



## Emulsion liquid membrane pertraction of Cr(III) from aqueous solutions using PC-88A as carrier



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### HIGHLIGHTS

- High stable ELM and Cr(III) removal performance (94%) was achieved after 5 min.
- Organic phase containing kerosene, PC-88A, Span 80, and paraffin was prepared.
- Primary emulsion consisted in different organic/stripping persulfate phase ratios
- Best ELM performance: 2% of Span, 2% paraffin, 0.5M PC-88A, and 0.1M persulfate
- Interfacial reactions and chromium facilitated transport through ELM were proposed.

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### ABSTRACT

Liquid membrane processes have emerged as alternative techniques to conventional processes for concentration and separation of metal ions from aqueous effluents. The removal of chromium(III) from synthetic aqueous solutions by an emulsion liquid membrane technique (ELM) was investigated. 2-Ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A) was used as carrier, Span 80 as surfactant, light paraffin as additive, and ammonium persulfate  $[(\text{NH}_4)_2\text{S}_2\text{O}_8]$  as stripping agent. Different physical and chemical parameters such as stirring speed, metal ion concentration and pH of the continuous phase, carrier concentration, organic/aqueous stripping ratio (O/S), and internal stripping agent concentration have been analyzed. The results demonstrated that working in a batch mode at the optimum ELM extraction–stripping condition 94% of chromium(III) was removed during the first 5 min of operational time. The ELM showed high stability up to 30 min. Different interfacial reactions involving the chromium complexes and the facilitated transport of Cr(III) through the ELM were proposed.

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### 1. Introduction

The environmental pollution caused by industrial waste waters is a current problem of our age. One of the main industries that produces and throws away chromium(III) to the environment is the tannery industry as well as metallurgy and electroplating industries. Cr(VI) and Cr(III) are the two most common oxidation states of chromium. Cr(VI) is much more toxic and environmental pollutant than the trivalent form due to its strong oxidizing nature. The maximum exposure limit to Cr(VI) is 0.05 mg/m<sup>3</sup> averaged over an 8 hour working day, exposures higher than that limit could cause toxicity not only to humans, but also to animals and vegetables [1]. Cr(III) is easily oxidized to Cr(VI) under thermal and chemical conditions of leather effluents. Besides, due to the fact that it cannot be absorbed, it can form complex with proteins in the external layer of skin and

accumulate in the lung causing lung cancer [2]. Regarding chromium removal from industrial effluents, several methods have been developed such as chemical precipitation [3,4], ionic exchange [5,6], solvent extraction [7,8], membrane systems [9,10] and absorption [11]. The most widespread conventional method for Cr(III) and Cr(VI) removal is precipitation. Another alternative is to use solvent extraction processes (SX) with liquid organic extractants [7,8]. This technology has been widely applied for recovery and removal of chromium in hydro-metallurgy and tanning wastewater [12]. However, all those conventional processes have many operational difficulties such as large inventory of extractants, fairly large plants to obtain the required separations, loss of solvent due to the organic compound solubility in aqueous solutions, volatilization of diluents and/or degradation of organic compounds [13]. Liquid membrane processes are suitably used as an alternative technique for concentration and separation of metal ions from aqueous solutions. The application of liquid membrane technique has been expanded in the last 30 years and its usage has become a treatment of alkali metals, actinides, lanthanides and transition ions [2,14–19]. Liquid membrane separation processes

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combine extraction and stripping of the solute in a single stage, low energy requirement, and small quantities of extractant, which makes it more profitable over other separation processes. From different types of liquid membranes available in literature, Emulsion Liquid Membrane (ELM) has the advantage of having high surface areas, fast extraction/stripping process and high efficiency. ELM has been recognized as an effective method for ion separation and concentration, when the component to be extracted is present in very low concentration. Choosing a suitable extractant or carrier, between other operational conditions is one of the key factors that control the ion extraction efficiency. In order to achieve the best extraction conditions at the minimum operational time different extractants have been used, among them, tertiary amines [20], TOPO/Cynex921 and cyamex923 (trioctylphosphine oxide) [21,22], trioctylamine [23], tributyl phosphate [24], aliquat-336 [25–27], D2EHPA (di(2-ethylhexyl) phosphoric acid) [28]. The size of the internal phase droplets and organic phase stability are important factors related with the ELM efficiency. To enhance the liquid membrane stability additives in the organic phase, such as surfactants and paraffin (higher interfacial surface tension and viscosity) have been used by several researchers [19,28–30].

In this study the removal of Cr(III) with an ELM containing PC-88A as carrier, light paraffin, and Span 80 as surfactant was investigated. PC-88A was chosen because it's appropriate characteristics to achieve an efficient transport of Cr(III) through ELM, such as: i) there are no present irreversible and degradation reactions with the Cr(III), given to ELM higher both, separation capacity and lifetime; ii) it has a fast reversible kinetic of complex reaction allowing ELM to operate in conditions near to equilibrium; and iii) it is an acidic carrier highly soluble in organic solvents and water insoluble.

The effect of PC-88A, light paraffin and Span 80 concentrations in the organic phase, aqueous/organic phase ratio of primary emulsion, stripping agent concentration and pH, and Cr(III) concentration in the feed solution, on Cr(III) removal performance was analyzed. Transport mechanism of chromium ion derived from the experimental results was proposed.

## 2. Experimental

### 2.1. Materials

All reagents used were of analytical grade. All aqueous solutions were prepared with deionized water. Carrier 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A) produced by Daihachi Chemical Co (Japón) was used without further purification. It features a molecular weight = 306.4 g mol<sup>-1</sup> and a density ( $\rho$ ) = 0.948 g cm<sup>-3</sup>. Pure kerosene b.p. = 200–300 °C,  $\rho$  = 0.8 g cm<sup>-3</sup>,  $\eta^{20}$  = 1.44 × 10<sup>-3</sup> kg m<sup>-1</sup> s<sup>-1</sup> and aromatic content <25 vol.%, was provided by Fluka and used as solvent. Highly-pure light paraffin  $\rho$  = 0.87 g cm<sup>-3</sup>,  $\eta^{20}$  = 0.11 kg m<sup>-1</sup> s<sup>-1</sup> was purchased from Riedel-de Haën. The surfactant sorbitan monooleate SPAN-80 molecular weight = 428.6 g mol<sup>-1</sup>,  $\rho$  = 0.995 g cm<sup>-3</sup> was purchased from ICI Surfactants. Feed chromium solutions were prepared with standard solutions of Cr(III) Tritisol AR grade (Merck). Other chemical reactants such as H<sub>2</sub>SO<sub>4</sub> and (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> were used without further purification.

### 2.2. Analytical measurements

The pH of aqueous solution was measured using Metrom pH-meter. The concentration of chromium was determined spectrophotometrically with an Atomic Absorption Spectrophotometer Varian AA-50 at wavelength of 356.7 nm, band width 0.5 nm and optimum range of work 0.2–20 µg/ml. Organic phase viscosities were determined with a Cannon-Fenske viscometer and emulsion viscosities were determined by using a rotational viscometer Brookfield DV III.

### 2.3. Liquid–liquid extraction–stripping experiments

In order to determine quantitatively the optimum conditions for Cr(III) removal with the ELM it is necessary to set up the appropriate experimental conditions. Liquid–liquid extraction and stripping partition steps and the possible reactions involved in complex formation and decomposition at 298 K were studied. It is well known that in aqueous solution the predominance of Cr(III) species depends on, among other factors, the pH of solution and the ionic strength. Fig. 1 shows the profile of abundance of each Cr(III) species along the pH range [31]. Preliminary experiments of liquid–liquid extraction were performed with a feed aqueous solutions containing 2.115 × 10<sup>-3</sup> mol L<sup>-1</sup> of Cr(III) (110 ppm) at different pH with or without buffer. The initial pH of the feed solutions without buffer was varied between 0.5 and 6 with sulfuric acid. In case of buffered feed solutions the pH was varied from 3 to 6 adjusted with NaCH<sub>3</sub>COO/HCl buffer. Higher pH values may cause the ion precipitation as chromium hydroxide, whereas, lower pH values prevent the formation of Cr(III)–PC88A complex. The organic phases consist of different PC-88A concentration (0–1 mol L<sup>-1</sup>) in kerosene. Equal volumes (0.01 L) of both phases were equilibrated in decantation vial (at 298 K) and mechanically shaken (Swip KL-2 shaker) for 2 h and then left to rest for 12 h. The Cr(III) extraction percentages, E (Cr) %, were evaluated from

$$E(\text{Cr})\% = \frac{[\text{Cr}]_{\text{a,i}} - [\text{Cr}]_{\text{a,e}}}{[\text{Cr}]_{\text{a,i}}} \times 100 = \frac{[\text{Cr}]_{\text{e}}}{[\text{Cr}]_{\text{a,i}}} \times 100 \quad (1)$$

being [Cr]<sub>a,i</sub> the Cr(III) initial concentration in the feed aqueous solution; [Cr]<sub>a,e</sub> and [Cr]<sub>e</sub> the Cr(III) remnant concentration in the feed aqueous solution and the chromium–carrier complex concentration in the organic phase, respectively, at the equilibrium conditions.

Stripping experiments were performed by using an organic phase of PC-88A loaded with 2.077 × 10<sup>-3</sup> mol L<sup>-1</sup> (108 ppm) of Cr(III). In order to obtain the best back-extraction performance, two different stripping solutions were tested, i) aqueous solutions with different concentration of sulfuric acid (0–5 M), and ii) aqueous solutions with different concentration of ammonium persulfate (0–0.5 M). The use of (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> as stripping agent was proposed because it is used as standard method to oxidize Cr(III) to Cr(VI) [7]. Equal volumes (0.01 L) of both phases were equilibrated in decantation vial (at 298 K) and mechanically shaken (Swip KL-2 shaker) for 2 h and then left to rest for 12 h. The percentage of chromium removed, S (Cr) %, from the organic phase was determined by

$$S(\text{Cr})\% = \frac{[\text{Cr}]_{\text{a,e}}}{[\text{Cr}]_{\text{i}}} \times 100 \quad (2)$$

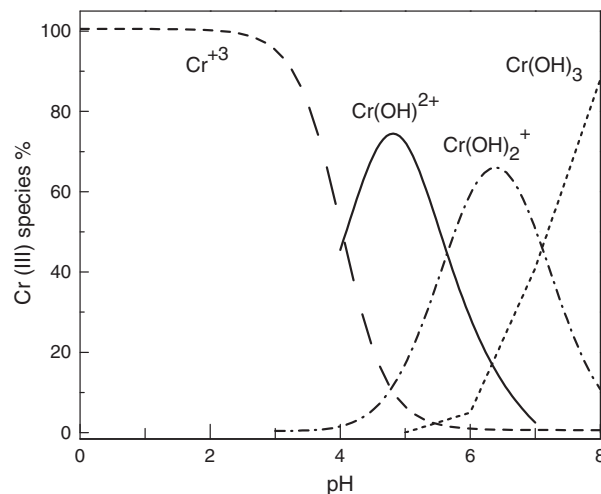


Fig. 1. Cr(III) species distribution as a function of pH.

**Table 1**  
Viscosity of the organic phase and primary emulsion.

Paraffin (% w/w)	Organic phase <sup>a</sup> $\eta$ (cp)	Primary emulsion <sup>b</sup> $\eta$ (cp)	Span 80 (% w/w)	Organic phase <sup>c</sup> $\eta$ (cp)	Primary emulsion <sup>d</sup> $\eta$ (cp)	PC-88A (M)	Organic phase <sup>e</sup> $\eta$ (cp)	Primary emulsion <sup>f</sup> $\eta$ (cp)
0	1.95	21.0	0	1.95	–	0.10	1.82	9.5
2	2.15	24.8	0.5	2.03	–	0.25	1.93	21.7
4	2.78	29.2	1	2.08	7.3	0.50	2.15	24.8
8	2.93	32.5	2	2.15	24.8	0.75	2.51	25.2
10	3.34	33.1	3	2.98	33.5	1.00	2.96	25.5

(a) Kerosene, 2% Span 80, PC-88A 0.5 M; (c) kerosene, 2% Paraffin, PC-88A 0.5 M; (e) Kerosene, 2% Paraffin, 2% Span; (b), (d), (f) 0.1 M of ammonium persulfate, O/S = 1.

where  $[Cr]_{a,e}$  is the chromium concentration in the stripping aqueous phase at the equilibrium condition, and  $[Cr]_i$  is the initial concentration of Cr(III) loaded in the organic phase.

## 2.4. Chromium recovery tests

### 2.4.1. ELM preparation

The stability of the ELM is one of the critical factors affecting the removal of metal ions. The emulsion rupture results in lowering extraction effectiveness and losing of the extracted components. The primary emulsion, water-in-oil type denoted as E, was formed by adding together the organic phase (O) and stripping aqueous phase (S) in a 0.5 L glass under an intense stirring (4500 rpm at 298 K) for 20 min by means of a high-speed stirrer (Wise Mix Homogenizer HG-15D). Preliminary test showed that lower droplet sizes and higher amount of droplets (higher interface area) of the primary emulsion were obtained with the increasing stirring rate. The droplet sizes of the primary emulsion were determined by optical microscopy of the secondary emulsions. Images were obtained on a Nano-Scope OMV-PAL optic system. The droplet size values varied approximately between  $\sim 7$ – $25 \mu\text{m}$ ,  $\sim 5$ – $17 \mu\text{m}$  and  $\sim 3$ – $10 \mu\text{m}$  for 1500, 2500 and 4500 rpm respectively. When the stirring rate surpassed 4500 rpm the coalescence and breakdown of droplets were produced, making the primary emulsion unstable. The O/S volume ratio is a factor that has an effect on both, the liquid membrane stability and the metal ion transport and recovery, thus primary emulsions with O/S volume ratios of 0.5–1–2 were prepared. The stripping solution or internal phase (S) was an ammonium persulfate aqueous solution in concentration varying from 0.025 to 0.25 mol L<sup>-1</sup>. The organic phase or liquid membrane consisted of solvent kerosene containing the proper quantity of carrier PC-88A (0.1–0.75 mol L<sup>-1</sup>), additive light paraffin (2–8% w/w), and surfactant Span-80 (1–3% w/w). The addition of a surfactant and paraffin aims to stabilize the liquid membrane by preventing the breakdown of the emulsion. Furthermore, the liquid paraffin prevents the swelling of the emulsion globules, avoiding the transfer of water from the feed water to the stripping phase. The amount of each component was adjusted in order to determine the optimum conditions for Cr(III) removal and ELM stability. The viscosities ( $\eta$ ) of organic phases and primary emulsions were measured and their values are given in Table 1.

### 2.4.2. Chromium permeation through ELM

Permeation experiments were carried out at 298 K by mixing the primary emulsion (E) and the feed solution (F) in a volume ratio of F/E = 10 (secondary emulsion) with a magnetic stirrer at 500 rpm. Higher stirring rate (>500 rpm) affects the stability of emulsion increasing the breakup of emulsion. Feed solution consisted of  $2.115 \times 10^{-3}$  mol L<sup>-1</sup> of Cr(III) aqueous solution adjusted at pH = 5 with NaCH<sub>3</sub>COO/HCl buffer. Once started the permeation experience testing samples of secondary emulsion were regularly taken at various time intervals for analysis. In order to find out the Cr(III) remnant in the aqueous phase, the secondary emulsion was filtered to separate the primary emulsion from feed solution. All permeation

trials were carried out in triplicate and mean values of chromium recovery were reported.

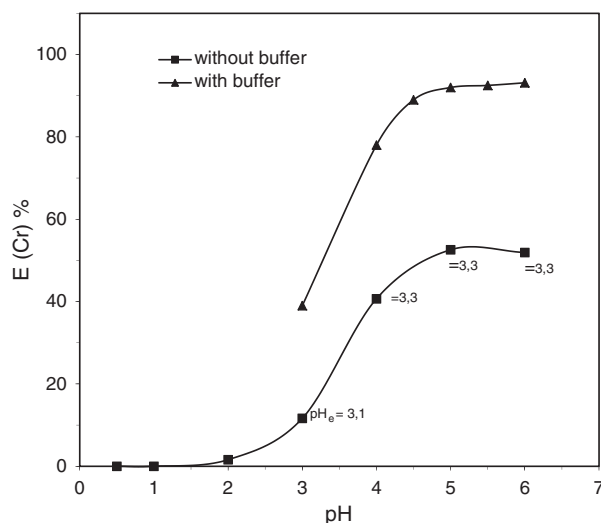
## 3. Results and discussion

### 3.1. Chromium liquid–liquid extraction and stripping

#### 3.1.1. Extraction

Results of Cr(III) liquid–liquid extraction percentage (E %, from Eq. (1)) as a function of pH are shown in Fig. 2. For clarity, the E (Cr) % data of feed solutions without buffer was plotted as a function of initial pH and the pH values at equilibrium (pH<sub>e</sub>) have been included in the figure. When buffered Cr(III) solutions were used, the pH values after Cr(III) extraction were the same of the initial solutions. In this case, protons produced by the complex extraction reaction were masked by the buffer. The most efficient operational condition for Cr(III) extraction (92–93%) was established at a feed aqueous phase buffered at pH  $\geq 5$ . To avoid ion precipitation as chromium hydroxide, the pH = 5 has been selected for further analysis of chromium extraction and transport through the ELM.

A series of extraction experiments were performed in order to analyze the effect of extractant concentration on Cr(III) extraction. In all tests, the aqueous solution consisted of  $2.115 \times 10^{-3}$  mol L<sup>-1</sup> of Cr(III) and pH = 5 buffered with NaCH<sub>3</sub>COO/HCl. The extractant PC-88A concentration loaded in the organic phase was varied from 0.1 to 1 M. The extraction experimental results are summarized in Table 2, where the best extraction performance (E = 92%) at PC-88A  $\geq 0.50$  M was achieved.



**Fig. 2.** pH effect on Cr(III) extraction with and without buffer. Aqueous phase (A): [Cr(III)] =  $2.115 \times 10^{-3}$  M, H<sub>2</sub>SO<sub>4</sub> or buffer NaCH<sub>3</sub>COO/HCl; organic phase: [PC-88A] = 0.5 M in kerosene; volume ratio O/A = 1.

**Table 2**  
Cr(III) extraction as a function of PC-88A concentration.

[PC-88A] (mol L <sup>-1</sup> )	[Cr] <sub>a,e</sub> × 10 <sup>3</sup> (mol L <sup>-1</sup> )	[Cr] <sub>e</sub> × 10 <sup>3</sup> (mol L <sup>-1</sup> )	E (Cr) %
0.1	1.769	0.346	16
0.15	1.423	0.692	32
0.25	0.781	1.334	63
0.35	0.369	1.746	83
0.45	0.231	1.884	89
0.50	0.173	1.942	92
0.75	0.171	1.944	92
1.00	0.171	1.944	92

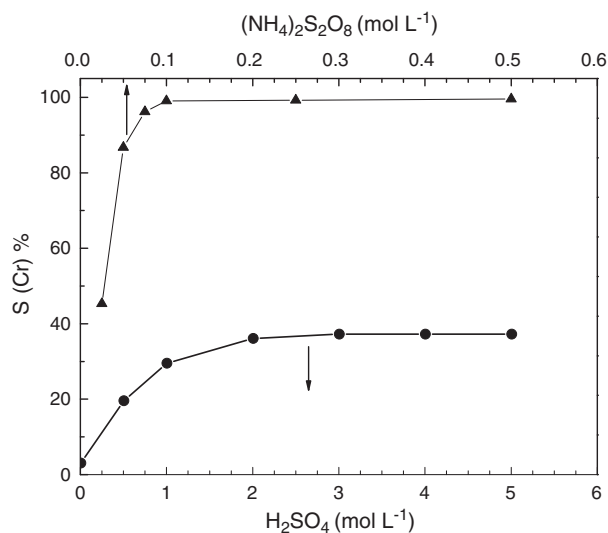
Feed solution: [Cr]<sub>ai</sub> = 2.115 × 10<sup>-3</sup> mol L<sup>-1</sup> buffered at pH = 5.

### 3.1.2. Stripping

The selection of suitable stripping reagent is considered to be one of the key factors to design an effective ELM. As it was mentioned in Section 2.3, the stripping tests were performed using an organic phase loaded with 2.077 × 10<sup>-3</sup> mol L<sup>-1</sup> of Cr(III) and two different stripping phases, sulfuric aqueous solution and ammonium persulfate aqueous solution. The effect of sulfuric acid and ammonium persulfate concentration on Cr(III) stripping (S%, Eq. (2)) is shown in Fig. 3. It can be observed that ammonium persulfate solutions are more effective for metallic ion recovery, reaching the highest Cr(III) stripping efficiency (R ≈ 99.5%) at [(NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] ≥ 0.1 M. The pH measurements of the stripping solutions before and after the back-extraction tests were practically the same. This can be attributed to the low amount of H<sup>+</sup> produced by the oxidation reaction of Cr(III) to Cr(IV) compared with the initial H<sup>+</sup> concentration in the stripping solution (pH ≈ 1, 1.6 and 1.9 for persulfate concentrations of 0.05, 0.1 and 0.5 M respectively). Based on back-extraction results, 0.1 M ammonium persulfate solution was chosen for further studies.

### 3.2. Analysis of parameters affecting the ELM stability and chromium recovery

Liquid membrane stability and chromium recovery rate are important factors in ELM processes since they directly affect its efficiency. As it can be noticed in the subsequent analysis of parameters, the chromium removal increases considerably during the first 5 min (70–94%) and after that it increases slightly approaching a limiting



**Fig. 3.** Effect of sulfuric acid and ammonium persulfate on Cr(III) back-extraction. Stripping phase (S): [(NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] = 0.025–0.5 M; organic phase (O): [PC-88A] = 0.5 M, [Cr(III)] = 2.077 × 10<sup>-3</sup> M in kerosene; volume ratio O/S = 1.

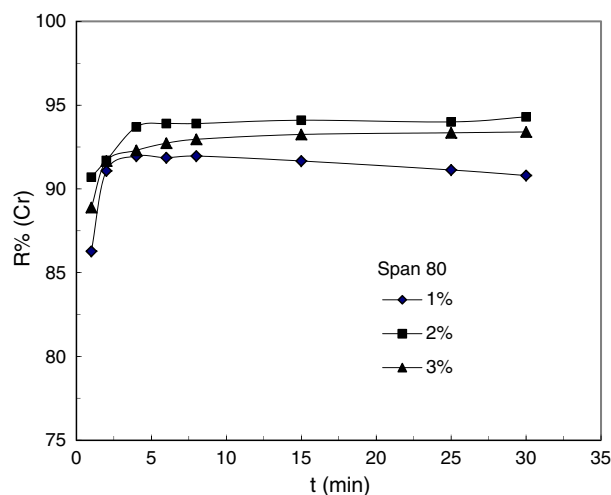
value (equilibrium condition). In the following sections, the chromium removal value at t = 5 min was used as reference recovery factor to evaluate the effect of surfactant, paraffin, O/S volume ratio, carrier PC-88A concentration, and ammonium persulfate concentration on ELM Cr(III) removal performance.

#### 3.2.1. Effect of surfactant

To determine the surfactant ability as carrier, preliminary test of Cr(III) transport using a primary emulsion with an organic phase containing 3 wt.% of surfactant, 2% paraffin, 0% PC-88A and solvent kerosene, was analyzed. The Cr(III) recovery results showed that chromium ion transfer was not accomplished (R% = 0) in absence of PC-88A extractant. The amount of surfactant added to the ELM must be considered to obtain stable emulsion. Low surfactant amount gives unstable emulsion and high surfactant concentration, above its critical micelles, and tends to form aggregates in the bulk solution. The aggregates promote water transport to external phase that causes breakage while to internal phase causes swelling [32,33]. In order to investigate this effect, the concentration of Span-80 was varied in the range of 0 to 3 wt.%. The primary emulsion consisted of: volume ratio O/S = 1; organic membrane phase (kerosene) containing 0.5 M PC-88A, surfactant and 2% paraffin; and stripping internal phase 0.1 M of ammonium persulfate. The secondary emulsion or ELM included the primary emulsion and feed aqueous solution containing 2.115 × 10<sup>-3</sup> M of Cr(III) buffered at pH = 5. Fig. 4 illustrates the percentage of Cr recovery, R (Cr) %, as a function of operational time, where

$$R(\text{Cr})\% = \frac{[\text{Cr}]_s}{[\text{Cr}]_f} \times 100 \quad (3)$$

being [Cr]<sub>s</sub> and [Cr]<sub>f</sub> the Cr concentration in the stripping and feed solution, respectively. When 0 and 0.5% w/w of surfactant were used a very unstable emulsion was attained (R% ≈ 0). Fig. 4 shows that emulsion stability increased with the increase of surfactant concentration up to 2–3 wt.%. In the case of organic phase with 1% of surfactant high removal of Cr(III) (≈92%) was achieved up to 5 min and then decrease steadily with operation time indicative of liquid membrane rupture. This could be due to a low interfacial tension between the phases, leading to droplets with thinner organic layer. High amounts of surfactant (3 wt.%) lead to “super-stable” primary emulsions being difficult to break after the whole permeation process.



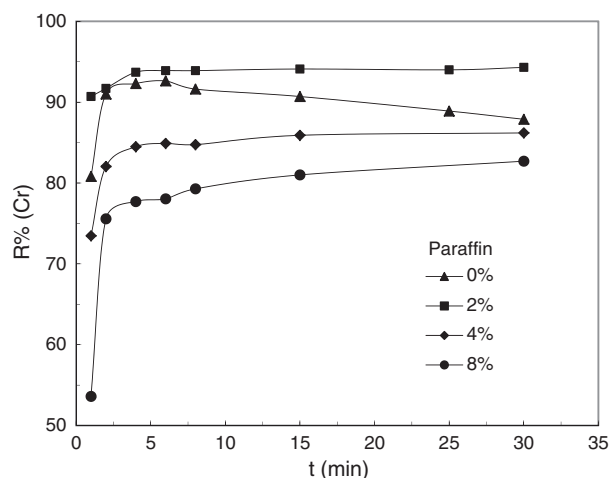
**Fig. 4.** Effect of surfactant concentration on ELM stability and Cr(III) removal. Primary emulsion (E): organic phase (O) 0.5 M PC-88A, 0–3 wt.% Span-80, 2% paraffin, kerosene; stripping phase (S) [(NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] = 0.1 M. Feed phase (F): [Cr(III)] = 2.115 × 10<sup>-3</sup> M buffered at pH = 5; volume ratios O/S = 1 and F/E = 10; stirring rate = 500 rpm.

These results and the above comments indicate that 2% w/w of Span 80 in the organic phase is the most adequate quantity to stabilize the primary emulsion. Analogous results were found by Goya et al. [34] who studied the influence of Span 80 on the % removal of Cr(VI) varying the surfactant concentration from 1 to 5%. These authors observed that with increase in surfactant concentration from 1 to 3% (w/w) the % removal of Cr increases. Nevertheless, the overall efficiency keeps on decreasing with further increase in Span 80 concentrations. They attributed this result to the enhancement of mass transfer resistance and osmotic swelling induced by a large amount of surfactant present in the system. Authors concluded that 3% (w/w) of surfactant concentration was found to be an optimum value in order to compensate the mass transfer resistance and osmotic swelling.

### 3.2.2. Effect of paraffin

The use of paraffin as additive of the organic phase allows controlling the viscosity and liquid membrane thickness. An augment of paraffin increases the membrane viscosity increasing emulsion stability and life time [19,28–30]. Chacravarti et al. [19] studied the effect of the variation of the oil-membrane constituents (kerosene and liquid paraffin) in ELM for removal of Cr(VI) from simulated waste water. They found that the increase in the paraffin content produces an increase in the emulsion viscosity and a decrease in the size of the internal phase droplets, hindering the Cr extraction. The same result was reported by He et al. [30] in their analysis of Cd(II) kinetic transport reactions in ELM. They found that the diffusion of the carrier-cadmium complex from debulk membrane to the membrane/stripping phase interface decreases with increase in paraffin content.

A series of Cr permeation-recovery tests were carried out to find out the optimum amount of paraffin to be added in the organic phase. The operating conditions were: paraffin in the range of 0–8%; PC-88A 0.5 M; 2% Span 80; kerosene; 0.1 M of ammonium persulfate; volume ratio O/S = 1; feed solution  $2.115 \times 10^{-3}$  M Cr(III) buffered at pH = 5 and F/E = 10. Fig. 5 shows that when organic phase without paraffin was used the percentage of chromium recovery increases during the first 5 min reaching a maximum value ( $\approx 93\%$ ) and then start to decline steadily with operation time. This was owing to the low stability of the ELM which makes the emulsion begins to break after few minutes of operation, allowing mixing up the stripping phase with the feed solution, reducing the recovery efficiency. Fig. 5 confirms that the presence of paraffin ( $\geq 2\%$ ) produces highly stable ELM within the operational time (30 min). However, when paraffin



**Fig. 5.** Effect of paraffin concentration on ELM stability and Cr(III) removal. Primary emulsion (E): organic phase (O) 0.5 M PC-88A, 2 wt.% Span-80, 0–8% paraffin, kerosene; stripping phase (S)  $[(\text{NH}_4)_2\text{S}_2\text{O}_8] = 0.1$  M. Feed phase (F):  $[\text{Cr}(\text{III})] = 2.115 \times 10^{-3}$  M buffered at pH = 5; volume ratios O/S = 1 and F/E = 10; stirring rate = 500 rpm.

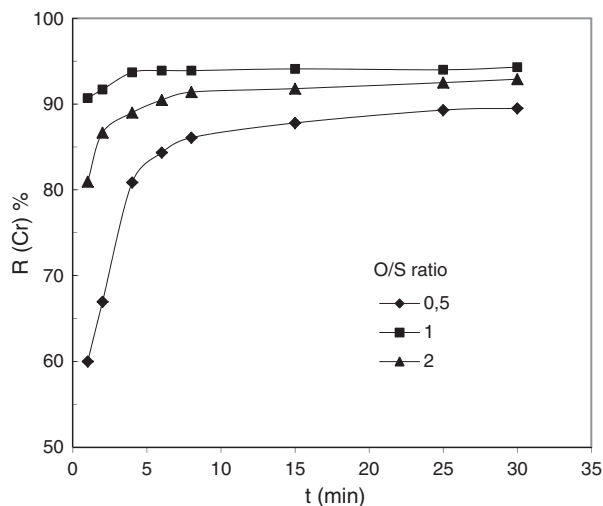
surpasses 2% it produces a decrease of the recovery rate of the metallic ion because of an increase in the viscosity of the ELM, which brings about a decrease in the chromium complex diffusion coefficients. As a conclusion, the addition of 2% of paraffin showed the best ELM efficiency; a very stable liquid membrane and 94% of chromium recovery during the first 5 min of operational time.

### 3.2.3. Effect of O/S volume ratio

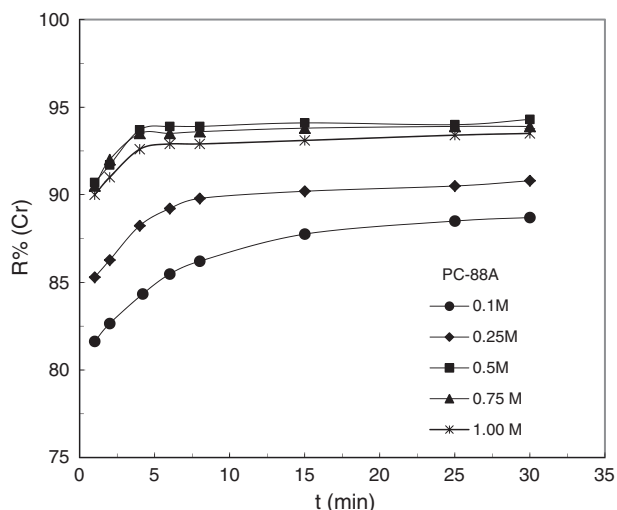
The organic phase to the stripping phase volume ratios of the primary emulsion was varied between 0.5 and 2, keeping the other parameters constant, PC-88A 0.5 M; 2% paraffin; 2% surfactant; 0.1 M of ammonium persulfate; feed solution  $2.115 \times 10^{-3}$  M Cr(III) buffered at pH = 5 and F/E = 10. The chromium recovery results are represented in Fig. 6. It can be observed that good emulsion stability was obtained in the range of O/S volume ratio analyzed, however the O/S = 1 showed the higher rate of chromium recovery. These results were similar to Chakravarti et al. [19]. They attribute this behavior to a less effective interfacial surface in the case of an O/S > 1 and, on the other hand, to the higher viscosity emulsion arising from a larger volume of stripping solution (O/S < 1). Comparable results were obtained by Kumbasar et al. [35]. In the case of O/S < 1 these authors assumed that increasing the stripping phase volume the emulsion becomes unstable and leads to a leakage of the internal phase into the external phase, increasing in viscosity, which leads to larger globules.

### 3.2.4. Effect of the carrier concentration

PC-88A concentration was varied from 0.1 to 1 M, and the other experimental conditions were: O/S = 1; 0.1 M solution of ammonium persulfate; 2% Span 80; 2% paraffin; kerosene; feed solution  $2.115 \times 10^{-3}$  M Cr(III) buffered at pH = 5, and F/E = 10. Fig. 7 shows that an increase in the PC-88A concentration favored the Cr(III) recovery rate until reaching a concentration of 0.5 M where the percentage of recuperation was  $R \approx 94\%$  during the first 5 min of operation time. Higher PC-88A concentration (0.75–1 M) showed a slight decrease in % R of Cr(III) removal rate. We account this behavior in part to the viscosity of the liquid organic membrane and its effect on chromium complexes transport through the ELM. When the PC-88A concentration increases there are two main factors involved in the chromium transport: i) an increase in the amount available of carrier which leads to a higher amount of chromium complex at feed aqueous-organic membrane interface and, ii) an increase in



**Fig. 6.** Effect of O/S volume ratio in the ELM stability and Cr(III) removal. Primary emulsion (E): organic phase (O) 0.5 M PC-88A, 2 wt.% Span-80, 2% paraffin, kerosene; stripping phase (S)  $[(\text{NH}_4)_2\text{S}_2\text{O}_8] = 0.1$  M. Feed phase (F):  $[\text{Cr}(\text{III})] = 2.115 \times 10^{-3}$  M buffered at pH = 5; volume ratios O/S = 0.5–2 and F/E = 10; stirring rate = 500 rpm.

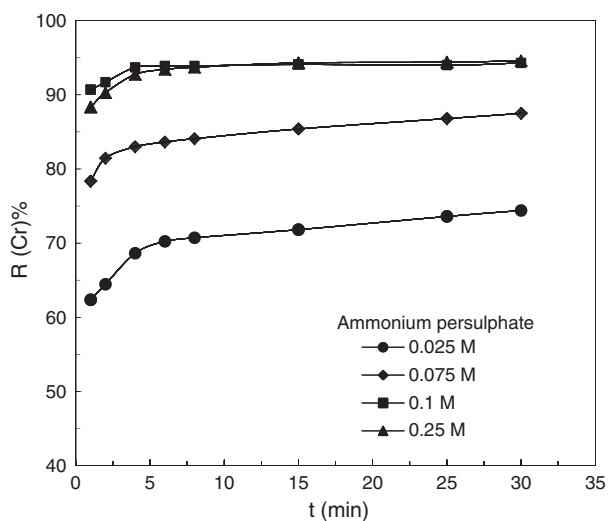


**Fig. 7.** Effect of PC-88A concentration in the organic phase on Cr(III) recovery. Primary emulsion (E): organic phase (O) 0.1–1 M PC-88A, 2 wt.% Span-80, 2% paraffin, kerosene; stripping phase (S)  $[(\text{NH}_4)_2\text{S}_2\text{O}_8] = 0.1$  M. Feed phase (F):  $[\text{Cr}(\text{III})] = 2.115 \times 10^{-3}$  M buffered at pH = 5; volume ratio O/S = 1 and F/E = 10; stirring rate = 500 rpm.

the organic phase viscosity (Table 1) which brings about a decrease in the complex coefficient diffusion (lower transport rate). These opposite effects result in a maximum chromium removal rate at PC-88A  $\geq 0.5$  M. Analogous results and conclusions related with the effect of carrier concentration on metal ion transport through different liquid membranes were obtained by other authors [15,34,36].

### 3.2.5. Effect of the $(\text{NH}_4)_2\text{S}_2\text{O}_8$ concentration in the stripping solution

Based on the chromium stripping studies, ammonium persulfate solutions in concentration from 0.025 to 0.1 M were examined. The other experimental conditions were: O/S = 1; PC-88A 0.5 M; 2% Span 80; 2% paraffin; kerosene; feed solution  $2.115 \times 10^{-3}$  M Cr(III) buffered at pH = 5, and F/E = 10. As can be expected, the recovery rate of Cr(III) increases as the ammonium persulfate concentration in the stripping phase increases up to 0.1 M (Fig. 8). When the persulfate concentration was 0.25 M the same removal rate of 0.1 M was practically achieved (94% in the first 5 min of operational



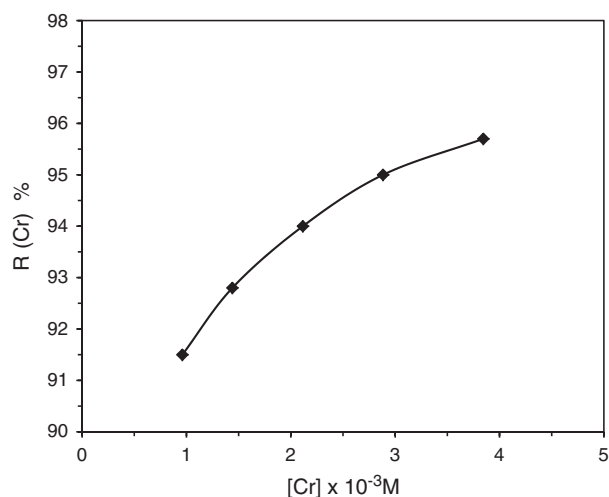
**Fig. 8.** Effect of the ammonium persulfate concentration on Cr(III) recovery. Primary emulsion (E): organic phase (O) 0.5 M PC-88A, 2 wt.% Span-80, 2% paraffin, kerosene; stripping phase (S)  $[(\text{NH}_4)_2\text{S}_2\text{O}_8] = 0.025$ –0.25 M. Feed phase (F):  $[\text{Cr}(\text{III})] = 2.115 \times 10^{-3}$  M buffered at pH = 5; volume ratio O/S = 1 and F/E = 10; stirring rate = 500 rpm.

time). This fact indicates that when the Cr(III) concentration in the feed solution was  $2.115 \times 10^{-3}$  mol L<sup>-1</sup>, strippant concentration of 0.1 M provides a sufficient amount of persulfate to oxidize Cr(III) to Cr(VI). These results are in agreement with the liquid–liquid chromium stripping tests. In their analysis of ammonium persulfate concentration effect on Cr(III) recovery using 1 M of D2EHPA as carrier Acosta et al. [28] also found that the chromium removal increases with the increase of the ammonium persulfate reaching similar recovery rate when persulfate concentration was higher than 0.7 M. Their results showed that a maximum of 60% and 98% of Cr recovery can be achieved after 35 min of operational time when 0.1 M and 1 M of persulfate were used respectively.

### 3.2.6. Effect of Cr(III) concentration in the feed solution

Effect of variation of Cr(III) concentration in the range of 0.961–3.845 M was studied. Experimental tests were carried out under the same previous optimized parameters, O/S = 1; PC-88A 0.5 M; 2% Span 80; 2% paraffin; kerosene; stripping solution 0.1 M; Cr(III) buffered at pH = 5, and F/E = 10; and stirring speed of 500 rpm. Fig. 9 shows R (Cr) % varies with metal concentration. It was observed that R (Cr) % increases with an increase in Cr(III) concentration. It is well known that many elementary steps are involved during the metal transport in both supported and emulsion liquid membranes [37], such as: i) diffusion of the metal ions through the stagnant layers of feed and stripping aqueous solutions; ii) complexation and de-complexation reactions at organic–aqueous interface; and iii) diffusion of the carrier and metal-carrier in the organic membrane phase; among others. Generally, the complexation and de-complexation reactions do not show chemical limitations, because reaction rates in the membrane are very large compared than diffusion rate. In this case, the metal ion transport through the liquid membrane is mainly governed by the i) and iii) steps, where the metal transport through the stagnant layer and organic membrane phase is usually represented by the Fick's law.

Fig. 9 shows that the recovery rate of chromium gradually increases with the augment of Cr(III) concentration in the feed. This behavior is in agreement with the above assumptions. According with the Fick's law, an increase in the chromium feed concentration will raise the chromium driving force in both, stagnant aqueous layer and organic phase, which in turn produce an increase in the overall chromium flux rate through the ELM. Related conclusions have been arrived by Alguacil et al. [38] and Venkateswaran and Palanivelu [39].



**Fig. 9.** Effect of Cr(III) concentration in the feed solution on Cr(III) recovery. Primary emulsion (E): organic phase (O) 0.5 M PC-88A, 2 wt.% Span-80, 2% paraffin, kerosene; stripping phase (S)  $[(\text{NH}_4)_2\text{S}_2\text{O}_8] = 0.1$  M. Feed phase (F):  $[\text{Cr}(\text{III})] = 0.96$ –3.845  $\times 10^{-3}$  M buffered at pH = 5; volume ratio O/S = 1 and F/E = 10; stirring rate = 500 rpm.

### 3.2.7. De-emulsification of primary emulsion

After every ELM pertraction experiment (30 min of operational time), the primary emulsion was separated from the feed solution by filtration under vacuum using a 0.5  $\mu\text{m}$  membrane filter. The primary emulsion was then broken using a Cole Parmer Ultrasonic Processor (500–750 W, 20 kHz). The organic phase and the stripping aqueous phase were separated by decantation. The chromium concentration in the stripping solution and in the feed solution was determined. The chromium mass balance closed within an error of  $\pm 10\%$ . The released organic phase containing the kerosene solvent with the carrier PC-88A, the light paraffin and the surfactant can be again used to prepare a new primary emulsion.

### 3.3. Transport mechanism of Cr(III)

The ELM system is formed by the organic phase and two aqueous phases, one is the Cr(III) feed solution and the other is the ammonium persulfate stripping solution. The organic phase or liquid membrane separates both aqueous phases forming two aqueous-organic interfaces. The transport of chromium ion from the feed solution to the stripping solution can be considered to be composed of many elementary steps, among them: chromium species diffusion through the stagnant layer of aqueous phases; interfacial transfer kinetics of the chromium species; interfacial reactions of chromium complexes; and diffusion of chromium complexes through the organic phase.

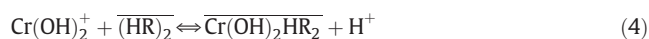
The kinetics of the extraction and stripping reactions play an important role in the Cr(III) transport. According with our experimental

results, the following extraction and stripping reactions were proposed:

#### 3.3.1. Extraction reactions

The Cr(III) ion species reacts with the carrier present in the organic phase. The carrier PC-88A is known to dimerize in nonpolar aliphatic solvents [40]. As reported in Fig. 1, the distribution of chromium (III) species in aqueous solution at different pH, indicates that at pH 5 the presence of  $\text{Cr}(\text{OH})_2^{2+}$  is nearly 75%, and that of  $\text{Cr}^{3+}$  and  $\text{Cr}(\text{OH})_2^+$  are around 7% and 18% respectively. Consequently, the complexes formed during the extraction process at pH = 5 are mainly concerned to the reactions between the dimer PC-88A (denoted as  $(\text{HR})_2$ ) with predominant ion specie  $\text{Cr}(\text{OH})_2^{2+}$  and in lesser extension with  $\text{Cr}^{3+}$  and  $\text{Cr}(\text{OH})_2^+$  species. From this, the following complex reactions at equilibrium were proposed:

Reaction 1



Reaction 2



Reaction 3



where the upper bar indicates organic phase condition.

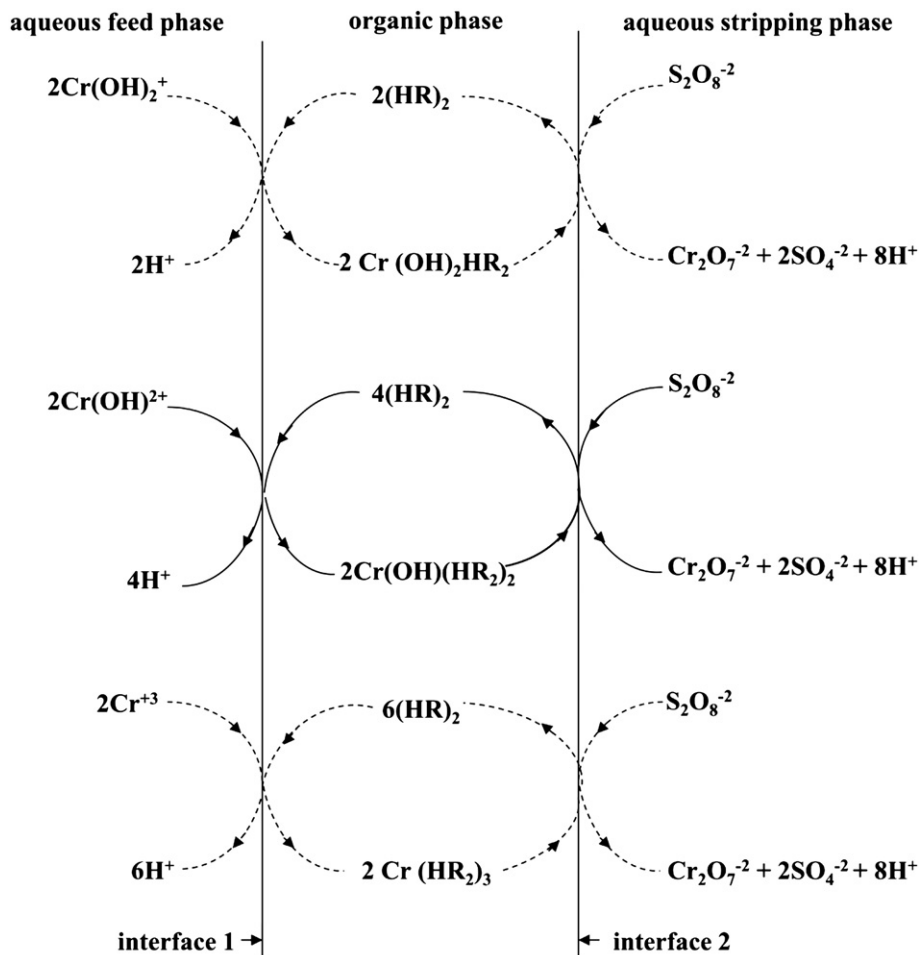
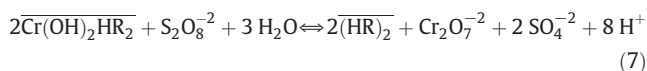


Fig. 10. Schematic representation of Cr(III) facilitated transport with PC-88A through the ELM.

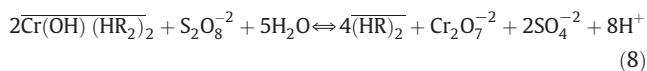
### 3.3.2. Stripping reactions

According with the extraction reactions assumed above, the following stripping reactions were suggested

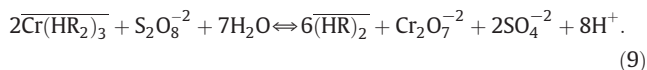
#### Reaction 4



#### Reaction 5



#### Reaction 6



### 3.3.3. Transport mechanisms of Cr(III)

From the above reactions, it can be considered that there is a facilitated transport of Cr(III) through the ELM represented by the following main steps: i) the Cr(III) species from the feed solution reacts with the carrier at the organic-feed aqueous interface according with Reaction 1 and in lesser extension with Reactions 2 and 3; ii) diffusion of the chromium-carrier complexes through the organic phase; iii) chromium-carrier complexes decomposition at organic-stripping aqueous interface due to oxidation of Cr(III) to Cr(VI) (Reactions 4, 5 and 6), allowing chromium ion removal and regenerating the PC-88A carrier; and iv) carrier diffusion from the organic-stripping interface to the organic-feed interface.

The proposed transport mechanism of Cr(III) is schematized in Fig. 10, in which the dashed lines indicate low contribution of the  $\text{Cr}^{3+}$  and  $\text{Cr}(\text{OH})_2^+$  species on the overall transport of Cr(III) through the ELM.

## 4. Conclusions

The results provide important experimental conditions for Cr(III) facilitated transport of PC-88A by using emulsion liquid membranes. The results indicated that: a gradual increase of light paraffin in the organic phase improved the ELM stability, however, this increase produced a decrease in the metal ion transport, being 2% the optimal amount of paraffin; the minimum amount of Span 80 to stabilize the membrane was 2%; the appropriated volume ratio between the stripping aqueous phase and organic phase (primary emulsion) for the extraction of Cr(III) was O/S = 1. Under the above operational conditions and using  $2.115 \times 10^{-3}$  M of Cr(III) in the feed solution, 0.5 M of PC-88A of carrier and 0.1 M of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  in the stripping phase, a total recovery of 94% of Cr(III) during the first 5 min can be achieved. These results show the potential application of the ELM technique to be used for Cr(III) ion recovery or removal from the effluents coming from industries such as electroplating, textile dyeing, and tannery.

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