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Removal and recovery of Cr (III) with emulsion liquid membranes

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ABSTRACT

This work is an experimental study of the removal and recovery of Cr(III) ion from aqueous solutions using the emulsion liquid membrane (ELM) technique. The ELM is a solution of di(2-ethylhexyl) phosphoric acid (D2EHPA) in kerosene as carrier and sorbitan monooleate SPAN 80 as surfactant. The transport capacity of the metallic ion in the ELM and the best conditions of the feed and stripping solutions in batch tests were determined. The results obtained show a good yield in Cr(III) recovery reaching 100% in a relatively short period of time (30 min) with the following operational conditions: feed solution of Cr(III) pH = 4, stripping solution of 5 mol L^{-1} sulfuric acid or 1 mol L^{-1} ammonium persulphate, and an ELM made up of 1 mol L^{-1} D2EHPA in kerosene; 4% (w/w) paraffin and 2% (w/w) SPAN 80.

Keywords: Chromium; Extraction; Emulsion liquid membrane

1. Introduction

Chromium is a heavy metal of common and extensive use in several industries such as textile, metal finishing, tanning, electroplating, etc. Its disposal as wastewater harms the environment.

With respect to chromium removal from industrial effluents, several methods have been developed such as chemical precipitation [1,2], ionic exchange [3,4], solvent extraction [5,6], membrane systems [7,8], absorption [9], etc. The most widespread conventional method for Cr(VI) removal is precipitation. Another alternative is the use of extraction processes (SX) [5,6] with solvents by using liquid organic extractants. This technology has been widely used for recovery and removal of chromium in hydro-metallurgy and tanning wastewater [10]. The reason for using this method in metal ion separation and enhancement from diluted solutions is the extractant high selectivity to metal. Nonetheless, there are many operational difficulties such as a large inventory of extractants, fairly large plants to obtain the required separations, loss of solvent due to organic compound solubility in aqueous solutions, volatilization of diluents and/or degradation of organic compounds [11].

Due to the advantages of these membranes, several recent studies on an alternative technique to traditional SX operations have been carried out using liquid membranes for chromium selected separation and concentration of effluents. Hochhauser and Cussler [12] studied the separation of Cr(VI) from aqueous solutions with emulsion liquid membranes having tertiary amines as extractant and Span 80 as surfactant. They developed an expression for chromium flow in this system considering that emulsion globules may be idealized as a flat film of constant thickness with a negligible film resistance in the aqueous phase. In this simplified system, it is assumed that all internal drops encapsulated in an emulsion globule are well mixed and they coalesce in a simple drop surrounded by a hollow spherical layer of membrane

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phase. Fuller and Li [13] analyzed Cr(VI) and zinc extraction of effluents from ELM cooling towers. The ELM was formed by polyamide as surfactant, Aliquat 336 as carrier and nonyl-dodecylalcohol as the complex solvent. Molinari et al. [14] studied the separation and concentration of Cr (III), Cr (VI) and Cd (II) in supported liquid membranes of DNNSA (dinonylnaphthalene sulfonic acid), Aliquat 336 and Alamine 336 in different solvents such as o-xylene, kerosene, n-heptane and their mixtures. They analyzed the stability and regeneration of membrane, the transmembrane flow of these ions and their separation factors. They concluded that both the SLM stability and ion flow in the membrane are functions of the physicochemical characteristics of solvent-carrier mixtures. Chakravarti et al. [15] showed the results of Cr(VI) and Cu(II) separation with ELM from simulated wastewater solutions. They studied the effect of variation of oil membrane constituents, different concentrations of sulfuric acid as stripping in the internal phase, pH and the ion concentration in the refine, and the Cu(II) content in the wastewater. They found out that the main cause of Cr(VI) transport was the ion-exchange behavior of carriers in the membrane and the coupled counter-transport resembling a "chemical pump". They found out that the application of the reaction site model and involvement of a pseudo-first-order process reasonably justified the transport method of Cu(II) separation. Bhowal et al. [16] developed a mathematical model for Cr(VI) extraction from acid solutions in ELM using Aliquat 336 as extractant and NaOH as acceptor internal phase. They discussed the simultaneous reactions involved between Cr(VI) and Aliquat 336 in the organic phase and Cr (VI) with hydroxyl anions in the aqueous phase. The charge balance equation takes into account the distribution of Cr(VI) with different pH values. The reversible reaction considered in this model is more realistic as exemplified by various researchers for non-carrier membrane.

The aim of the present work is to obtain the better experimental conditions for Cr(III) transport using the ELM technique. The ELM contains D2EHPA in kerosene as carrier and SPAN 80 as surfactant. The effect of carrier concentration on the membrane and H_2SO_4 or $(NH_4)_2S_2O_8$ concentrations in the stripping solution was analyzed. Also, the influence of paraffin addition to the ELM, the effect of aqueous/organic ratios on the primary emulsion, and feed solution/emulsion ratios in both, the ELM stability and Cr(VI) transport were examined.

2. Experimental

2.1. Materials

Extractant carrier di (2-ethyl-hexyl) phosphoric acid (D2EHPA) AR grade, molecular weight = 322,43 g. mol^{-1} density $\rho = 1.06$ g/cm^3, and pure kerosene b.p. = 200–300°C, $\rho = 0.8$ g/cm^3, $\eta^{20} = 1.44$ kg m^{-1} s^{-1} and aromatic content <25 vol %, were provided by Fluka. Highly-pure light paraffin $\rho = 0.87$ g.cm^{-3}, $\eta = 0.11$ kg m^{-1} s^{-1} was purchased from Riedel-de Haën. The surfactant sorbitan monooleate SPAN-80 molecular weight = 428,6 g mol^{-1}, $\rho = 0.995$ g/cm^3 was purchased from ICI Surfactants. The feed chromium solutions were prepared with standard solutions of Cr(III) Tritisol AR grade (Merck). Other chemical reactants such as H_2SO_4 and $(NH_4)_2S_2O_8$ were analytically graded.

2.2. Liquid–liquid equilibrium extraction and stripping tests

In a decantation vial, equal 10-mL volumes of Cr(III) aqueous solutions and organic phase were contacted and mechanically agitated for 6 h at 298 K. The extraction aqueous solutions consisted in Cr solutions 1.92×10^{-3} mol L^{-1} (100 ppm) at different pH. The range of pH values was 0.5 to 5 adjusted with sulfuric acid. The extraction organic phase was a D2EHPA solution 0.1 mol L^{-1} in kerosene.

For stripping tests, an organic phase D2EHPA 0.1 mol L^{-1} in kerosene containing 1.9×10^{-3} mol. L^{-1} of Cr(III) was used. Two different reactants as stripping aqueous solutions were used, namely: (1) H_2SO_4 in a range of 0.5 to 5 mol L^{-1}, and (2) $(NH_4)_2S_2O_8$ in a range of 0 to 2 mol L^{-1}.

Total chromium contained in the aqueous phase was determined by atomic absorption spectrometry using a Varian 50AA spectrometer. The pH of the aqueous solution was determined by a Metröm pHmeter.

2.3. Preparation of primary emulsion

The primary emulsions, water-in-oil type denoted as E, were prepared at 298K according with the following experimental protocol:

1. The organic phase (O) was prepared using kerosene as solvent, containing the following compounds: 0–10% (w/w) of light liquid paraffin, extractant D2EHPA in a range of 0.1 to 1.25 mol L^{-1}, and 2% (w/w) of surfactant Span 80. According to preliminary tests, this amount of surfactant was the most adequate to stabilize the primary emulsion.

2. The proper amounts of the organic phase (O) and the stripping aqueous phase (S) were placed into in a 0.25 L glass. Volume ratios of the organic phase and the internal aqueous phase (O/S) used in the experiments, were:

- E(1):O/S = 25 mL/62.5 mL = 0.4;
- E(2):O/S = 40 mL/40 mL = 1;
- E(3):O/S = 50 mL/25 mL = 2

3. Both liquid phases were intensely stirred at a constant stirring speed of 4500 rpm during 20 min by

Table 1
Paraffin concentration, organic phase viscosity, and diffusion coefficient of metallic complex

Paraffin liquid (% w/w)	0	1	2	4	8	10
Viscosity, η_B (cp)	38	40	425	48	65	75
Diffusion coefficient, D_{AB} ($\times 10^9$ m/s^2)	874	830	782	692	511	443

means of a high-speed digital stirrer LabTech model. LHG-15D (maximum speed 25,000 rpm; rotor = ϕ12.7 mm, stator = ϕ18 mm).

4. Organic phases and emulsion viscosities were measured with a Cannon-Fenske viscometer and a Brookfield DVIII rotational viscometer, respectively. The viscosity values are given in Table 1.

2.4. Chromium permeation and recovery tests

Secondary emulsions were prepared in a 1 L precipitation vessel mixing 50 mL of the primary emulsion (E) with 500 mL of the feed aqueous phase of Cr(III) at pH = 4 (F). This volume ratio (F/E = 10) is the most convenient for Cr(III) permeation recovery tests at laboratory scale according to the literature [12,15,16]. Both solutions were mixed by a magnetic bar at a mixing speed of 600–700 rev. min^{-1} measured with an optic tachometer. This results in a system of three liquid phases stabilized by the emulsionant. The three phases are the following: stripping aqueous phase, organic phase of extractant/membrane, and the feed aqueous phase. The experimental Cr mass transport from the feed solution to the stripping aqueous droplets was carried out at 298K.

Samples of 5 mL were gathered periodically until equilibrium conditions were reached. Secondary emulsions were filtered to separate the primary emulsion from feed solution. The chromium concentration in the feed phase was determined by atomic absorption spectrophotometry.

3. Results and discussion

3.1. Chromium extraction and stripping at equilibrium

To establish adequate operational conditions of Cr(III) extraction and stripping, and to determine representative chemical reactions in interfaces, tests of liquid–liquid extraction stripping were carried out. The values of metal extraction (Ex%) and stripping (St%) percentages were estimated as follows:

$$Ex\% = \frac{[Cr]_{ia} - [Cr]_{a}}{[Cr]_{ia}} \times 100 \quad (1)$$

$$St\% = \frac{[Cr]_{a}}{[Cr]_{io}} \times 100 \quad (2)$$

where $[Cr]_{ia}$ and $[Cr]_a$ are initial and final concentrations of Cr ion in the aqueous phase, respectively, and $[Cr]_{io}$ the initial concentration of Cr loaded in the organic phase.

The extraction curve obtained for Cr(III) ion solutions in a pH range of 0.5–4.5 with D2EHPA is shown in Fig. 1. These results indicate that the Cr extraction percentage is dependent on operation pH. Cr(III) extraction increased as equilibrium pH increased as well. It reached its maximum value (Ex =100%) around pH 4 and then decreased. This behavior is consistent with a high stability of Cr(III) aqueous and hydroxyl complexes, according to the following reactions [20]:

$$\mathrm{pH} \cong \left[\mathrm{Cr(H_2O)_6}\right]^{3+}_{aq} + 3\left[\mathrm{(HR)_2}\right]_{org} \Leftrightarrow \left[\mathrm{Cr(HR_2)_3}\right]_{org} + 3\left(\mathrm{H^+}\right)_{aq} + 6\mathrm{H_2O} \quad (3)$$

$$\mathrm{pH} > 4.5 \left[\mathrm{Cr(H_2O)_6}\right]^{3+}_{aq} + 3\left(\mathrm{OH^-}\right)_{aq} \Leftrightarrow \left[\mathrm{Cr(OH)_3(H_2O)_3}\right]_{aq} (\mathrm{pptate}) + 3\mathrm{H_2O} \quad (4)$$

where HR denotes the extractant D2EHPA, and (aq) and (org) subscripts indicate aqueous and organic phase conditions, respectively. When pH >4.5, the formation of a $Cr(OH)_3$ precipitate tends to decrease the effective aqueous concentration of Cr(III) decreasing the extraction.

A qualitative analysis of Fig. 1 shows the selection of pH operational conditions on both sides of the ELM to reach the maximum transport of chromium. In this case, a feed solution (external aqueous phase of the ELM) with a pH around 4 is convenient. On the other hand, the stripping solution (internal aqueous phase of the ELM) should be strongly acid leading to $Cr(HR_2)_3$ complex dissociation [inverse reaction, Eq. (3)].

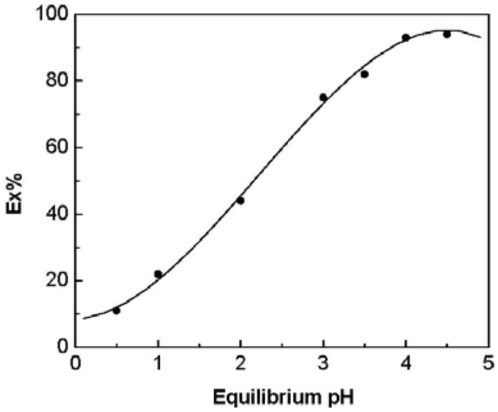

Fig. 1. Extraction of Cr(III) with D2EHPA: effect of pH.

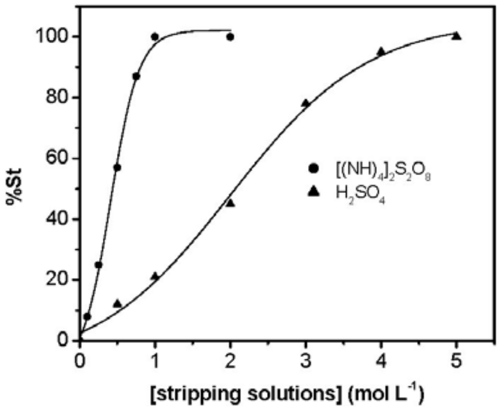

Fig. 2. Stripping of Cr(III): effect of $[H_2SO_4]$ and $[(NH_4)_2S_2O_8]$.

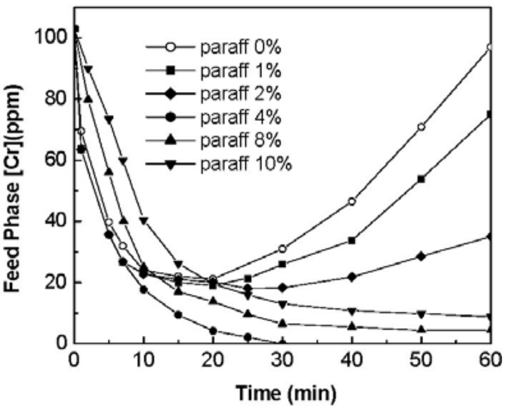

Fig. 3. Effect of paraffin concentration on Cr(III) recovery.

Another method of Cr(III) ion stripping is by means of Cr(III) oxidation to Cr(VI). A standard method for oxidizing the Cr(III) to Cr(VI) is the use of ammonium persulphate [5,21] according to the following reaction:

$$2[Cr(HR_2)_3]_{org} + 3\,[S_2O_8^{-2}]_{aq} + 7\ H_2O \Leftrightarrow (Cr_2O_7^{-2})_{aq} + 6\,(SO_4^{-2})_{aq} + 6[(HR)_2]_{org} + 8\ H^+ \tag{5}$$

Taking into account this analysis, we propose the use of two different stripping solutions in this study: (1) aqueous solutions with different concentrations of sulfuric acid (0.5–5mol L^{-1}), and (2) aqueous solutions with different concentrations of ammonium persulphate (0.1–2 mol L^{-1}).

The effect of sulfuric acid and ammonium persulphate concentration in Cr(III) stripping is shown in Fig. 2. It can be observed that both solutions are effective for metallic ion stripping, reaching a total removal of Cr(III) at a sulfuric acid concentration of 5 mol L^{-1} and an ammonium persulphate concentration of 1 mol L^{-1}.

3.2. Tests of Cr(III) permeation in the ELM

3.2.1. Effect of paraffin concentration

The use of paraffin as additive allows controlling the viscosity and liquid membrane thickness. An increase of the membrane viscosity increases emulsion stability and its permeation life time. However, when this increase surpasses certain percentage of additive, it produces a decrease of the extraction rate of the metallic ion due to the increase of the resistance to mass transport in the liquid membrane [20].

A number of Cr permeation recovery tests were carried out to find out the influence of paraffin liquid on the stability of the organic phase. In all these experiments, the following conditions were kept constant: feed aqueous phase Cr(III) 1.92×10^{-3} mol L^{-1} pH = 4, stripping internal aqueous phase of $(NH_4)_2S_2O_8$ 1 mol L^{-1}, and volume ratio of phases O/S = 1 for primary emulsion and F/E = 10 for the ELM. The organic phase consisted of D2EHPA 1 mol L^{-1}, 2% Span 80 and paraffin with kerosene as solvent. The amount of paraffin varied from 0 to 10% w/w.

The data of Cr(III) recovery in the ELM are shown in Fig. 3 where the concentration of chromium in the feed solution vs. time, and the percentage of paraffin loaded in the organic phase were outlined. Within paraffin range of 0–2%, the amount of Cr in the feed solution decreases with operation time, reaching a minimum and then it increases. This last increase in chromium concentration indicates a drop breakdown of primary emulsion.

A good stability of ELM and a satisfactory recovery of Cr(III) were obtained after an hour of operation using a paraffin concentration of 4% or higher. With this concentration, total recovery of Cr(III) was reached after 30 min. The addition of a higher percentage of paraffin in the organic phase produces a decrease of chromium rate recovery. As it was mentioned previously, this may be attributed to the increase of the viscosity in the organic phase (η_B) with the increase amount of paraffin (Table 1) which, in turn, produces a decrease of the diffusion coefficient of metallic complex (D_{AB}). The diffusion coefficient was evaluated from the Stoke–Einstein equation:

$$D_{AB} = \frac{\kappa T}{6\pi r_A \eta_B} \tag{6}$$

where κ is the Boltzman constant, T the absolute temperature, and r_A = 657 Å is the molecular complex ratio.

In the following permeation tests carried out to study other operational variables, paraffin concentration in the organic phase was set at 4% w/w.

3.2.2. Effect of volume ratio O/S on ELM performance

According to literature [23], a decrease of volume ratio between the organic and internal aqueous phases produces a decrease of the primary emulsion stability.

This may be due to both a decrease in the emulsion viscosity and an increase of the drop diameter. Consequently, to obtain a homogeneous distribution of drops and a more stable emulsion, it is necessary to find the adequate proportion between the organic phase and the internal aqueous phase.

Permeation and Cr recovery tests were carried out to establish the correct O/S volume ratios of the primary emulsion. The following experimental conditions were kept constant: the feed aqueous phase of Cr(III) 1.92×10^{-3} mol L^{-1} pH = 4, stripping internal aqueous phase of $(NH_4)_2S_2O_8$ 1 mol L^{-1}, and the volume ratio between the feed and primary emulsion is F/E=10. The organic membrane phase consisted of D2EHPA 1 mol L^{-1}, 2% Span 80 and 4% w/w paraffin in kerosene as solvent.

Fig. 4 shows the data of total chromium concentration in the feed solution versus operation time for O/S ratios of 1/2.5; 1/1; 1/0.5. The results obtained show that the ratio O/S = 1/1 is the more adequate for metallic ion recovery, extracting 100% of the ion in 30 min. These results are consistent with those obtained by other authors [3,10,15].

3.2.3. *Effect of D2EHPA concentration*

The effect of D2EHPA concentration in liquid membranes on Cr recovery is shown in Fig. 5. The D2EHPA concentration was set in a range of 0.1–1 mol L^{-1}, the other experimental conditions were the following: feed aqueous phase, solution of Cr(III) 1.92×10^{-3} mol L^{-1} at pH = 4; stripping internal aqueous phase, solution of $(NH_4)_2S_2O_8$ 1 mol L^{-1}; volume ratios O/S = 1 for primary emulsion and F/E=10 for the ELM; and organic membrane phase consisting of D2EHPA, 2% Span 80 and 4% w/w of paraffin with kerosene as solvent.

Fig. 5 shows that D2EHPA increase in the membrane favors Cr(III) separation with a maximum ion depletion in the feed solution after 30 minutes with 1 mol L^{-1} of carrier concentration.

3.2.4. *Effect of H_2SO_4 concentration in the stripping phase*

To study the effect of sulfuric acid concentration in the internal phase, it was varied in a range of 0.5–5 M in the acceptor phase, keeping the other experimental conditions as follows: feed phase, aqueous solution of Cr(III) 1.92×10^{-3} mol L^{-1} at pH = 4; internal acceptor phase, aqueous solution of H_2SO_4; membrane phase: D2EHPA 1 mol L^{-1}, 2% Span 80, and 4% paraffin and kerosene; volume ratio of phases: O/A= 1 and F/E = 10.

The effect of sulfuric acid concentration in the internal phase is shown in Fig. 6. It can be observed that a higher

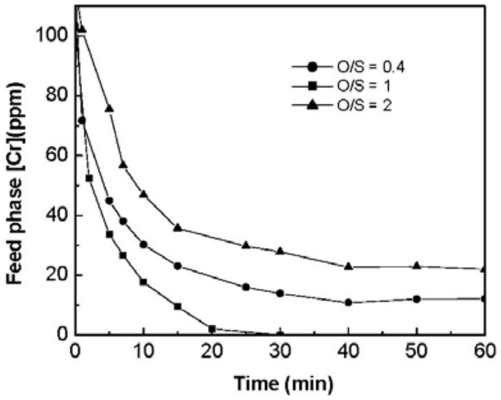

Fig. 4. Effect of O/S ratios on ELM stability.

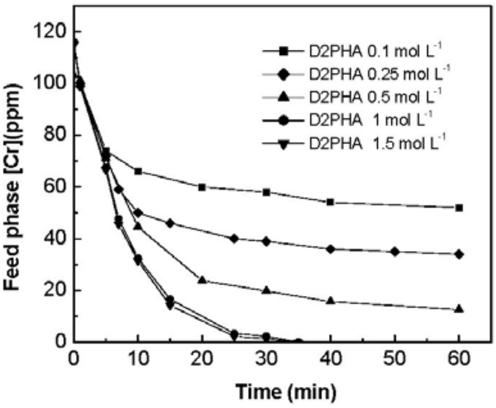

Fig. 5. Effect of [D2EHPA] on Cr(III) recovery.

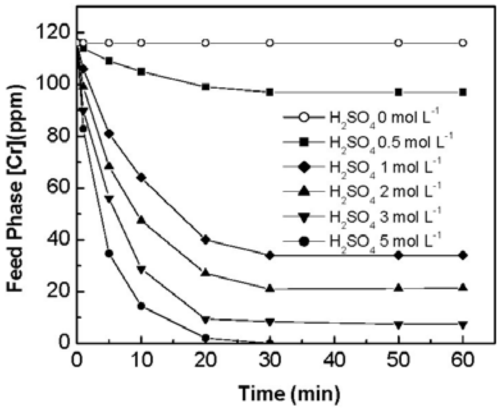

Fig. 6. Effect of $[H_2SO_4]$ on Cr(III) recovery.

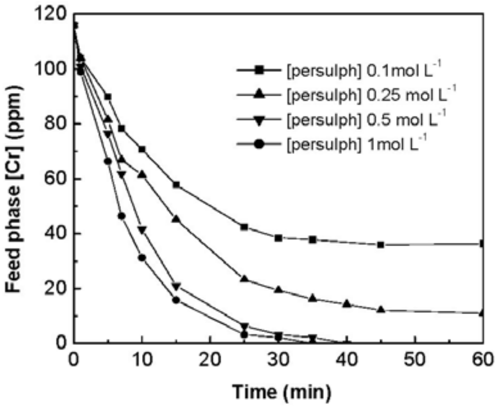

Fig. 7. Effect of $[(NH_4)_2S_2O_8]$ on Cr(III) recovery.

concentration of sulfuric acid in the stripping phase favors Cr(III) separation. A total recovery of Cr is observed when the sulfuric acid concentration in the acceptor or stripping phase is higher than 5 mol L^{-1} corroborating that it is necessary a medium strongly acid in the acceptor phase to break the metal-extractant complex in the extraction stage [Eq. (3)]. Permeation tests using pure H_2O as acceptor phase were carried out for long periods of 2–3 h with the result that Cr is not at all transported through the liquid organic membrane.

3.2.5. *Effect of $(NH_4)_2S_2O_8$ concentration in the stripping phase*

In our analysis in Section 3.1, we propose the use of ammonium persulphate as stripping solution. Aqueous solutions of persulphate in a range of 0.5–1 M were used keeping the other experimental variables as follows: feed phase, aqueous solution of Cr(III) 1.92×10^{-3} mol L^{-1} at pH = 4; internal acceptor phase, aqueous solution with different $(NH_4)_2S_2O_8$ concentrations; membrane phase formed by D2EHPA 1 mol L^{-1}, 2% Span 80 and 4% paraffin, and solvent kerosene; volume ratio of phases O/A = 1 and F/E = 10.

Fig. 7 shows the effect of ammonium persulphate concentration in the acceptor solution on Cr(III) permeability. The extraction of chromium increases with the increase of the persulphate in the internal acceptor phase until reaching its maximum at a concentration of about 1 mol L^{-1} of ammonium persulphate.

4. Conclusions

This work deals with the experimental conditions of a facilitated transport of Cr(III) using emulsified liquid membranes. Experimental results of liquid–liquid extraction indicate that a higher extraction of chromium is obtained when the pH of the feed solution has a value of 4. Under these conditions, there is a better availability of the metallic ion for the formation of complex D2EHPA-Cr in the feed aqueous-organic interphase.

The results of the liquid–liquid stripping tests indicate that total removal of Cr(III) can be achieved using a strongly acid medium (sulfuric acid) as stripping solution, or with ammonium persulphate (Cr(III) oxidant agent) in the stripping solution. Sulfuric acid allows the complex $Cr(HR_2)_3$ dissociation at the organic-stripping solution interphase. The presence of ammonium persulphate in the stripping solution promotes the oxidation of Cr (III) to Cr (VI) allowing the back-extraction of Cr(III) from the organic phase to the aqueous solution.

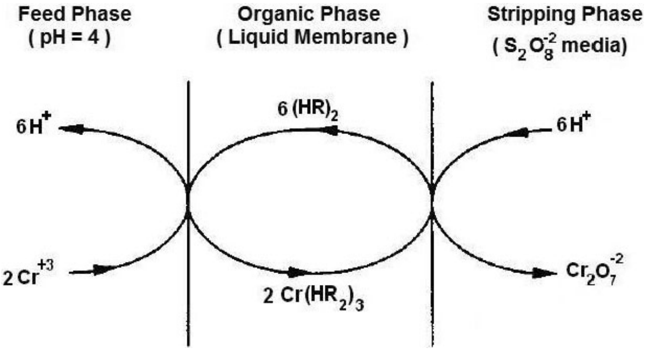

Fig. 8. Schematic representation of Cr (III) facilitated transport with D2EHPA through the ELM.

The experimental results obtained from Cr(III) permeation through the ELM indicate a significant recovery of Cr(III) with sulfuric acid in the acceptor solution, reaching a total removal of the metallic ion from the feed phase when the acid concentration is 5 mol L^{-1}. The presence of $(NH_4)_2S_2O_8$ in the internal acceptor solution promotes the Cr(III) transport reaching its maximum when its concentration is around 0.5 mol L^{-1}. These results show more convenient experimental conditions of Cr(III) removal from acid technique since the metallic ion can be extracted without using high concentrations of acid in the stripping solution. The possible transport mechanism of chromium ion in the emulsified liquid membrane is outlined in Fig. 8.

The experimental conditions to achieve the best ELM performance for chromium recovery and liquid membrane stability were as follows: volume ratio of organic-stripping phases O/S=1 for primary emulsion (E), with an organic phase formed by 1 mol L^{-1} of extractant D2EHPA, 2% of emulsificant Span 80 and 4% w/w of liquid paraffin in kerosene; ELM from a volume ratio of aqueous feed-primary emulsion F/E = 10, with the feed chromium solution at pH = 4.

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