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Extraction of Chromium(VI) From Aqueus Solution by Liquid Surfactant Membrane

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The extraction of chromium(VI) through a liquid surfactant membrane with tri-butylphosphate and tri-octylphinoxide dissolved in dodecane considered as a carrier, was investigated. Tri-ethanolamine was used as inner phase reagent. The effects of the reaction time, pH of external phase, the concentration of extractant in the organic phase, the inner phase concentration and the Cr(VI) concentration in aqueous solution were also investigated. The extraction of Cr(VI) increases with the increase of external phase pH. This study has revealed that there exists an optimal range of tri-octylphinoxide concentrations added to tri-butylphosphate in the membrane phase where a maximum metal extraction can be achieved. The complexes $H_2CrO_4(TBP)_2$ and $H_2CrO_4(TOPO)_2$ formed in the membrane phase are proposed to describe the transport of Cr(VI); the interfacial interaction organic phase-inner phase including the equilibria among $H_2CrO_4(TBP)_2$, $H_2CrO_4(TOPO)_2$, OH^-, $(CrO_4^{2-})_{aq}$, $2(TOPO)_{org}$, $2(TBP)_{org}$ and H_2O are proposed to describe the striping of Cr(VI).

Key Words: Chromium(VI), Membrane liquid; wastewater.

INTRODUCTION

Due to its corrosive resistance and special properties of high resistance alloys, chromium has been widely usd in the electrodeposition process; it is highly toxic so that it has to be removed from wastewater before draining it into water surface[1].

In nature, chromium exists in two main valencics, namely, Cr(III) and Cr(VI). The toxic effects of these two elements are well known[2]. Hexavalent chromium is more toxic than trivalent form; the former exists in aqueous phase in different ionic forms with total chromate concentration and depending on the pH[3] as shown in Fig. 1.

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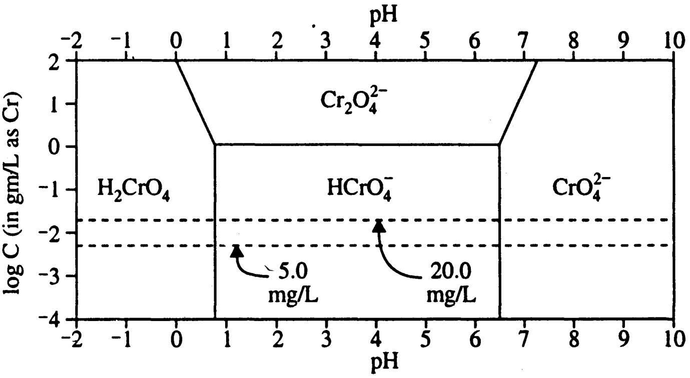

Fig. 1. Schematic representation of total chromate and dichromate

Liquid membranes containing extractants have been used for the concentration and separation of metal ions; this simultaneous extraction and stripping operation is very attractive because metal ions can move from low to high concentration regions[4]. The separation of Cr(VI) from wastewater is known to be efficient by using organophosphorus neutral esters as carriers[1, 5]. In fact, the fraction of various forms of Cr(VI) in the aqueous phase varies with the concentration of the solution pH.

It is worth noticing that the diffusivities of various forms of Cr(VI) are different from each other. In the present work, the liquid surfactant membrane (LSM) technique has been applied to investigate the extraction mechanism, the influence of various parameters affecting extraction and the addition of tri-octyl phinoxide (TOPO) as second carrier in the membrane with tri-butyl phosphate (TBP) as the main extractant.

EXPERIMENTAL

Chromium solution of potassium dichromate (feed) was prepared by dissolving a known amount of this chemical in water (98% purity purchased from Prolabo, France) for extraction using LSM technique; the treated solution was diluted to a given extent.

Emulsion preparation

The emulsions used for metal extraction were prepared with triethanolamine (TEA) as a stripping solution with the concentration ranging from 0.12–0.5 M and organic phase (membrane). The membrane consists of a paraffin solvent dodecane (99% purity, Prolabo, France); two extractants were used, namely, tri-butylphosphate (TBP) (98% purity, Aldrich) and tri-octylphosphineoxyde (TOPO), Prolabo, France, a non-anionic surfactant Span 80 (sorbitan mono-oleate). This mixture was homogenized using a high-speed stirrer (type Kjank and Kunkel T.8, Germany) for 5 min as the total mixing time and controlled to a 6000-rmp-rotation speed[6].

Permeation experiments

Emulsion prepared was dispersed in the feed solution ($K_2Cr_2O_7$). NaOH (99% purity product, Merck) and H_2SO_4 (96% purity, Cheminova) were used to adjust the pH of the feed phase. The agitation procedure was performed by a Kjank and Kunkel RW20, Germany type stirrer at 250 rpm rotation speed. At the end of extraction, the loaded emulsion phase separates from the raffinate phase. The separation of phase was effected 10 min after ending the agitation.

Analyses

The analyses of metal ions Cr(VI) in the raffinate were performed on a UV-Visible spectrophotometer (Shimadzu, Japan).

RESULTS AND DISCUSSION

Some results of Cr(VI) permeation with TBP and TOPO as carriers were obtained in a previous work[1, 5]. Using the LSM method, it was reported that the TEA as a stripping solution has been stable and can be used for rich solution in Cr(VI) content[5]. The concentration of Span 80 in the organic phase should be between 5 and 6% in order to achieve good recovery of cations (good stability of emulsion) and a rapid demulsification. A high concentration of surfactant in membrane increases the transport resistance of Cr(VI) across the membrane[7]. Thus, it was decided to carry out a first set of experiments with the operating concentrations (Table-1).

TABLE-1
OPERATING CONDITIONS FOR METALS EXTRACTION

1. Emulsion:	
(a) Membrane composition (mass%)	
TBP	3–8
Span 80	5
TOPO	1.5–3
Dodecane	rest
(b) Internal phase composition TEA	0.12–0.5
(c) Stirring speed (emulsion preparation)	6000 rpm
(d) Total stirring time	5 min
(e) Phase ratio (emulsion volume)/(inner phase volume)	3
2. Metal extraction:	
(a) Mixing speed	250 rpm
(b) Phase ratio (feed volume)/(emulsion volume)	10
(c) Temperature	25°C
(d) Feed volume	100 mL
(e) Feed acidity (pH)	1.5–8
(f) Cr(VI) concentration	100 rpm

The effect of TBP concentration in organic phase

The effect of TBP concentration (carrier) in the organic phase on the recovery of Cr(VI) is shown in Fig. 2. It can be seen that an increase in extractant concentration leads to a better extraction due to the increase of the ratio [TBP]/[Cr(VI)]. An increase in TBP concentration beyond 8% by mass in membrane decreases the rate of Cr(VI) recovery. This is attributed to the instability of the emulsion. For 8% by mass of TBP concentrations in the membrane, the rate of extraction has been found to be equal to 83%. The obtained experimental values for the rate of Cr(VI) recovery as a function of the TBP concentration are presented in Table-2.

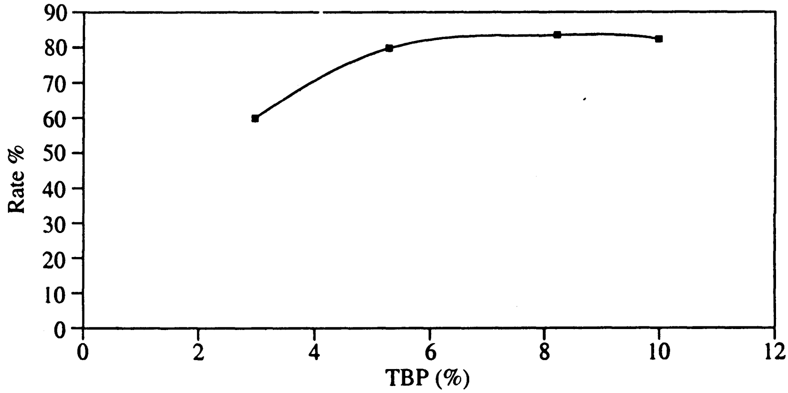

Fig. 2. Effect of TBP on the extraction of Cr(VI)

TABLE-2
RESULTS FOR THE RATE OF Cr(VI) RECOVERY AS A FUNCTION OF TBP CONCENTRATION

TBP (%)	3	5	8	10
Rate (%)	60.03	77.20	83.2	82.12

The effect of TOPO concentration

The model presented above with maintaining the TBP concentration in the membrane at 8% by mass is used to study the effect of TOPO as a second carrier. The addition of TOPO to the membrane phase is aimed to enhance the rate of metal extraction *via* the so-called synergism[8]. The results of the extraction of Cr(VI) by TBP and TOPO are listed in Tables 3a–3d and their illustrations are shown in Fig. 3.

TABLE-3a
RESULTS FOR THE RATE VARIATION AS A FUNCTION OF CONTACT TIME, WITH 8% OF TBP AND 0% OF TOPO

t (min)	0	2	4	6	8	10
Rate (%)	0	83.81	76.87	82.12	82.12	78.55

TABLE-3b
RESULTS FOR THE RATE VARATION AS A FUNCTION OF CONTACT TIME, WITH 8% OF TBP AND 1.5% OF TOPO

t (min)	0	2	4	6	8	10
Rate (%)	0	85.91	84.02	96.8	94.43	70.77

TABLE-3c
RESULTS FOR THE RATE VARIATION AS A FUNCTION OF CONTACT TIME, WITH 8% OF TBP AND 3% OF TOPO

t (min)	0	2	4	6	8	10
Rate (%)	0	82.75	74.34	75.82	69.51	72.45

TABLE-3d
RESULTS FOR THE RATE VARIATION AS A FUNCTION OF CONTACT TIME, WITH 8% OF TBP AND 5% OF TOPO

t (min)	0	2	4	6	8	10
Rate (%)	0	87.13	80.06	73.10	69.77	63.14

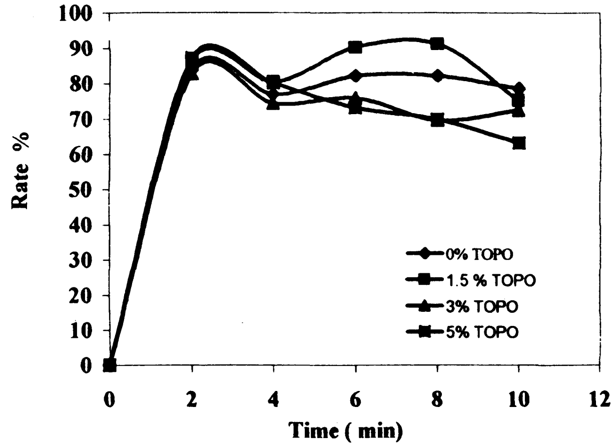

Fig. 3. Effect of TOPO on the extraction of Cr(VI)

The extraction of Cr(VI) increases with increasing TOPO concentration ranging from 1.5–3% by mass however, a further increase of TOPO concentration beyond 3% by mass decreases the extraction of Cr(VI). It was found that when the concentration of the neutral ester in the membrane phase exceeds a certain limit, the emulsion stability is likely to be affected[9]. The optimal concentration of TOPO that gives a maximum rate of extraction of 97% is fixed to a value of 1.5% by mass in the membrane.

Effect of TEA concentration

Experiments were carried out using emulsions of 0.12, 0.24 and 0.5 M of amine solution concentration and the obtained permeation rate of this experiment is shown in Fig. 4 with results listed in Tables 4a–c. It can be seen from this figure that an increase in stripping phase concentration leads to a better extraction. This fact is attributed to the capacity of stripping phase (TEA solution) to dissociate the complexes: Cr(VI)-TBP and Cr(VI)-TOPO in the interface membrane-receiving phase.

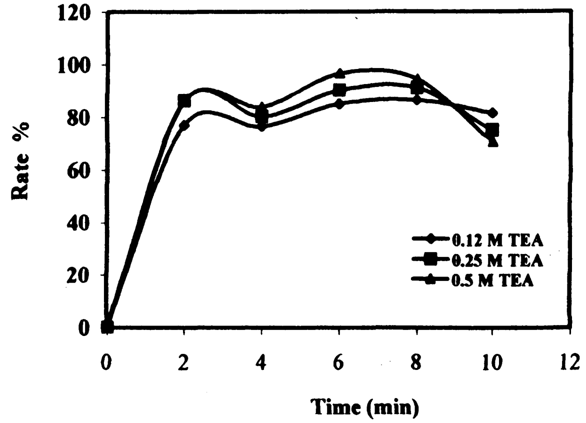

Fig. 4. Effect of TEA on the extraction of Cr(VI)

TABLE-4a
RESULTS FOR THE RATE VARIATION AS A FUNCTION OF CONTACT TIME, WITH INTERNAL PHASE CONCENTRATION OF [TEA] = 0.12 mol/L

t (min)	0	2	4	6	8	10
Rate (%)	0	77.12	76.53	85.17	86.63	81.70

TABLE-4b
RESULTS FOR THE RATE VARIATION AS A FUNCTION OF CONTACT TIME, WITH INTERNAL PHASE CONCENTRATION OF [TEA] = 0.24 mol/L

t (min)	0	2	4	6	8	10
Rate (%)	0	86.3	80.41	90.23	91.19	75.17

TABLE-4c
RESULTS FOR THE RATE VARIATION AS A FUNCTION OF CONTACT TIME, WITH INTERNAL PHASE CONCENTRATION OF [TEA] = 0.50 mol/L

t (min)	0	2	4	6	8	10
Rate (%)	0	85.91	84.02	96.60	94.43	70.77

It is, therefore, possible to write the following stripping mechanism as follows:

$$[H_2CrO_4(TBP)_2] + 2(OH^-)_{in} \longrightarrow (CrO_4^{-2})_{in} + 2(TBP)_{org} + H_2O$$

$$[H_2CrO_4(TOPO)_2 + 2(OH^-)_{in} \longrightarrow (CrO_4^{-2})_{in} + 2(TOPO)_{org} + H_2O$$

On the other hand, when the concentration of TEA is greater than 0.5 M, the degree of Cr(VI) extraction was affected by the so called swelling phenomena which result from the transport of water from the feed phase into emulsion.

The increase in the emulsion volume may give rise to significant changes in the globules and internal phase droplet sizes as well as their distribution, thus, affecting the rate of solute extraction[10]. In this case, inner phase (TEA) pH > pKa is necessary to dissociate the formed complexes: Cr(VI)-TBP and Cr(VI)-TOPO.

Effect of pH value of the feed phase

The experimental results of the rate of extraction variation with contact time are listed in Tables 5a–d; these experimetnal values are presented in Fig. 5, which illustrates the effect of pH value of feed solution on the permeation rates. It is clear from Fig. 5 that when the pH value present in the feed solution is equal to 8, the extraction rate reaches a maximum 97%. Thus all the dichromate ions present initially in the feed solution were converted to chromate ions (Fig. 1).

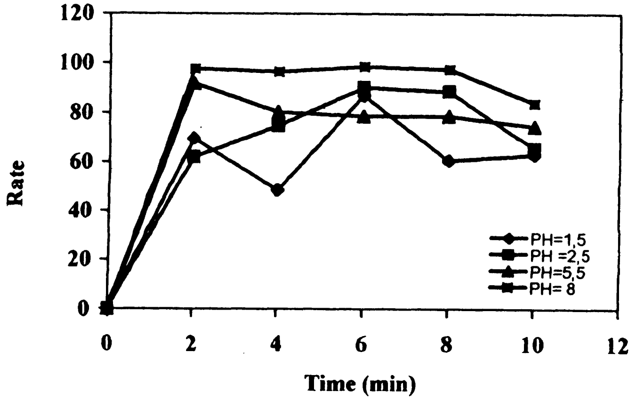

Fig. 5. Effect of pH in the feed phase on the extraction of Cr(VI)

TABLE-5a

RESULTS FOR THE RATE VARIATION AS A FUNCTION OF CONTACT TIME, WITH AN EXTERNAL PHASE pH = 1.5

t (min)	0	2	4	6	8	10
Rate (%)	0	69.60	48.56	87.08	60.75	63.20

TABLE-5b

RESULTS FOR THE RATE VARIATION AS A FUNCTION OF CONTACT TIME, WITH AN EXTERNAL PHASE pH = 2.5

t (min)	0	2	4	6	8	10
Rate (%)	0	62.16	74.77	90.25	88.74	65.69

TABLE-5c
RESULTS FOR THE RATE VARIATION AS A FUNCTION OF CONTACT TIME, WITH AN EXTERNAL PHASE pH = 5.5

t (min)	0	2	4	6	8	10
Rate (%)	0	91.76	80.32	78.81	78.82	74.63

TABLE-5d
RESULTS FOR THE RATE VARIATION AS A FUNCTION OF CONTACT TIME, WITH AN EXTERNAL PHASE pH = 8

t (min)	0	2	4	6	8	10
Rate (%)	0	97.64	96.49	98.65	97.47	83.88

It is well known that the fraction of $Cr_2O_7^{2-}$ is the predomimant form of Cr(VI) in solution; from a practical point of view the diffusivity of CrO_4^{2-} from feed phase through the membrane is larger than that of $Cr_2O_7^{2-}$ at low pH; this is due to the fact that the mass of CrO_4^{2-} is greater than that of $Cr_2O_7^{2-}$.

Effects of Cr(VI) concentration in the feed phase

Generally speaking, the permeation process is controlled by the diffusion of solute through the membrane phase, mass transfer through the external phase and the chemical reaction between the solute and the membrane phase[11]. The experimental values of the rate variation with contact time (Tables 6a–c) are illustrated in Fig. 6, which shows the effect of concentration of Cr(VI) in the aqueous feed solution on the permeation rate. It is clear that an increase in Cr(VI) concentration decreases the extraction rate; this is due to the ratio [extractant]/[Cr(VI)] decrease, so that the mass transfer of Cr(VI) through the external phase and the chemical reaction between Cr(VI) and the membrane phase may govern the permeation process.

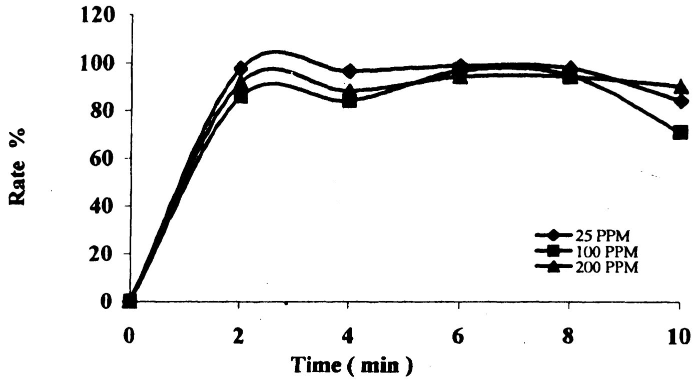

Fig. 6. Effect of Cr(VI) concentration in the feed phase on the extraction of Cr(VI)

TABLE-6a
RESULTS FOR THE RATE VARIATION AS A FUNCTION OF CONTACT TIME, WITH A CONCENTRATION OF [Cr(VI)] = 200 ppm IN THE FEED PHASE

t (min)	0	2	4	6	8	10
Rate (%)	0	91.91	88.24	94.19	93.96	90.08

TABLE-6b
RESULTS FOR THE RATE VARIATION AS A FUNCTION OF CONTACT TIME, WITH A CONCENTRATION OF [Cr(VI)] = 100 ppm IN THE FEED PHASE

t (min)	0	2	4	6	8	10
Rate (%)	0	85.91	84.02	96.6	94.43	70.77

TABLE-6.c
RESULTS FOR THE RATE VARIATION AS A FUNCTION OF CONTACT TIME, WITH A CONCENTRATION OF [Cr(VI)] = 25 ppm IN THE FEED PHASE

t (min)	0	2	4	6	8	10
Rate (%)	0	97.64	96.49	98.65	97.47	83.88

Conclusion

The extraction of Cr(VI) through LSM containing both TBP and TOPO as mobile carriers were investigated. Because of the high extraction yield of 97%, it can be concluded that, when TBP and TOPO are mixed together, they are very suitable for the extraction of Cr(VI). The addition of TOPO in LSM process should be limited to 1.5% mass to achieve the best extraction rates, whereas, any further increase in TBP concentration beyond the threshold value will seriously affect the emulsion stability. The trietanolamine (TEA) as an internal stripping reagent has been recommended for the extraction of Cr(VI) and the study has established that a concentration of 0.5 M of amine solution is the optimum concentration for maximum extraction. Accordingly, much work must be done in order to clarify the transport mechanism of Cr(VI) and the stability of emulsion.

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