



## Studies on the extraction of chromium(III) by emulsion liquid membrane

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### ABSTRACT

This paper presents a comprehensive study on removal of chromium(III) from aqueous waste solution using emulsion liquid membrane (ELM). The study has highlighted the importance of emulsion stability for maximizing the removal of chromium(III). The ELM consists of tri-*n*-butyl phosphate (TBP) as a carrier, commercial kerosene as organic solvent, sulfonated liquid polybutadiene (LYF) as surfactant agent, sulfuric acid, deionized water or sodium hydroxide as stripping phase. The important factors studied which affected the ELM stability and removal of chromium(III) were the concentrations of surfactant (2–8% w/w), carrier (2–10% w/w), internal phase H<sub>2</sub>SO<sub>4</sub> [pH 0–6], deionized water [pH 6.65] and NaOH (0–0.8% w/w), transfer time (5–35 min) and the effect of volume ratio of the feed solution to the emulsion phase (R<sub>f</sub>) (5:1–9:1). At the optimum condition it was possible to remove 99.71–99.83% of chromium(III) by using ELM. LYF was not only the surfactant but also played a key auxiliary effect for TBP combining with chromium(III) by studying on the transport mechanism.

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### 1. Introduction

The extensive use of chromium in leather tanning, metal-lurgy, electroplating and other industries has resulted in the release of aqueous chromium to the subsurface at numerous sites [1]. Chromium is an element with muta-, terato- and cancerogenic properties [2–5]. The most common oxidation states for chromium are +3, +6. Chromium(III) cannot be absorbed, it can form complex with protein in the external layer of skin and accumulated in the lung causing lung cancer. Thus, the removal and recovery of chromium(III) of increasing interest because of the growing importance given to environmental protection problems.

One of the promising methods for the separation of such effluents is the ELM process, invented by Li and Norman [6], about 30 years ago. ELM combines a single step extraction and stripping processes which are generally carried out in two separate steps in conventional solvent extraction processes. ELM is created by forming a stable emulsion, such as a water-in-oil emulsion, between two immiscible phases, followed by dispersion of the emulsion into a third, continuous phase by agitation for extraction. The membrane phase is the oil phase that separates the encapsulated, internal aqueous droplets in the emulsion from the external, continuous phase [6,7].

The main advantages of the ELM system are: (1) high interfacial area for mass transfer due to the small size of the aqueous phase

droplets; (2) high diffusion rate of the metal ion through the membrane; (3) simultaneous performance of extraction and stripping in the same system; and (4) capability of treating a variety of elements and compounds in industrial setting at a greater speed and with a high degree of effectiveness.

TBP was one of the most widely used organophosphorous extractants in the solvent extraction process. TBP has been showed to be an effective carrier for the separation and purification of a number of metals and organic acids due to its excellent chemical stability, high boiling point and low solubility in water. There are only a few reports about the facilitated transport of chromium(III) using TBP as mobile carrier through ELM. There are many studies having been carried out using ELM for the recovery of metal ions [8–14], aniline [15], phenol [16], organic acids [17], sephalexin from dilute solution [18]. Then there is no available information in the published literatures on the removal study of chromium(III) transport through ELM using TBP as carrier. Only some attention has been paid to the facilitated transport of chromium(III) using a liquid membrane [19–23]. Our laboratory group have studied on removal of chromium(III) from aqueous waste solution by liquid membrane using *p*-tert-butylcalix[4]arene acetate as extractant and obtained some experience [24–27]. However, the removal efficiency of chromium(III) was very low and cannot meet the requirement of the standards of national wastewater discharge.

The main objective of this work was to investigate the influence of various parameters affected the ELM formation and test the performance of the prepared ELM on removal of chromium(III) by using synthetic solution. It was possible to remove 99.71–99.83% of chromium(III) by using ELM at the optimized condition.

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## 2. Experimental

### 2.1. Materials

The following inorganic salts, acids, and organic solvent are used in the experiments without further purification: sulfonated liquid polybutadiene (synthesized in our laboratory), tributyl phosphate (TBP,  $\geq 98.5\%$ ), phosphoric acid ( $\text{H}_3\text{PO}_4$ ,  $\geq 85\%$ ), sulfuric acid ( $\text{H}_2\text{SO}_4$ , 95–98%), sodium hydroxide ( $\text{NaOH}$ ,  $\geq 99\%$ ), commercial kerosene (density,  $0.8 \text{ kg L}^{-1}$ ), chromic nitrate ( $\text{Cr}(\text{NO}_3)_3$ ,  $\geq 99\%$ ). Deionized water is used for preparing all the aqueous solutions.

### 2.2. Procedure

In specific volume beaker (250 ml or 500 ml), a 15 g portion of tributyl phosphate [2–10% w/w], sulfonated liquid polybutadiene [2–8% w/w] in organic solvent (commercial kerosene) are emulsified at stirring speed (3000 rpm) by means of a motor-driven emulsifier. 15 g of  $\text{H}_2\text{SO}_4$  [pH 0–6], deionized water [pH 6.65] or  $\text{NaOH}$  [0–8% w/w] is added drop wise to the stirred organic phase until O/A [the weight ratio of the oil phase to the aqueous (stripping) phase] 1. The solution is stirred continuously for 5 min to obtain a white ELM. The prepared ELM is added to specific volume of external aqueous solution. The contents are stirred by means of motor-driven at 300 rpm speed for a different transfer time.

### 2.3. Analytical method

The chromium(III) concentration is determined by visible-infrared spectrometer (721, Shanghai, China) at 540 nm wavelength. 1,5-diphenylcarbazide is used as indicator. The chromium(III) concentration in the stripping phase is calculated from mass balance. All experiments were carried out at ambient temperature. Reproducibility was confirmed as  $\pm 3\%$  or better.

## 3. Results and discussion

### 3.1. Optimization of process parameters for the extraction of chromium(III) by ELM

The results and discussion of the effect of surfactant concentration 2–8% (w/w), carrier concentration 2–10% (w/w), internal phase concentration  $\text{H}_2\text{SO}_4$  [pH 0–6], deionized water [pH 6.65] or  $\text{NaOH}$  [0–8% w/w], transfer time 5–35 min and the volume ratio of the feed solution to the emulsion phase (Rf) (5:1–9:1) on the stability of the prepared ELM and removal of chromium(III) from synthetic solutions which is  $20 \text{ mg L}^{-1}$  are prepared as follows:

#### 3.1.1. Effect of sulfuric acid concentration in the internal phase on the removal efficiency of chromium

The influence of sulfuric acid concentrations [pH 0–6] and deionized water [pH 6.65] on the emulsion stability at emulsification speed (3000 rpm), emulsification time 5 min at constant surfactant concentration 8% (w/w), carrier concentration 7% (w/w), organic solvent (commercial kerosene) O/A ratio 1, Rf 5, mixing speed 300 rpm and transfer time 20 min was shown in Fig. 1. It was observed that the removal efficiency passed 99% and kept constant with the  $\text{H}_2\text{SO}_4$  pH 0 to pH 6.65. Generally there are two kinds of driving force in the ELM process, the first is the differences of hydrogen ion chemical potentials between the aqueous phases, the second is the mental concentration gradient between internal and external phase. Chromium(III) is amphoteric oxide which dissolves in acid and alkali and precipitates in water. From these results we concluded that hydrogen ion concentration was the main driving force at  $\text{H}_2\text{SO}_4$  pH 0 and chromium(III) concentration gradient was the main driving force at pH 6.65 which was deionized water.

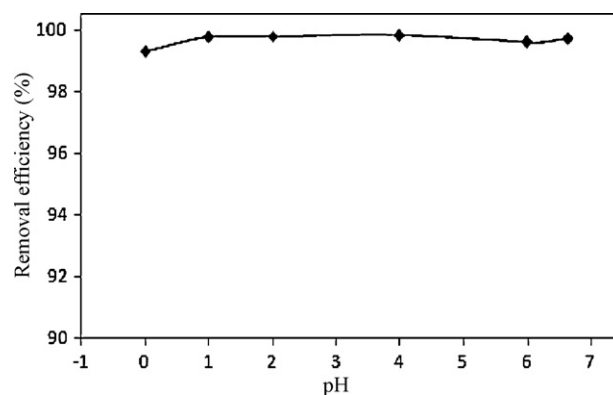


Fig. 1. Effect of sulfuric acid concentration in internal phase on the removal efficiency of chromium(III) at surfactant concentration 8% (w/w), carrier concentration 7% (w/w), O/A 1, Rf 5, mixing speed 300 rpm and transfer time 20 min.

Although chromium(III) precipitated in internal phase, the ELM was enough stability to achieved so high removal efficiency.

#### 3.1.2. Effect of sodium hydroxide concentration in the internal phase on the removal efficiency of chromium

The effect of  $\text{NaOH}$  (0–8% w/w) as the stripping phase on the removal efficiency of chromium(III) was investigated. The operating parameters were: emulsification speed (3000 rpm) and emulsification time 5 min at constant surfactant concentration 8% (w/w), carrier concentration 7% (w/w), organic solvent (commercial kerosene) O/A ratio 1, Rf 5, mixing speed 300 rpm and transfer time 20 min. The results are represented in Fig. 2. As seen from Fig. 2, the removal efficiency nearly kept constant with increasing the sodium hydroxide concentration from 0% to 0.4% (w/w), 0% concentration of sodium hydroxide is deionized water. With further increased sodium hydroxide concentration from 0.4% to 0.8% (w/w), the removal efficiency decreased sharply. So it was concluded that deionized water was selected as the internal phase.

#### 3.1.3. Effect of surfactant concentration on the emulsion stability and the removal efficiency of chromium

The effect of surfactant concentration on the behavior of the emulsion stability and the removal efficiency of chromium(III) was investigated. The operating parameters were: emulsification speed 3000 rpm, emulsification time 5 min, internal phase deionized water, carrier concentration 7% (w/w), organic solvent (commercial kerosene) at O/A 1, Rf 5, transfer speed 300 rpm and transfer time 20 min. The concentration of the surfactant was varied from 2% to 8% (w/w). The effect of surfactant on emulsion stability was

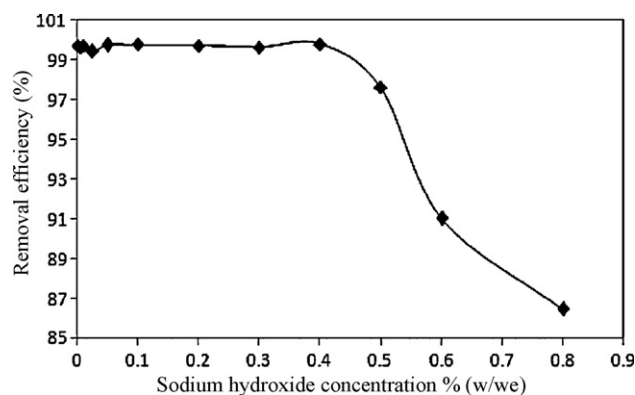
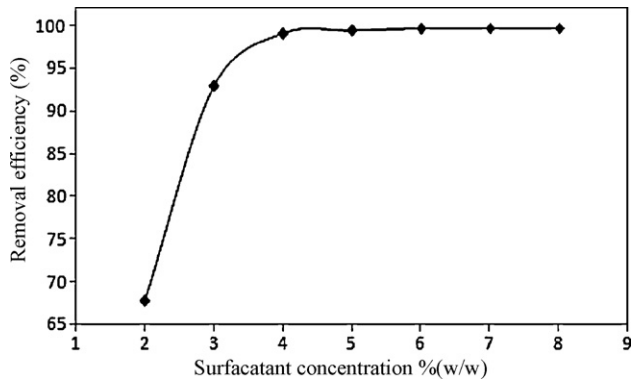
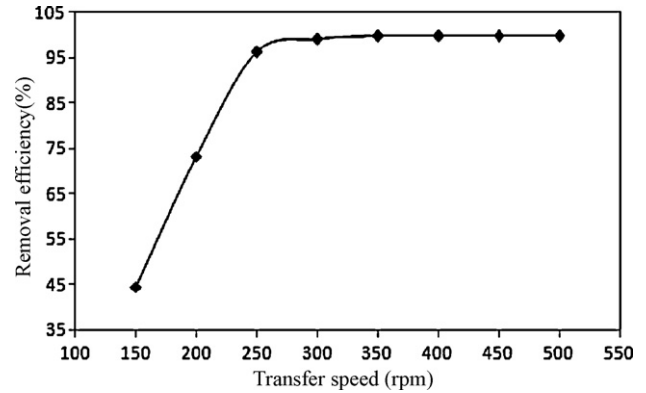


Fig. 2. Effect of sulfuric acid concentration in internal phase on the removal efficiency of chromium(III) at surfactant concentration 8% (w/w), carrier concentration 7% (w/w), O/A 1, Rf 5, mixing speed 300 rpm and transfer time 20 min.



**Fig. 3.** Effect of surfactant concentration on the removal efficiency of chromium(III) at internal phase deionized water, carrier concentration 7% (w/w), O/A 1, Rf 5, mixing speed 300 rpm and transfer time 20 min.



**Fig. 5.** Effect of transfer speed on the removal efficiency of chromium(III) at internal phase deionized water, surfactant concentration 4% (w/w), carrier concentration 7% (w/w), O/A 1, Rf 5, and transfer time 20 min.

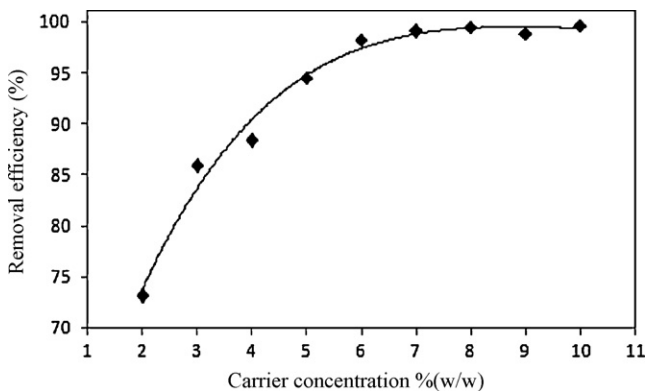
presented in Fig. 3. It was observed that the removal efficiency increased sharply and was 99.07% at the surfactant concentration 4% (w/w). When the surfactant concentration from 4% to 8% (w/w), the removal efficiency passed 99% and kept constant. From this result, 4% (w/w) concentration of the surfactant was selected, which was enough to stabilize the emulsion and kept high removal efficiency.

#### 3.1.4. Effect of carrier concentration on the removal efficiency of chromium

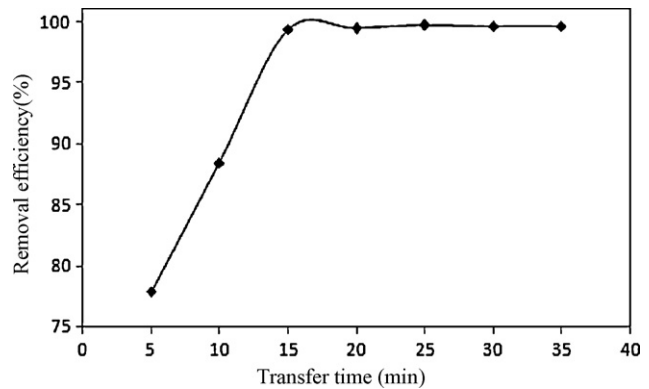
It was observed that the carrier concentration also played a key role on the removal efficiency of chromium(III). The experimental conditions was kept constant at emulsification speed 3000 rpm, emulsification time 5 min, internal phase deionized water, surfactant concentration 4% (w/w), organic solvent (commercial kerosene) at O/A ratio 1, Rf 5, transfer speed 300 rpm and transfer time 20 min. The effect of carrier concentration (2–10% w/w) on the removal efficiency of chromium(III) was shown in Fig. 4. As seen from Fig. 4, the removal efficiency increased sharply by increasing the carrier concentration from 2% to 6% (w/w) was from 73.08% to 98.19%. When the carrier increased from 7% to 10% (w/w), the removal efficiency passes 99% and kept constant. Therefore, 7% (w/w) concentration of the carrier was selected.

#### 3.1.5. Effect of transfer speed on the removal efficiency of chromium

The influence of transfer speed (150–500 rpm) on the removal efficiency at emulsification speed (3000 rpm) and emulsification time 5 min at constant surfactant concentration 4% (w/w), carrier



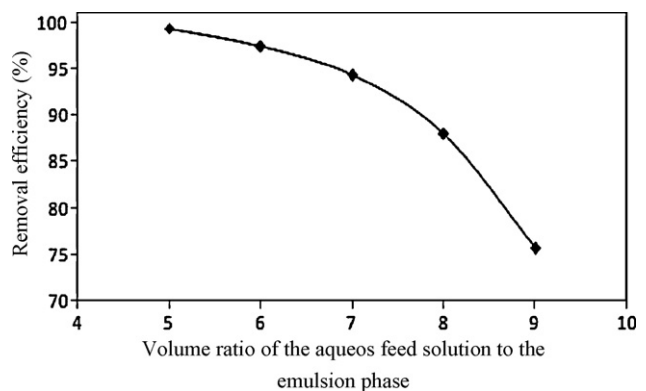
**Fig. 4.** Effect of carrier concentration on the removal efficiency of chromium(III) at internal phase deionized water, surfactant concentration 4% (w/w), O/A 1, Rf 5, mixing speed 300 rpm and transfer time 20 min.



**Fig. 6.** Effect of transfer time on the removal efficiency of chromium(III) at internal phase deionized water, surfactant concentration 4% (w/w), carrier concentration 7% (w/w), O/A 1, Rf 5 and mixing speed 350 rpm.

concentration 7% (w/w), commercial kerosene 89% (w/w), internal phase deionized water, O/A 1, Rf 5, and transfer time 20 min have been studied.

The removal efficiency of chromium(III) at different transfer speeds was shown in Fig. 5. It was observed that the removal efficiency increased by increasing the transfer speed from 150 to 250 rpm, chromium(III) removed from 44.52% to 96.25%, when the transfer speed increased from 300 to 500 rpm, the removal efficiency of chromium(III) passed 99% and remained nearly constant. It achieved 99.83% of chromium(III) efficiency at 350 rpm. We selected 350 rpm as transfer speed.



**Fig. 7.** Effect of Rf on the removal efficiency of chromium(III) at internal phase deionized water, surfactant concentration 4% (w/w), carrier concentration 7% (w/w), O/A 1, Rf 5, mixing speed 350 rpm and transfer time 15 min.

### 3.1.6. Effect of transfer time on the removal efficiency of chromium

The effect of transfer time (5–35 min) on the removal efficiency at emulsification speed (3000 rpm) and emulsification time 5 min at constant surfactant concentration 4% (w/w), carrier concentration 7% (w/w), commercial kerosene 89% (w/w), internal phase deionized water, O/A 1, Rf 5, and transfer speed 350 min have been studied.

The removal efficiency of chromium(III) at different transfer times was shown in Fig. 6. It showed that when the removal efficiency increased by increasing the transfer time from 5 to 15 min, chromium(III) removed from 77.89% to 99.38%, then when the transfer time increased from 20 to 35 min, the removal of chromium(III) remained nearly constant. Therefore, the transfer time 15 min was selected.

### 3.1.7. Effect of volume ratio of the feed solution to the emulsion phase on the removal efficiency of chromium

The effect of volume ratio of the feed solution to the emulsion phase (Rf) (5:1–9:1) on the removal efficiency of chromium(III) was studied at emulsification speed 3000 rpm, emulsification time 5 min, internal phase deionized water, surfactant concentration 4% (w/w), carrier concentration 7% (w/w), O/A 1, transfer speed 350 rpm, transfer time 15 min as shown in Fig. 7. It was clear that the removal efficiency of chromium(III) decreased gradually in the range of Rf from 5:1 to 9:1 and was 75.70% at Rf 9:1.

## 3.2. Theoretical aspects

We have studied the transport mechanism of chromium(III) on ELM by solvent extraction. The effect of TBP, the sulfonation degree and concentration of LYF on the extraction of chromium(III) from synthetic solutions which contains 20 mg L<sup>-1</sup> chromium(III). The effect of different surfactant agents Span-80 and LYF on removal efficiency of chromium(III) using ELM.

### 3.2.1. Effect of TBP and LYF on the extraction efficiency of chromium(III)

In specific volume beaker (50 ml), TBP and LYF were mixed at 300 rpm speed by means of a motor-driven stirrer for 5 min. The prepared organic solution was added to 100 ml of 20 mg L<sup>-1</sup> chromium(III) solution in 250 ml volume beaker. The contents were stirred by means of motor-driven stirrer at 50 rpm speed for 30 min. It was easy to be emulsified when there was LYF in the organic solution so that the mixing speed cannot surpass 50 rpm. The results were represented in Table 1. As seen in Table 1 the extraction efficiency was low if only there was TBP or LYF and kerosene as organic solution, however it passed 95% when there were TBP and LYF as organic solution, LYF itself did not have extraction ability. So it was

these negative groups would attract certain amount of Cr<sup>3+</sup> at the interface so that TBP could combine with Cr<sup>3+</sup>.

### 3.2.2. Effect of LYF concentration in organic solution on the extraction efficiency of chromium(III)

In specific volume beaker (50 ml), TBP and LYF were mixed at 300 rpm speed by means of a motor-driven stirrer for 5 min. The prepared organic solution was added to 100 ml of 20 mg L<sup>-1</sup> Cr<sup>3+</sup> solution in 250 ml volume beaker. The contents were stirred by means of motor-driven stirrer at 50 rpm speed for 30 min. The results were represented in Table 2. It was observed that extraction efficiency increased by increasing the LYF from 0.2 to 1.5 g, and -OSO<sub>3</sub><sup>-</sup> groups were also increased. There must be certain amount -OSO<sub>3</sub><sup>-</sup> which could attract Cr<sup>3+</sup>, then TBP could bind with Cr<sup>3+</sup>. Finally TBP combined mostly Cr<sup>3+</sup> from the aqueous solution.

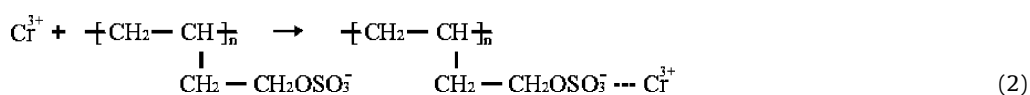
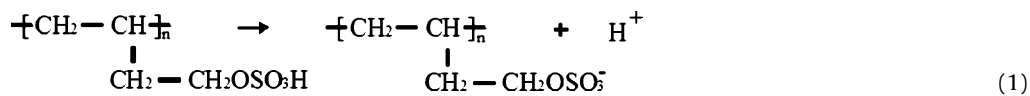
There must be certain amount hydrophilic groups -OSO<sub>3</sub><sup>-</sup> of LYF at the interface, it was not necessary to increase sulfonation degree of LYF. The results were presented in Table 3. Therefore, 5% degree of sulfonation was selected.

### 3.2.3. Effect of different surfactants on the removal efficiency of chromium(III) using EML

The operating procedure was the same as in Section 2.2 and parameters were: emulsification speed 3000 rpm, emulsification time 5 min, internal phase deionized water, carrier concentration (TBP) 7% (w/w), organic solvent (commercial kerosene) at O/A 1, Rf 5, transfer speed 300 rpm and transfer time 20 min. TBP or LYF was 7% (w/w). The effect of different surfactants on the removal efficiency was presented in Table 4. Span-80 was one of the most widely used surfactant. Surfactant concentration 7% (w/w) was enough stability for membrane, however the removal efficiency was nearly zero, there were three OH<sup>-</sup> in Span-80, but H<sup>+</sup> cannot dissociate from OH<sup>-</sup> to aqueous solution. At the external interface there was not enough negative groups attracting certain amount of chromium(III) cation. So it was clear that LYF was not only the surfactant but also played a key auxiliary effect for TBP combining with chromium(III) at the interface which just proved the conclusion of Section 3.2.2.

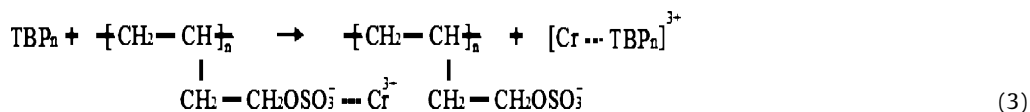
According to the above experiment phenomenon, the transport mechanism of chromium(III) from external phase to internal phase in EML may be represented by the scheme shown in Fig. 8. The following steps are involved in transport process:

- (1) The -OSO<sub>3</sub>H of LYF is on the external interface and H<sup>+</sup> dissociate from -OSO<sub>3</sub>H into aqueous solution. Cr<sup>3+</sup> is attracted by -OSO<sub>3</sub><sup>-</sup>.



concluded that TBP was difficulty to combine chromium(III), when LYF was added into TBP as organic solution, the -OSO<sub>3</sub>H of LYF was on the interface and H<sup>+</sup> dissociate from -OSO<sub>3</sub>H to aqueous solution. There were lots of -OSO<sub>3</sub><sup>-</sup> groups at the interface and

- (2) TBP binds with Cr<sup>3+</sup> at the external interface to form a complex, [Cr-TBP<sub>n</sub>]<sup>3+</sup>. The complex is transported to internal interface because of concentration gradient between external and internal interface.



**Table 1**  
Effect of TBP and LYF on the extraction efficiency of chromium(III).

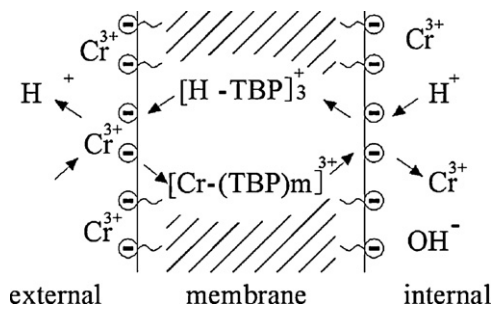
No.	TBP (g)	LYF (g)	Kerosene (g)	Efficiency
1	10	0	0	9.47%
2	0	1.0	10	18.68%
3	10	1.0	0	95.66%

**Table 2**  
Effect of LYF concentration on the extraction efficiency of chromium(III).

No.	TBP (g)	LYF (g)	Efficiency
1	10	0.2	21.84%
2	10	0.5	84.01%
3	10	1.0	96.84%
4	10	1.5	97.5%

**Table 3**  
Effect of sulfonation degree of LYF on the removal efficiency of chromium(III) by ELM.

No.	1	2	3	4	5
Sulfonation degree	100	50	25	10	5
Efficiency	>99%				

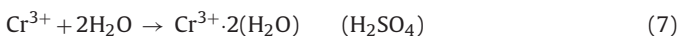
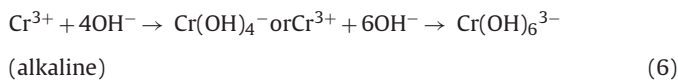
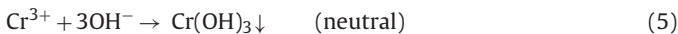


**Fig. 8.** Scheme diagram of the transport mechanism in EML process for chromium(III) separation.

- (3) At internal interface ion-exchange reaction takes place thereby this complex releasing  $\text{Cr}^{3+}$  into internal phase, TBP returns to the external interface with  $\text{H}^+$  to recombine  $\text{Cr}^{3+}$  and  $\text{H}^+$  releases into external phase.



- (4)  $\text{Cr}^{3+}$  reacts with internal solvent, the concentration gradient of  $\text{Cr}^{3+}$  between external and internal phase provides the driving force for the transport via membrane phase.



**Table 4**  
Effect of different surfactants on the removal efficiency of chromium(III) using EML.

No.	Surfactant	Efficiency
1	LYF	>99.5%
2	Span-80	<1%

## 4. Conclusion

The influence of the effect of the surfactant concentration 2–8% (w/w), carrier concentration 2–10% (w/w), internal phase  $\text{H}_2\text{SO}_4$  [pH 0–6], deionized water [pH 6.65] and NaOH [0–0.8% w/w], Rf ratio 5:1–9:1, transfer time 5–35 min on the stability of the prepared ELM and removal of chromium(III) from synthetic solutions were investigated. The optimum conditions for preparation stable emulsion which capable of 99.71–99.83% chromium(III) removal were 3000 rpm emulsification speed, 5 min emulsification time, internal phase  $\text{H}_2\text{O}$ , surfactant concentration 4% (w/w), carrier concentration 7% (w/w), Rf 5, O/A 1, transfer speed 350 rpm and transfer time 20 min. LYF was played a key auxiliary effect for TBP combining with chromium(III) by studying on transport mechanism.

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## References

- [1] N.K. Djane, K. Ndungu, C. Johnsson, H. Sartz, T. Tornstrom, L. Mathiasson, Chromium speciation waters using serially connected supported liquid membranes, *Talanta* 48 (1999) 1121–1132.
- [2] T.J. O'Brien, S. Ceryah, S.R. Paterino, Complexities of chromium carcinogenesis: role of cellular response, repair and recovery mechanism, *Mutat. Res.* 533 (2003) 3.
- [3] K.C. Tagliari, V.M. Vargas, K. Zimiani, R. Cecchini, Oxidative stress damage in the liver of fish and rats receiving an intraperitoneal injection of hexavalent chromium as evaluated by chemiluminescence, *Environ. Toxicol. Pharmacol.* 17 (2004) 149.
- [4] R. Swietlik, Speciation and Transformations of Anthropogenic Chromium in the Environment Polluted by Tannery Wastes (in Polish), Publishing House of Radom University of Technology, Radom, 2001.
- [5] A. Molik, J. Siepak, R. Swietlik, J. Dojlido, Identification of chromium species in tanning solutions, *Pol. J. Environ. Stud.* 13 (2002) 311.
- [6] N. Li, Norman, Separating hydrocarbons with liquid membranes, Exxon Research and Engineering Company, U.S. Patent 3,410,794.119, Assinee (1968).
- [7] W.S. Ho, K.K. Sirkar, *Membrane Handbook*, Chapman and Hall, Eds, New York, 1992.
- [8] F. Valenzuela, C. Fonseca, C. Basualto, O. Correa, C. Tapia, J. Spag, Removal of copper ions from a waste mine water by a liquid emulsion membrane method, *Mineral Eng.* 18 (2005) 33–40.
- [9] S. Bourenane, M.E.H. Samar, A. Abbaci, Extraction of cobalt and lead from wastewater using a liquid surfactant membrane emulsion, *Ac. Chem. Solv.* 50 (2003) 663–675.
- [10] A.K. Charavarti, S.B. Chowdhury, D.C. Mukherjee, Liquid membrane multiple emulsion process of separation of copper (II) from wastewater, *Colloids Surfaces* 166 (2000) 7–25.
- [11] R.A. Kumbasar, Extraction of chromium (VI) from multicomponent acidic solutions by emulsion liquid membranes using TOPO as extractant, *J. Hazard. Mater.* 167 (2009) 1141–1147.
- [12] M.S. Gasser, N.E. El-Hefny, J.A. Daoud, Extraction of Co(II) from aqueous solution using emulsion liquid membrane, *J. Hazard. Mater.* 151 (2008) 610–615.
- [13] R.A. Kumbasar, Separation and concentration of cobalt from zinc plant acidic thiocyanate leach solutions containing cobalt and nickel by an emulsion liquid membrane using triisooctylamine as carrier, *J. Hazard. Mater.* 333 (2009) 118–124.
- [14] M. Rajasimman, R. Sangeetha, Optimization of process parameters for the extraction of chromium (VI) by emulsion liquid membrane using response surface methodology, *J. Hazard. Mater.* 168 (2009) 291–297.
- [15] R. Devulapalli, F. Jones, Separation of aniline from aqueous solutions using emulsion liquid membranes, *J. Hazard. Mater.* 70 (1999) 157–170.
- [16] X. Zhang, J.H. Liu, T.S. Lu, Industrial application of liquid membrane separation for phenolic wastewater treatment, *Water Treat. J.* (1987) 127–135.
- [17] C.C. Wang, A.L. Bunge, Multisolute extraction of organic acids by emulsion liquid membranes—batch experiments and models, *J. Membr. Sci.* 53 (1990) 71–103.
- [18] G.C. Sahoo, N.N. Dutta, Studies on emulsion liquid membrane extraction of Cephalaxin, *J. Membr. Sci.* 145 (1998) 15–16.
- [19] B. Wionczyk, W. Apostoluk, Solvent extraction of chromium(III) from alkaline media with quaternary ammonium compounds, Part I, *Hydrometallurgy* 72 (2004) 185.
- [20] R. Molinari, E. Drioli, G. Pantano, Stability and effect of diluents in supported liquid membranes for Cr(III), Cr(VI) and Cd(II) recovery, *Sep. Sci. Technol.* 24 (12–13) (1989) 1015.

- [21] A.M. Chaudry, S. Ahmad, M.T. Malik, Supported liquid membrane technique applicability for removal of chromium from tannery wastes, *Waste Manage.* 17 (4) (1997) 211.
- [22] J. Gega, W. Walkowiak, Separation of Cr(VI) and Cr(III) ions from sulfuric acid solutions with TOPO by bulk and supported liquid membranes, *Pol. J. Appl. Chem.* XLIII (3–4) (1999) 147.
- [23] R. Gawro'nski, P. Religa, Transfer of chromium(III) ions in systems with liquid membrane (in Polish), *Monogr. PAN* 22 (2004) 295.
- [24] D. Fei, J. Luo, Y. Dang, Extraction of Cr<sup>3+</sup> with p-tert-butylcalix[4]arene acetate from artificial tannery wastewater, *J. Appl. Chem. China* 25 (2) (2008) 157–161.
- [25] D. Fei, J. Luo, Y. Dang, Study on interfacial reaction of internal phase in process of extracting Cr<sup>3+</sup> by emulsion liquid membranes, *J. Chem. Eng. China* 36 (3) (2008) 35–37.
- [26] D. Fei, Y. Dang, J. Luo, Study on the phase interfacial reactions in the process of extracting Cr<sup>3+</sup> by emulsion liquid membranes, *J. Sichuan Univ. (Sci.) China* 39 (6) (2007) 71–75.
- [27] J. Luo, D. Fei, M. Yang, Study on the mathematic models of emulsion liquid membrane with carrier extracting Cr<sup>3+</sup> from tannery wastewater, *J. Membr. Sci. Technol. China* 28 (1) (2008) 60–65.