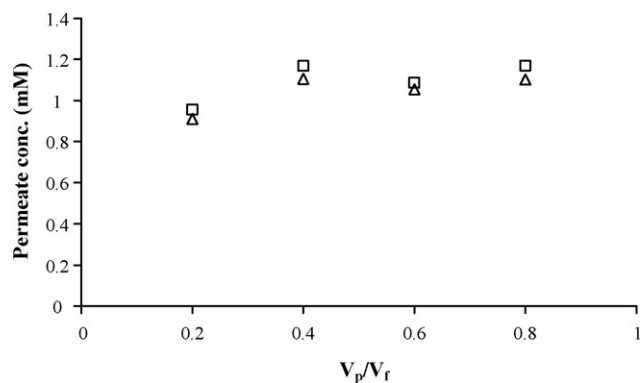


Fig. 2. Effect of absence of SDS on rejection of metal ions.  $[\text{Ni}]_F = 1$  mM,  $[\text{Co}]_F = 1$  mM,  $[\text{SDS}]_F = 0$  mM,  $[\text{NaCl}]_F = 0$ ,  $T = 27^\circ\text{C}$ , pH 8, inlet flow rate = 150 mL/min,  $V_p/V_f = 0.8$ . ( $\Delta$ ) Permeate concentration of Co, ( $\square$ ) permeate concentration of Ni.

ratio (S/M) = 10,  $V_p/V_f = 0.5$ . The inlet flow rate was varied as 50 mL/min, 100 mL/min, 150 mL/min and 200 mL/min. Before each run the membrane was back flushed with deionized water. Then again deionized water was passed through it to check the membrane permeability.

As shown in Fig. 3, at inlet flow rate of 150 mL/min the percentage rejection for the cobalt was obtained maximum as 99.7% and for the nickel 99.74%. Thus, the flow rate was empirically optimized as 150 mL/min at which maximum rejection for the nickel and cobalt was observed. This flow rate was then used as the standard for the rest of the experiments. The drop in rejection after 150 mL/min flow rate may be attributed to the fact that some of the micelles may get forcibly pumped through the membrane pores along with the monomeric surfactant and unbound metal ions.

#### 3.3. Effect of surfactant to metal ion (S/M) ratio on performance of MEUF

Fig. 4 shows the effect of variation of surfactant to metal ion ratio (S/M) on the rejection of  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  ions. The feed metal ion concentration was 1 mM each of  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$ .

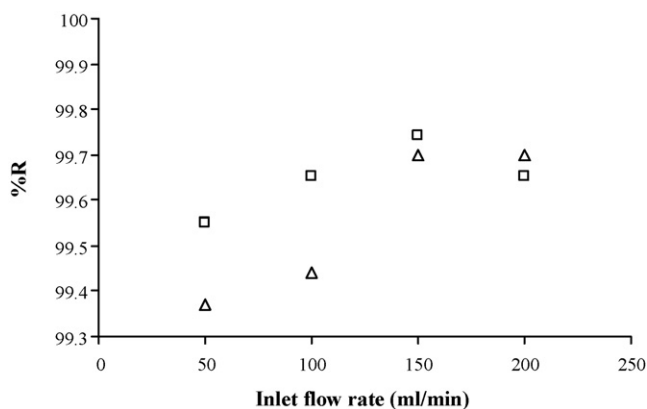


Fig. 3. Effect of inlet flow rate on % rejection of  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$ .  $[\text{Ni}]_F = 1$  mM,  $[\text{Co}]_F = 1$  mM,  $[\text{SDS}]_F = 20$  mM,  $[\text{NaCl}]_F = 0$ ,  $T = 27^\circ\text{C}$ , pH 8,  $V_p/V_f = 0.5$ . ( $\Delta$ ) % Rejection of Co, ( $\square$ ) % rejection of Ni.

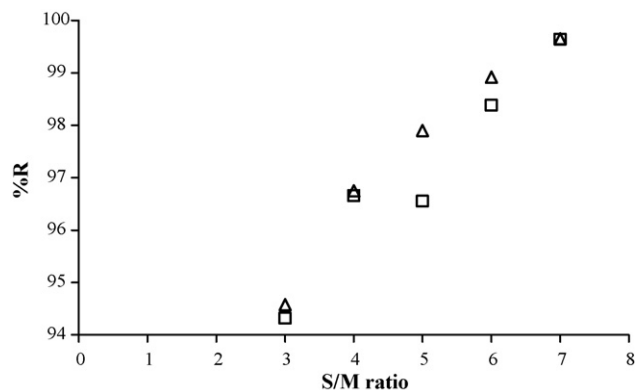


Fig. 4. Effect of  $S/M$  ratio on % rejection of  $Ni^{2+}$  and  $Co^{2+}$ .  $[Ni]_F = 1$  mM,  $[Co]_F = 1$  mM,  $[NaCl]_F = 0$ , inlet flow rate = 150 mL/min,  $T = 27^\circ C$ , pH 8,  $V_p/V_f = 0.8$ . (Δ) % Rejection of Co, (□) % rejection of Ni.

At very low  $S/M$  ratio equal to 3 where SDS concentration was 6 mM which is less than its CMC (8 mM) rejection for  $Ni^{2+}$  and  $Co^{2+}$  was found to be about 94%, which may be explained on the basis that, SDS being a long chain molecule even in monomeric form gets rejected by the membrane due steric hindrance. Many such molecules get accumulated on the membrane surface and concentration of SDS just above membrane increases to a considerably higher value to form the micelles resulting into considerable rejection. Thus, this rejection of 94% can be attributed to steric hindrance and adsorption [7]. The experimental results show that the extent of increase in rejection of  $Ni^{2+}$  and  $Co^{2+}$  beyond  $S/M$  ratio of 5 is less and reaches to a maximum at  $S/M$  equal to 7. This is in agreement with Huang et al. [8].

As the  $S/M$  ratio was increased the rejection also increased. From Fig. 4, the increase in rejection up to  $S/M$  ratio of 5 is more pronounced although it is maximum at 7. Thus, we can conclude that critical  $S/M$  ratio is 5 while the optimal value of  $S/M$  is 7.

In dead end system maximum rejection was obtained at  $S/M$  ratio equal to 10 [6], where as for cross flow system  $S/M$  ratio of 7 gives maximum rejection. This means surfactant requirement is reduced in cross flow continuous ultrafiltration.

### 3.4. Effect of pH

Fig. 5 shows the effect of pH on the rejection of  $Ni^{2+}$  and  $Co^{2+}$  ions in MEUF. The pH of the feed solution was varied from 3 to 10. The rejection of  $Ni^{2+}$  and  $Co^{2+}$  remained nearly constant in a broad pH range between 3 and 10. Compared to the rejection obtained at high pH  $Ni^{2+}$  rejection was found to be decreased by around 1.5% at pH < 4 which is in agreement with results published by Juang et al. [9]. This is because at low pH (pH 3) the concentration of  $H^+$  ions becomes greater than feed  $Ni^{2+}$  and  $Co^{2+}$  concentration (=1 mM); therefore  $Ni^{2+}$  and  $Co^{2+}$  ions now have to compete with  $Na^+$  as well as  $H^+$  ions for their binding with SDS micelles. The  $H^+$  ions being smallest in size among  $Na^+$ ,  $Ni^{2+}$  and  $Co^{2+}$ ,  $H^+$  binds to micelles more selectively. Because of bivalence  $Ni^{2+}$  and  $Co^{2+}$  ions are still strongly adsorbed on micelles. However, because of small size

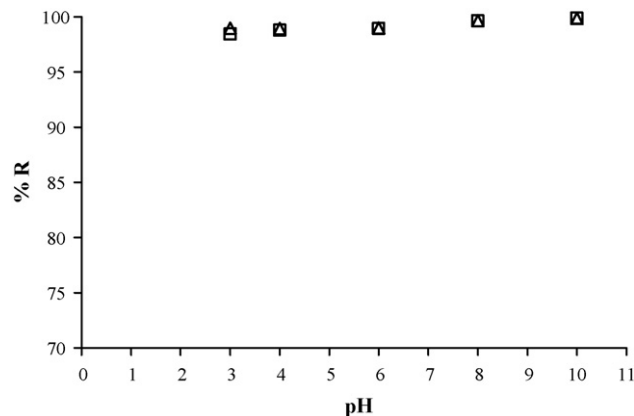


Fig. 5. Effect of pH on % rejection of  $Ni^{2+}$  and  $Co^{2+}$ .  $[Ni]_F = 1$  mM,  $[Co]_F = 1$  mM,  $[SDS]_F = 14$  mM, inlet flow rate = 150 mL/min,  $[NaCl]_F = 0$ ,  $T = 27^\circ C$ ,  $V_p/V_f = 0.8$ . (Δ) % Rejection of Co, (□) % rejection of Ni.

$H^+$  ions compete strongly with  $Ni^{2+}$  and  $Co^{2+}$  to bind to the micelles and this is reflected in the corresponding decrease in rejection [9].

In the present study, pH was empirically optimized at the value of 8 as there is marginal increase in %  $R$  from pH 8 to 10.

### 3.5. Effect of feed metal ion concentration on MEUF

Fig. 6 shows effect of increase in feed concentration of  $Ni^{2+}$  and  $Co^{2+}$  on performance of MEUF (%  $R$ ). In order to explain the behavior of MEUF in present situation, consider a micellar system containing micelles surrounded by a completely dissociated electrolyte  $NiSO_4$  in the form  $Ni^{2+}$  and  $SO_4^{2-}$  and  $CoSO_4$  in the form of  $Co^{2+}$  and  $SO_4^{2-}$ . The local distribution of these ions surrounding the micelles is determined by the relative magnitude of electrical potential energy (given by product of total protonic charge on the ion and electric potential at that point due to micelle) and the kinetic energy of the molecule (given by product of Boltzmann's constant and absolute temperature) and the bulk concentration [10]. Owing to these driving forces and high charge density of the micellar surface the randomly moving  $Ni^{2+}$  and  $Co^{2+}$  ions in the solution are trapped in the

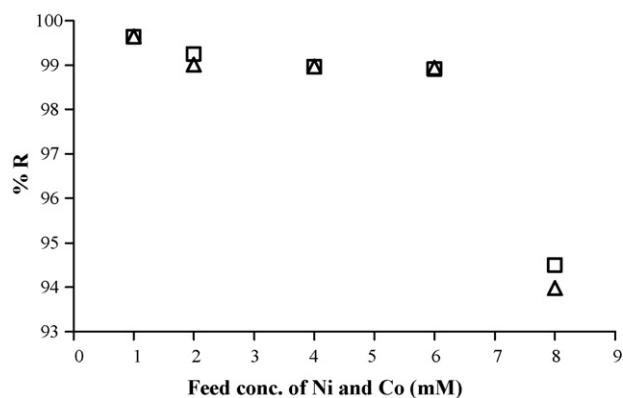


Fig. 6. Effect of feed concentration of  $Ni^{2+}$  and  $Co^{2+}$  on rejection coefficient of  $Ni^{2+}$  and  $Co^{2+}$ .  $S/M = 7$ , pH 8,  $[NaCl]_F = 0$ , inlet flow rate = 150 mL/min,  $T = 27^\circ C$ ,  $V_p/V_f = 0.8$ . (Δ) % Rejection of Co, (□) % rejection of Ni.

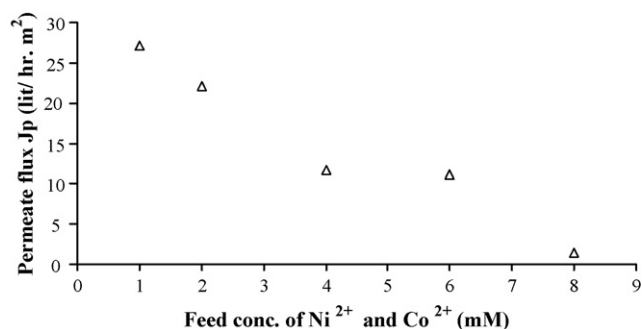
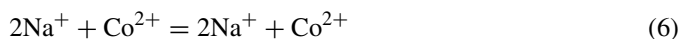
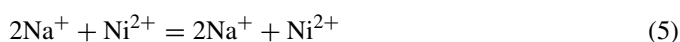


Fig. 7. Variation of permeate flux with feed concentration of Ni<sup>2+</sup> and Co<sup>2+</sup>. S/M=7, pH 8, [NaCl]<sub>F</sub>=0, inlet flow rate = 150 mL/min, T=27 °C, V<sub>p</sub>/V<sub>f</sub>=0.8. (Δ) Permeate flux (L/h m<sup>2</sup>).

electric field of the micelle and get bound to it. These ions are then bound to the micelles to the extent that they move with the micelles and are no longer osmotically active [11]. Now as the magnitude of electrical interaction between micelles and Ni<sup>2+</sup> and Co<sup>2+</sup> ions is dependent on charge as a driving force most of the Ni<sup>2+</sup> and Co<sup>2+</sup> ions displace Na<sup>+</sup> ions from micellar surface (i.e. they undergo selective counterion binding). This effect is quite prominent as can be seen from Fig. 6 that the rejection coefficient over the entire range of concentration (1–6 mM each) of Ni<sup>2+</sup> and Co<sup>2+</sup> was greater than 99%. The ion exchange between Na<sup>+</sup> and Ni<sup>2+</sup> and Co<sup>2+</sup> takes place as per the reaction given in Eqs. (5) and (6), and equilibrium is established between the bound and unbound Ni<sup>2+</sup> and Co<sup>2+</sup> ions.



Subscripts 'm' and 'w' denote ions in bound and unbound state respectively in bulk solution. As the feed concentration increases there is a corresponding increase in the concentration of unbound Ni<sup>2+</sup> and Co<sup>2+</sup> ions and hence, the permeate concentration also increases. At very high concentrations of Ni<sup>2+</sup> and Co<sup>2+</sup> ions in the feed (>6 mM) the rejection considerably drops down to about 94%. Reduction in rejection at higher feed concentration can be attributed to the lack of availability of binding sites. Thus, a multistage MEUF can be employed for high feed concentration to bring down the permeate concentration in the desired range on the similar grounds of staged mass transfer operations.

Since the experiments were carried out keeping S/M ratio constant at 7, as metal ion concentration increased the surfactant concentration also increased. At Ni<sup>2+</sup> and Co<sup>2+</sup> each equal to 8 mM (total metal ion concentration equal to 16 mM) the SDS concentration was 112 mM which is 14 times CMC of SDS. At this high concentration the micellar shape changes from spherical to cylindrical or plate like and thus these can be easily passed through the membrane pores resulting into considerable drop in rejection of the metal ions. The permeate flux was calculated for this experiment and it was drastically decreased to 1.45 L/h m<sup>2</sup> as shown in Fig. 7. This can be attributed to the adsorption of micelles on the membrane and in the pores

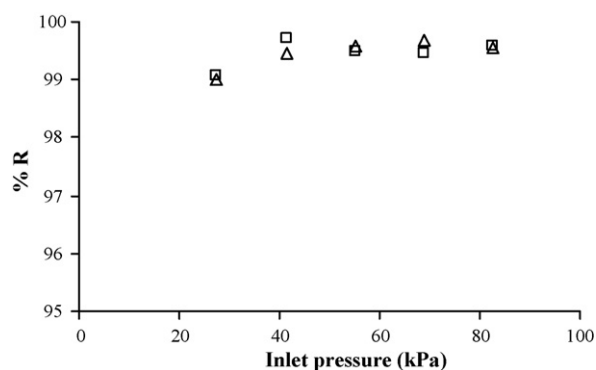


Fig. 8. Effect of inlet pressure on rejection coefficient of Ni<sup>2+</sup> and Co<sup>2+</sup>. [Ni]<sub>F</sub> = 1 mM, [Co]<sub>F</sub> = 1 mM, [SDS]<sub>F</sub> = 14 mM, [NaCl]<sub>F</sub> = 0, pH 8, T = 27 °C, V<sub>p</sub>/V<sub>f</sub> = 0.8. (Δ) % Rejection of Co, (□) % rejection of Ni.

resulting into pore blockage and thus drop in rejection occurs [12,13].

### 3.6. Effect of inlet pressure on performance of MEUF

At standard set of condition such as feed solution 250 mL, [Ni]<sub>F</sub> and [Co]<sub>F</sub> 1 mM each, pH 8, S/M=7. The inlet pressure was varied between 27.58 kPa and 82.76 kPa (4–12 psi). Before each run the membrane was back flushed with deionized water. Then again deionized water was passed through it to check the membrane permeability. For deionized water permeate flux was almost constant.

From Fig. 8, at inlet pressure of 55.15 kPa (8 psi) the maximum rejection for Ni<sup>2+</sup> and Co<sup>2+</sup> was observed. This inlet pressure coincides with inlet pressure at optimum flow rate of 150 mL/min.

The transmembrane pressure in cross flow system proportionally increases as the inlet pressure increases and correspondingly the rejection of both Ni<sup>2+</sup> and Co<sup>2+</sup> ions increases giving more than 99% rejection.

Fig. 9 shows the effect of transmembrane pressure on rejection efficiency. The rejection is almost constant at the range of transmembrane pressure from 100 to 600 kPa. Thus, cross flow MEUF can be carried out at a constant transmembrane pres-

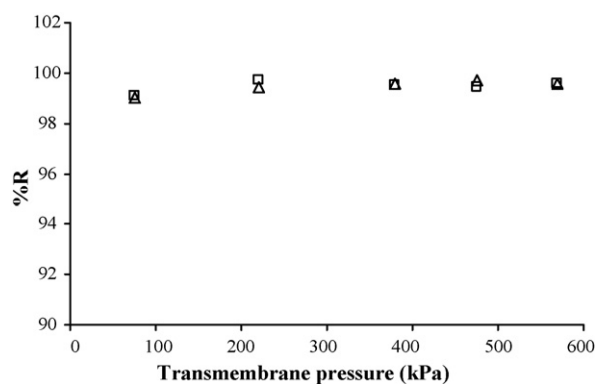


Fig. 9. Effect of transmembrane pressure on % rejection. [Ni]<sub>F</sub> = 1 mM, [Co]<sub>F</sub> = 1 mM, [SDS]<sub>F</sub> = 14 mM, [NaCl]<sub>F</sub> = 0, inlet flow rate = 150 mL/min, pH 8, T = 27 °C, V<sub>p</sub>/V<sub>f</sub> = 0.8. (Δ) % Rejection of Co, (□) % rejection of Ni.



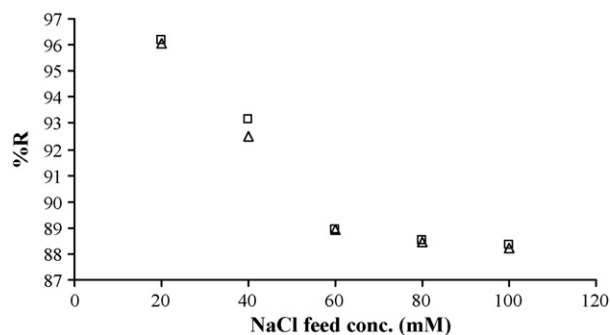


Fig. 10. Effect of feed NaCl concentration on % rejection.  $[\text{Ni}]_F = 1 \text{ mM}$ ,  $[\text{Co}]_F = 1 \text{ mM}$ ,  $[\text{SDS}]_F = 14 \text{ mM}$ , inlet flow rate = 150 mL/min, pH 8,  $T = 27^\circ\text{C}$ ,  $V_p/V_f = 0.8$ . (Δ) % Rejection of Co, (□) % rejection of Ni.

sure as low as 100 kPa. This is in agreement with Xu et al. [15].

### 3.7. Effect of electrolyte on $\text{Ni}^{2+}$ and $\text{Co}^{2+}$ rejection efficiency

The presence of electrolyte can decrease the CMC of ionic surfactants because the electrolyte can weaken the repulsive forces between the head groups, which are normally fighting against the aggregation of surfactant monomers. Therefore, micelles can form comparatively easier in the presence of electrolyte [14,15].

Fig. 10 shows the effect of electrolyte, which is NaCl in this experiment on the  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  rejection efficiency. Salts are used in electroplating and metal finishing industry for making buffer solutions, and hence can be easily found in the wastewater streams coming from these units.

The rejection efficiency decreases with the increase in NaCl concentration from 10 to 100 mM and reaches an unvarying low value of 88%. The result does not comply with what is pointed out in the literatures [14–16]. This may be because of the increase in the concentration of the counter ions due to salt addition the concentration of  $\text{Na}^+$  ions in the stern layer increases and the probability of  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  ions being found in the vicinity of micelles reduces. As the  $\text{Na}^+$  is monovalent ion it can readily bind with the negative charge head of the micelle. Therefore, one can expect rejection coefficient to decrease with increase in the salt concentration. Also, the anions of electrolyte, namely  $\text{Cl}^-$ , can form the complexes with metal ions [15–17]. In this experiment, the two negative effects of the presence of NaCl may exceed the positive effect of the decrease of CMC due to the presence of NaCl [6–15]. However, the rejection efficiency

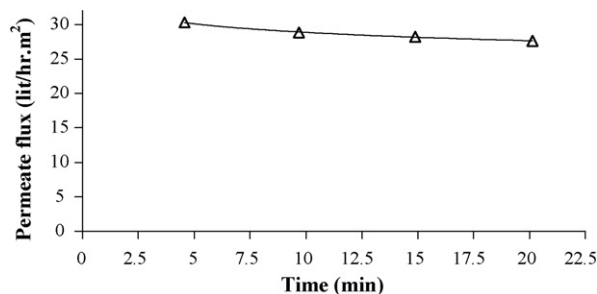


Fig. 11. Effect of operating time on permeate flux.  $[\text{Ni}]_F = 1 \text{ mM}$ ,  $[\text{Co}]_F = 1 \text{ mM}$ ,  $[\text{SDS}]_F = 14 \text{ mM}$ ,  $[\text{NaCl}]_F = 0$ , pH 8,  $T = 27^\circ\text{C}$ ,  $V_p/V_f = 0.8$ . (Δ) Permeate flux ( $\text{L/h m}^2$ ).

as high as up to 88% was found with 100 mM NaCl as shown in Fig. 10.

### 3.8. Dynamic analysis and flux variation in MEUF

At  $[\text{Ni}]_F = 1 \text{ mM}$  and  $[\text{Co}]_F = 1 \text{ mM}$  and standard optimum conditions such as  $S/M = 7$ , pH 8, inlet flow rate = 150 mL/min samples were collected dynamically at different  $V_p/V_f$  ratio and corresponding time was recorded to calculate the permeate flux.

At the beginning of the experiment, deionized water was ultrafiltered at the transmembrane pressure of 47 kPa and the permeate flux was 43  $\text{L/h m}^2$ . Then the effect of operating time on permeate flux was investigated at the fixed SDS,  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  concentration. As shown in Fig. 11, the initial permeation flux is 30  $\text{L/h m}^2$  which is much less than the permeation flux of deionized water. This may be attributed to the adsorption of micelles on the membrane surface and in pores. Table 1 shows the permeate flux in MEUF process. Initially there is some drop in permeate flux and later on it is almost constant. This behavior may be attributed to the concentration polarization, namely SDS micelles deposit on the membrane surface in short time. When the micelle concentration on the membrane surface reaches an adequately high value, the gel layer will form. During the process of concentration polarization, SDS micelles block the membrane pores and cause a resistance to flow, so the permeation flux decreases quickly in the first 10 min in this study. Later on the deposited micelles at the membrane surface do not increase, so the permeation flux reaches a plateau [15].

## 4. Evaluation of MEUF

The performance of MEUF can also be judged from the micelle loading, micelle binding constant and the distribution

Table 1  
Dynamic analysis and flux variation in MEUF at optimum conditions

$V_p/V_f$	Water flux $J_w$ ( $\text{L/h m}^2$ )	Time for collection of sample (min)	Permeate flux $J_p$ ( $\text{L/h m}^2$ )	Normalized flux $J_p/J_w$ ( $\text{L/h m}^2$ )
0.2	42.85714	4.57	30.30303	0.707071
0.4	42.85714	10.9	28.84615	0.673077
0.6	42.85714	15.28	28.21317	0.658307
0.8	42.85714	20.53	27.60736	0.44172

Table 2  
Performance of MEUF for nickel

$V_p/V_f$	Concentration of Ni in permeate $C_p$ (mM)	Concentration of Ni in retentate $C_R$ (mM)	Distribution coefficient ( $D$ )	Loading of micelles ( $L_m$ ) (mol/mol)	Micellar binding constant ( $K_P$ ) (1/mol)	%R for Ni
0.2	0.009786	1.24755	127.48314	0.13173308	13.4613814	99.21
0.4	0.01211	1.66	137.0768	0.11067092	9.1388043	99.25
0.6	0.016513	2.406	145.70339	0.0933521	5.65324889	99.34
0.8	0.017459	4.7955	274.67209	0.08333841	4.77337814	99.64

Table 3  
Performance of MEUF for cobalt

$V_p/V_f$	Concentration of Co in permeate $C_p$ (mM)	Concentration of Co in retentate $C_R$ (mM)	Distribution coefficient ( $D$ )	Loading of micelles ( $L_m$ ) (mol/mol)	Micellar binding constant ( $K_P$ ) (1/mol)	%R for Co
0.2	0.009566	1.247609	130.42113	0.13176272	13.7740663	99.23
0.4	0.011865	1.659526	139.86734	0.11065554	9.32621497	99.27
0.6	0.015393	2.481593	161.21565	0.09634909	6.25927959	99.38
0.8	0.017387	4.948798	284.62633	0.08601348	4.94699963	99.65

coefficient of solutes in micellar phase and aqueous phase obtained from distribution coefficient [18,19].

Micelles of surfactants are dynamic aggregates and they are in equilibrium with individual surfactant molecules, passing through the pores of a membrane. The residence time and micelle lifetime, which characterize an exchange of one surfactant molecule between the micelle and the bulk, and the micelle breakdown are very low, i.e. in the order of  $\mu$ s and ms, respectively, although it is impossible to give general values as these characteristic times depend significantly upon the surfactant type and its hydrophobicity. In the present study, ultrafiltration occurred continuously and 15–30 min were required to filter a volume of 250 mL. Thus, the distribution of the  $Ni^{2+}$  and  $Co^{2+}$  in both the pseudophases (micellar and aqueous) and then in the permeate and retentate was in equilibrium. As a result, the ultrafiltration could be used to estimate the distribution coefficients ( $D$ ) of the  $Ni^{2+}$  and  $Co^{2+}$  between the retentate and permeate, defined as the ratio of  $Ni^{2+}$  and  $Co^{2+}$  concentrations in the retentate  $[Ni^{2+}]_R$  and  $[Co^{2+}]_R$  and the permeate  $[Ni^{2+}]_P$  and  $[Co^{2+}]_P$ , with the volume fraction the distribution coefficient increases considerably but the rejection increases only marginally which means that maximum rejection of the metal ions occurs in the early stage of the ultrafiltration. This shows the dynamism of process with respect to retentate concentration conforming efficiency of separation by MEUF.

The reproducibility of the results can be confirmed from the micelle loading ( $L_m$ ) and micelle binding constant ( $K_P$ ). To calculate these values SDS in retentate was analyzed by two-phase titration method using CTAB.

For Ni

$$L_m = \frac{[Ni^{2+}]_R - [Ni^{2+}]_P}{[S]_R - CMC} \frac{\text{mol}}{\text{mol}} \quad (7)$$

For Co

$$L_m = \frac{[Co^{2+}]_R - [Co^{2+}]_P}{[S]_R - CMC} \frac{\text{mol}}{\text{mol}} \quad (8)$$

The ultrafiltration data enabled the micellar binding constant ( $K_P$ ) to be estimated:

For Ni

$$K_P = \frac{[Ni^{2+}]_M}{([Ni^{2+}]_W S)} \frac{1}{\text{mol}} \quad (9)$$

For Co

$$K_P = \frac{[Co^{2+}]_M}{([Co^{2+}]_W S)} \frac{1}{\text{mol}} \quad (10)$$

where the subscripts M and W denote the micellar and aqueous pseudophases, respectively, and  $S$  is the concentration of the surfactant in the surfactant pseudophase forming micelles. As ultrafiltration continues, values of surfactant will increase and will result in drop in  $K_P$ .

Actually  $[Ni^{2+}]_M = [Ni^{2+}]_R - [Ni^{2+}]_P$ ,  $[Ni^{2+}]_W = [Ni^{2+}]_P$  and  $S = [S]_R - CMC$  and  $[Co^{2+}]_M = [Co^{2+}]_R - [Co^{2+}]_P$ ,  $[Co^{2+}]_W = [Co^{2+}]_P$  and  $S = [S]_R - CMC$ .

From Tables 2 and 3, the values of  $D$  and  $L_m$  confirm that the micelles did not leak and equilibrium between solutes in both the pseudophases at any time of ultrafiltration can be assumed [18,19]. Thus, ultrafiltration can be considered as a research method helpful to characterize micellar solutions. The residence time characterize an exchange of surfactant molecule between the micelle and the bulk. The micelle lifetime is very low of the order of  $\mu$ s. An increase in value of  $D$  indicates that more and more surfactant molecules join the micellar phase, binding more and more metal ions as evidenced from the value of  $C_R$  in Tables 2 and 3.

## 5. Conclusion

Micellar enhanced ultrafiltration (MEUF) was used to remove  $Ni^{2+}$  and  $Co^{2+}$  simultaneously from synthetic wastewater using polysulfone ultrafiltration membrane and SDS as surfactant.

The results show that high rejection of  $Ni^{2+}$  and  $Co^{2+}$  can be obtained above 99% when the inlet flow rate is 150 mL/min and the concentrations of  $Ni^{2+}$  and  $Co^{2+}$  1 mM each. The S/M

ratio was optimized as 7 giving maximum rejection for  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$ . Though the presence of electrolyte decreases the efficiency of MEUF, considerable rejection is obtained even in presence of salt. The micelle loading, micellar binding constant and the distribution coefficient can be evaluated to confirm the reproducibility of the results.

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