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Process Intensification: Extraction of Chromium(VI) by Emulsion Liquid Membrane

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Abstract: Electroplating is one of the important processes involved in surface finishing and metal deposition for better life of articles and for decoration. Chromium(VI) is the most commonly used metal for electroplating. Thus, the waste water of such industries contains Chromium(VI) ions. Emulsion Liquid Membrane (ELM) separation technique provides a potentially powerful technique for the removal of Chromium(VI) ions from the waste water. In the present study, the effect of different parameters such as pH, different carriers concentration, synergistic effect caused by a mixture of two appropriate carriers concentration, effect of electrostatic surface potential and effects of composition of a dilute polymer solution; which will intensify the extraction efficiency of Chromium(VI); are systematically investigated using Aliquat 336 and tri-n-octyl amine as extractant, sorbitan mono-oleate (span 80) as surfactant, kerosene as membrane phase and sodium hydroxide as stripping solution.

Keywords: Emulsion liquid membrane, mass transfer, facilitated transport, chromium(VI) ion extraction

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INTRODUCTION

Electroplating is one of the important processes involved in surface finishing and metal deposition for better life of articles and for decoration. Copper(II), Nickel(II), and Chromium(VI) are the three most commonly used metals for electroplating. There are number of articles available in published literature on individual separation of Copper(II) (1, 2), Nickel(II) (3–5) ions and simultaneous separation of Copper(II) and Nickel(II) from their mixed solutions and from industrial waste water by Emulsion Liquid Membrane (ELM) (6, 7). The ELMs allow faster permeation rates of metals due to a large specific interfacial area. Compared to conventional processes, ELM process has certainly some attractive features, e.g., simple operation, high efficiency, extraction, and stripping in one stage; larger interfacial area, and scope of continuous operation.

In recent years, there has been a considerable interest in treating polluted water generated by industrial processes. Chromium(VI), coming from sulfuric acid baths employed in electroplating industry, as chromic acid is one of the most toxic elements to be discharged to the environment. The economic recovery and concentration of chromium from waste water is important, both for the hydrosphere and to ensure safe environment. The development of amine reagents in the early 1960s allowed the application of solvent extraction procedure for the removal of chromate anion from the aqueous solutions. Further development in extraction process followed with the discovery of ELM by Li (8). Emulsion liquid membranes are formed by first making an emulsion of two immiscible phases and then dispersing the emulsion in third phase. The resulting emulsion system can be either water/oil/water (W/O/W) or oil/water/oil (O/W/O) type. The liquid membrane phase is that which separates the encapsulated drops in the emulsion from the external continuous phase. Emulsion liquid membranes have also been applied to a variety of separations including the removal of contaminants from waste water; fractionation of hydrocarbons; in biochemical and biomedical fields; and recovery and purification of metal ions. Several preliminary results of the separation concentration of hexavalent chromium, Chromium(VI), with ELMs have been reported in the literature. Hochhauser and Cussler (9) studied the separation-concentration of Chromium(VI) from aqueous solution with ELMs containing tertiary amine as extractant and SPAN-80 as surfactant. Fuller and Li (10) analyzed the extraction of Chromium(VI) and Zinc(II) from cooling tower effluents by ELMs containing a polyamine as surfactant, Aliquat 336 as extractant and nonyl-decyl alcohols for the solublization of the complex in the solvent phase. Mori et al. (11) used an ELM containing tri-n-octyl amine as extractant, SPAN-80 or ECA-4360 as surfactant, and LiOH as the stripping reagent in the recovery and concentration of Chromium(VI) from aqueous sulfuric acid solutions. Salazer et al. (12, 13) have investigated the influence of the membrane composition and of the surfactant on the recovery of the Chromium(VI). Bhowal and Datta (14) studied the extraction of Chromium(VI) from aqueous acidic solution by emulsion liquid membrane using Aliquat 336 as extractant and NaOH as stripping agent and developed a mathematical model which accounted for the existence of different forms of Chromium(VI) ions in the aqueous phase depending on pH conditions. Banerjea et al. (15) also studied the batch extraction of Chromium(VI) ions from aqueous solution by ELMs using Aliquat 336 as extractant and NaOH as stripping agent and developed model based on advancing reaction front model. All important variables affecting the ELM process; including feed phase acid concentration, Chromium(VI) concentration in feed phase, carrier concentration, surfactant concentration, volume ratio of emulsion to aqueous feed phase and internal strip acid concentration are systematically investigated by them.

The extraction efficiency of Chromium(VI) is also dependent on a few other parameters. In the present study, attempts have been made to investigate the effect of a few other parameters such as pH, different carriers concentration, synergistic effect caused by a mixture of two appropriate carriers concentration, effect of electrostatic surface potential, and effects of composition of a dilute polymer solution on the extraction efficiency of Chromium(VI). In view of this, application of this technique is investigated for removal of Chromium(VI), from aqueous solution using Aliquat 336 and tri-n-octyl amine as extractant, sorbitan mono-oleate (Span 80) as surfactant, kerosene as membrane phase, and sodium hydroxide as stripping solution.

Experimental Procedure

Chemicals

Summary of experimental conditions for ELMs batch tests are given in Table 1. For the study of transport of Chromium(VI) ions through emulsion liquid membrane, potassium dichromate (99.99% pure, Merck make) salt is used. Commercial kerosene of specific gravity 0.798 and boiling point range between 145 to 250°C is used as a membrane phase. The extractant used is Aliquat 336 and tri-n-octyl amine having 98.5% purity, Span 80 (sorbitan mono-oleate containing O_2 based moleties) as surfactant; n-heptane as a diluent and stabilizer for the membrane phase. Prior to the extraction reaction, the extractant (Aliquat 336), which is commercially available in chloride form, was converted to the hydroxide form. Sodium dodecyl sulphate (BDH, England) and (n-dodecyl) trimethylammonium chloride (97% pure, Lancaster, England) was used as anionic and cationic surfactant. The polymer used was styrene/butadiene block copolymer (MW $\approx$ 140, 000, 30% styrene, Scientific Polymer Co.).

Method

Emulsion is prepared by emulsifying aqueous solution of acid (strip phase) with an organic phase (membrane phase). The membrane consists of fixed

Table 1. Summary of experimental conditions for ELMs batch tests

Membrane phase (O):	
Volume	25 mL
Carrier(aliquat 336 and tri-n-octylamine)	10% V/V
Diluent (n-heptane)	5%,V/V
Surfactant Span 80	5%,V/V
Kerosene	80%.V/V
Exterior phase (W):	
Volume	400–800 mL
Cr(VI)	100 ppm
pH	1–12
Interior phase (W):	
Volume	25 mL
Base conc.	1 N (NaOH)

For preparation of aqueous solutions double distilled water has been used.

proportions of surfactant Span 80, diluent (n-heptane) and varying proportions of carriers. The mixer is stirred at 5000 rpm for 15 min using a homogenizer (six-blade turbine impeller of 30 mm diameter) to form a uniform mixture and then the internal strip phase is added. The contents are again stirred at 5000 rpm for 15 min. An excellent milky-white and stable emulsion is obtained. The emulsion is dispersed in feed phase containing Chromium(VI) ions from which chromium is to be extracted. A six-blade paddle impeller of 50 mm diameter rotating at 400 rpm is used for stirring. For measuring speed of the agitator and homozeniser a hand tachometer having a range of 0–10000 rpm has been used. Samples of about 5 mL are withdrawn from the extractor at different intervals of time and are filtered through a sintered glass plug to separate emulsion and aqueous feed phase.

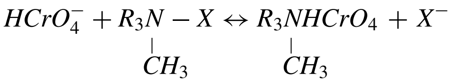
Analysis

Samples of aqueous phase, containing Chromium(VI), have been analyzed by a spectrophotometer (CE1020, 1000 series manufactured by CECIL, England) according to the standard methods (16).

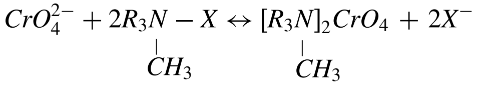
Results and Discussion

Mechanism of Chromium(VI) Extraction Process Using ELM

The equations given next show the extraction and stripping reactions of Chromium(VI) occurring in ELM process. The extraction reactions of monovalent $HCrO_4^-$ and divalent CrO_4^{2-} with quaternary amine Aliquat 336 (methyl tricaprylyl ammonium chloride) are as follows (15):



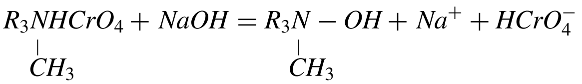
$$HCrO_4^- + \underset{\overset{|}{CH_3}}{R_3N} - X \leftrightarrow \underset{\overset{|}{CH_3}}{R_3NHCrO_4} + X^- \tag{1}$$



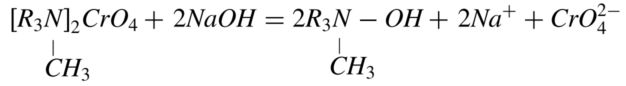
$$CrO_4^{2-} + 2\underset{\overset{|}{CH_3}}{R_3N} - X \leftrightarrow \underset{\overset{|}{CH_3}}{[R_3N]_2CrO_4} + 2X^- \tag{2}$$

where $R = (CH_2)_6CH_3$ and $X = Cl$ or OH

The complex formed in Eqs. (1) and (2) breaks down by reaction with NaOH:



$$\underset{\overset{|}{CH_3}}{R_3NHCrO_4} + NaOH = \underset{\overset{|}{CH_3}}{R_3N} - OH + Na^+ + HCrO_4^- \tag{3}$$



$$\underset{\overset{|}{CH_3}}{[R_3N]_2CrO_4} + 2NaOH = 2\underset{\overset{|}{CH_3}}{R_3N} - OH + 2Na^+ + CrO_4^{2-} \tag{4}$$

Equations (1) and (2) represent the complexation reaction, which occurs at the membrane-external phase interface, whereas Eqs. (3) and (4) show stripping reaction at the membrane-internal aqueous phase interface.

RESULTS AND DISCUSSION

Effect of pH

The effect of external phase pH on extraction of Chromium is shown in Fig. 1. It can be seen from Fig. 1 that if pH in the external phase is kept low, then the extraction will be faster and high in percentage. The chromate ion may exist in aqueous phase in different ionic forms ($HCrO_4^-$, CrO_4^{2-}, $Cr_2O_7^{2-}$, $HCr_2O_7^-$). The total amount of chromium and pH will dictate that particular chromium species of the above said ions will be predominant in the aqueous phase. CrO_4^{2-} anion prevails in basic or slightly acidic solution, while $Cr_2O_7^{2-}$ anions dominate in acidic Chromium(VI) aqueous solution. Moreover, $Cr_2O_7^{2-}$ convert into $HCrO_4^-$ anions in acidic aqueous solution at a lower Chromium(VI) concentration. Strzelbicki et al. (17) reported that the distribution coefficient decreases sharply when the equilibrium pH exceeds 6 for the extraction of Chromium(VI) oxyanions with Aliquat 336. This is because the quaternary ammonium salts exhibit reasonable extraction abilities only toward monovalent oxyanions, i.e., $HCrO_4^-$, while CrO_4^{2-} is the dominant species at that pH. This anion is predominant only at low pH and hence the faster depletion of solute occurs if the external phase is acidic.

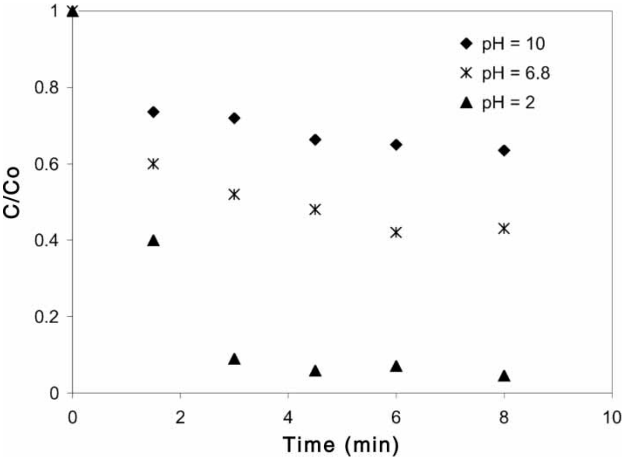


Figure 1. Effect of external phase pH on extraction of chromium.

Effect of Carriers and Carrier Concentration

The experimental observations on the variation of external phase chromium ion concentration with different types of carriers we shown in Fig. 2. It shows the degree of Chromium(VI) extraction as a function of time in acidic pH with the extractants Aliquat 336, tri-n-octyl amine, and their mixtures. Furthermore, a slight synergistic effect was observed when the

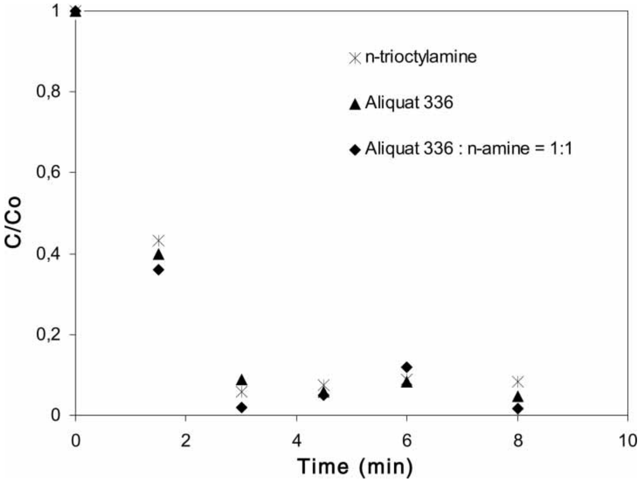


Figure 2. Variation of external phase chromium ion concentration with different types of carriers.

two extractants were mixed. Coordinating the two extractants formed a highly extractable complex. The degree of Chromium(VI) extraction vs. the ratio of extractant mixtures of Aliquat 336 to tri-n-octyl amine at acidic pH of 2.0 is shown in Fig. 3. The mixture of Aliquat 336 and tri-n-octyl amine shows a slight synergistic effect than that of individual carrier. Synergistic extraction may be attributed due to the formation of a mixed ligand complex. As shown in Fig. 3, when the concentration ratio of the two extractants approaches are close to 1.0, a maximum extraction percentage was obtained.

Effect of Electrostatic Surface Potential on Chromium(VI) Extraction

It has been found from the literature that the reaction at the interface between the external aqueous phase and the W/O emulsion drops are rate determining when internal phase acid or base concentration is considerably high. Therefore, under this condition the rate of the extraction may be increased by increasing the rate of the interfacial reaction. The aim of this study was to study the effects of the electrostatic surface potential on Chromium(VI) extraction interfacial reaction. Cationic surfactant (n-dodecyl) trimethylammonium chloride (DTAC) and anionic surfactant sodium dodecyl sulphate (SDS) was added to the membrane phase of the emulsion. The effect of adding charged surfactants (5 wt%) to the system is shown in Fig. 4.

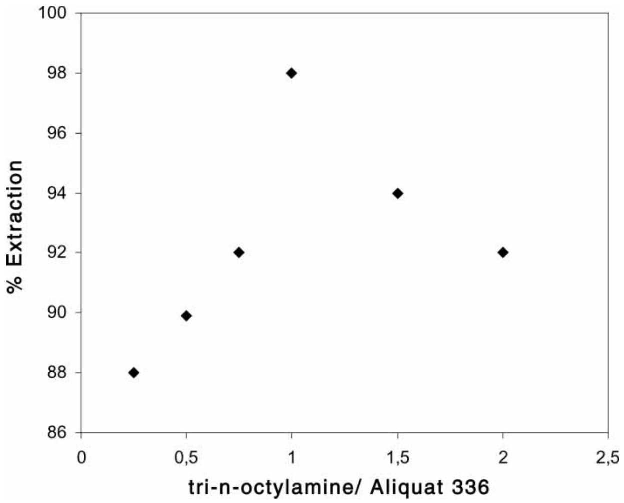


Figure 3. Effect of the mixed ratio of tri-n-octylamine and aliquat 336 on chromium extraction.

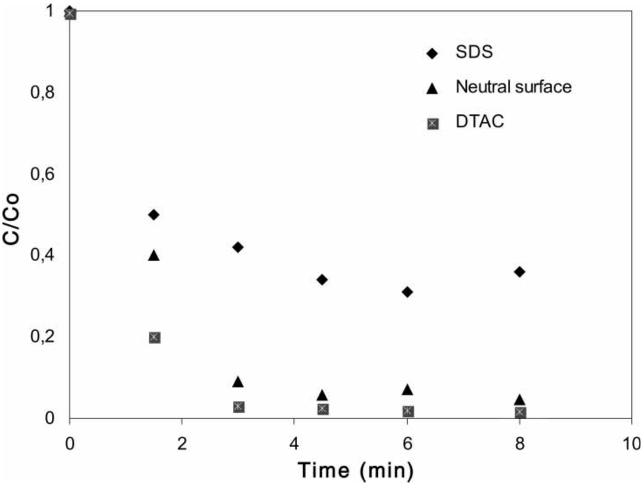


Figure 4. Effect of SDS and DTAC concentration on chromium extraction.

The addition of DTAC induces positive surface potential, while SDS induces negative surface potential. The effect of introducing a positive and negative charge to the micelle interface on the extraction of copper(II) by 1-phenylbutane-1,3-dione has been previously observed by Miyake et al. (18). This electrostatic surface potential induces a local change in the aqueous concentrations of charged species close to the surface. It has been observed that in the presence of cationic surfactant DTAC, complete removal of Chromium(VI) is possible at a faster rate. At acidic pH of 2, $HCrO_4^-$ and CrO_4^{2-} are the dominant species. The positively charged interface attracts all those anionic species by electrostatic force, resulting in a much higher Chromium(VI) concentration at the interface than in the bulk liquid. The rate of extraction was remarkably enhanced by the addition of a very small amount of DTAC. From Fig. 5, it has been observed that the extraction reaction kinetics will be altered according to the change in DTAC concentration (Cs).

Extraction Efficiencies of Chromium(VI) with Dilute Polymer Solutions

Stevens et al. (19) investigated the extraction of chromium in ELM systems. The membrane phase was a concentrated polymer solution prepared by dissolving polyisobutylene and polybutene in kerosene. From the viewpoint of membrane breakage, they showed that a polymer-stabilized membrane was more stable than surfactant-stabilized membranes. Unfortunately, they overlooked the very low extraction rate of chromium in the ELM system with

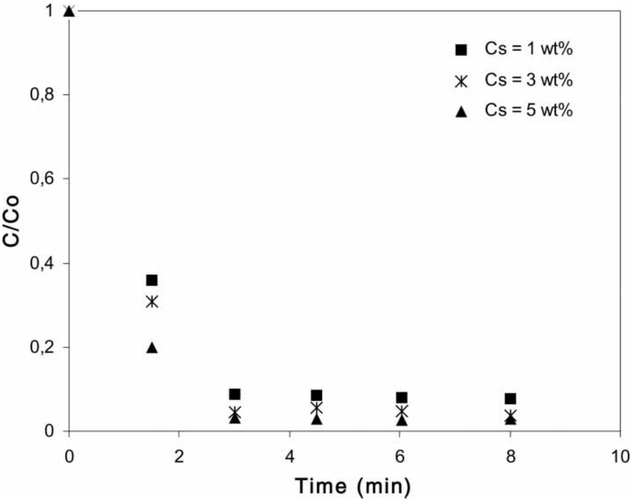


Figure 5. Effect of variation of DTAC concentration on chromium extraction.

the polymer-stabilized membrane of a high polymer concentration. S.C. Lee (20) used a dilute polymer solution as the organic membrane phase to improve emulsion stability during extraction of penicillin G in emulsion liquid membrane (ELM) systems. Simultaneously, he studied emulsion swelling and membrane breakage in order to analyze the ELM system. It was observed that use of the dilute polymer solution resulted in an increase in enrichment ratio of penicillin G concentration due to improvement of emulsion stability, independent of the w/o ratio. Following the work of S.C. Lee (20), in this study a dilute polymer solution as the organic membrane phase was used to improve emulsion stability during extraction of Chromium(VI) in ELM systems, and the effects of composition of a dilute polymer solution on the extraction efficiency of Chromium(VI) in ELM systems have been investigated.

The effects of concentration of the polymer in the membrane phase on the degree of extraction of Chromium(VI) at three different treat ratios; viz. 1:8, 1:12, 1:16; are shown through Figs. 6 to 8, respectively. It has been observed that the similar extraction behavior occurred, independent of the treat ratio. It has been observed that the initial degree of extraction of Chromium(VI) decreased with the increase in the polymer concentration, and there were no big differences between the degrees of extraction at the polymer concentrations 0.5 wt% and 1 wt% and when the polymer concentration is more than 1 wt%, the degree of extraction will be lowered. The higher viscosity in a higher polymer concentration produced a lower mass transfer rate due to higher thickness of the membrane phase, thereby resulting in lower degree of extraction.

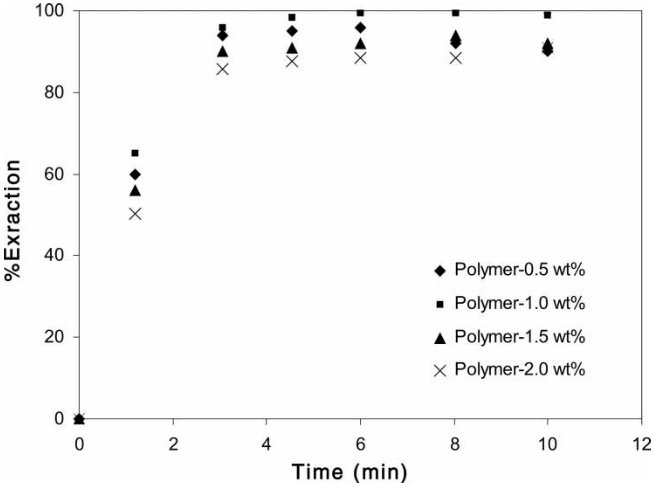


Figure 6. Effect of polymer concentration on degree of chromium extraction at the treat ratio 1:8.

CONCLUSION

Emulsion liquid membranes are a boon to process industry. Using ELM technique heavy metal ions, acid-base and hydrocarbons can easily be removed from waste water. The removal of Chromium(VI) from its dilute aqueous solution through ELM is studied with respect to various parameters

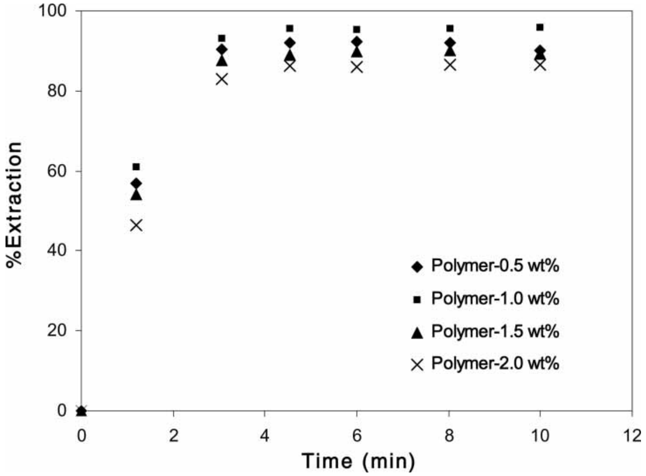


Figure 7. Effect of polymer concentration on degree of chromium extraction at the treat ratio 1:12.

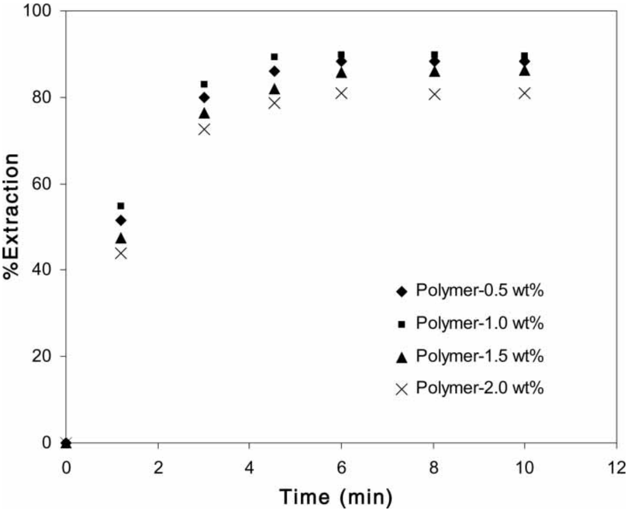


Figure 8. Effect of polymer concentration on degree of chromium extraction at the treat ratio 1:16.

using different carriers. Here, the diffusion of the complex in the membrane phase, the extraction and stripping reactions between Chromium(VI) ion and carrier molecule, and the reaction of Chromium(VI) with the sodium ion in the internal phase to yield Sodium Chromate and dichromate incapable of permeating through the membrane phase are taken into account. The important factor for getting maximum recovery of metal ions is the use of optimized quantity of carrier, ionic surfactant, treat ratio, and polymer concentration.

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