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Transport of Cr(VI) using an advanced membrane technology and ($PJMTH^+NO_3^-$) ionic liquid derived from amine Primene JMT as green chemicals

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ABSTRACT

The extraction of Cr(VI) from acidic solutions through pseudo-emulsion-based membrane strip dispersion (PEMSD) was conducted in a microporous hydrophobic polyvinylidenedifluoride (PVDF) membrane support and permeation cell. As organic extractant ionic liquids derived from the primary amine Primene JMT in cumene was used. The acidic feed solution containing Cr(VI) was placed in one side of the permeation cell, whereas the pseudo-emulsion of Primene JMT/cumene and acidic solution was placed in the other side of the cell, using a single microporous hydrophobic PVDF membrane support for extraction and stripping. In PEMSD the aqueous acidic (HNO_3) solution was dispersed into the organic (Primene JMT/cumene) membrane solution with a mixing arrangement (impeller stirrer) designed to form a strip dispersion. This operation mode provides a constant supply of the ionic liquid extractant/cumene solution to the membrane pores. Various hydrodynamic and chemical parameters, either in the feed or in the pseudo-emulsion phases, were investigated. Results showed that from feed solutions in the pH 3 range, chromium removal efficiencies exceeding 90% are achieving after 3 h, whereas chromium recovery in the strip solution is dependent upon the strippant concentration. Furthermore, the performance of this carrier against other extractants was evaluated.

Keywords: Pseudo-emulsion-based membrane strip dispersion; Liquid membranes; Primene JMT; Ionic liquid; Chromium(VI); Nitrate

1. Introduction

The removal of metal ions from dilute or concentrated solutions has received a great deal of attention for the recovery of valuable metal or decontamination of effluents.

Among the various metals considered as hazardous for living organism, chromium (VI) is one of the most dangerous due to its effect on development of cancer and non-cancer diseases and therefore this metal must be removed from wastewaters [1]. Chromium is a common pollutant introduced into natural waters due to the discharge of a variety of industrial wastewaters. It is widely used in various industries (leather tanning, paint, metallurgy, electroplating, anodizing aluminum, chromate preparation, etc.)

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which could possibly contaminate the environmental waters and enter in human body.

Several technologies are being using in the removal of this element from various liquid effluents, wastewaters or aqueous solutions [2–6], though in recent years a remarkable increase in the application of liquid membranes-based technology in order to separate and/or recover this metal from different solutions is observed [1,7–13]. There are two types of liquid membranes: (1) non-supported liquid membranes, category that includes bulk liquid membranes (BLMs) and emulsion liquid membranes (ELMs), and (2) supported liquid membranes (SLMs).

In supported liquid membrane systems (SMLs), the organic solution containing carriers is placed in porous support materials and is kept there by capillary forces. Compared with other liquid membrane methods, the major advantage of the SMLs, compared with the other liquid membrane methodologies, is that the SMLs requires less organic solution for the formation of the liquid membrane, its low operation costs, minimum product contamination, no phase separation problem, selectiveness and flexibility. Though these processes are normally effective, their use have been hampered by their apparent lack of stability under long-term operation basis. Normally, this decreasing in stability is due to the loss of the organic phase filling the membrane pores that results in carrier lost. However the introduction of the new technology of SLMs with strip dispersion apparently has solved the stability problem. In this operation mode, the aqueous feed solution, containing the species to be extracted is in contact with one side of the support, whereas the aqueous strip solution is dispersed in an organic solution, containing the corresponding carrier and a diluent, in a mixer and the pseudo-emulsion formed is put into contact with the other side of the microporous support [14].

On the other hand, ionic liquids (ILs) or "green solvents" have been proposed for separation process as new solvents. They are organic salts that are liquid below 100°C and usually consist of an organic cation and a polyatomic inorganic anion. Due to their non-measurable vapor pressure, combined with the greater capillary force associated with their relatively high viscosity and the possibility of minimizing their solubility in the surrounding phases by adequate selection of the cation and the anion, it is possible to obtain very stable and environmentally friendly supported liquid membrane using ionic liquids as supported liquid phase [15].

This investigation presented the results about the transport of Cr(IV) in acidic media using the ionic liquid $PJMTH^+NO_3^-$ generated in the pseudo-emulsion phase by an *in situ* reaction between the primary amine Primene JMT and the corresponding strippant reagent (HNO_3). Various hydrodynamic conditions and chemical parameters, such as concentration of Cr(VI) and acid in the feed phase, carrier concentration in the organic solution, the strippant reagent concentration (HNO_3), variation of the stirring speed in the feed phase and the effect of varying the organic diluent, were investigated in order to obtain the most efficient transport conditions. Furthermore, the performance of the present transport system was compared against other carriers.

2. Experimental

Primary amine Primene JMT (RNH_2, where R represented highly branched aliphatic carbon chains in the C16–22 range, it is also worth to note here that the nitrogen atom is bonded to a tertiary carbon atom) was used as carrier for transport experiments in the present investigation. PJMT was supplied by the Rohm and Haas Co. This and the other extractants: Primene 81-R (Rohm and Haas Co.) (primary aliphatic amine), Hostarex A-324 (Hoechst) (tertiary amine), Cyanex 923, C-923 (Cytec Ind.) (trialkylphosphine oxide), Tri-n-butylphosphate, TBP (Fluka) (phosphoric ester), and Tri-n-decylamine, TDA (Fluka) (tertiary aliphatic amine) were used without further purification. The analytical grade diluents cumene, toluene, n-decane, and xylene (Fluka) were used. The organic phase was prepared by mixing a measured volume of the Primene JMT or the corresponding extractant with reagent grade cumene or the corresponding diluents. The ionic liquid is then generated, instantaneously, in the same pseudo-emulsion compartment by mixing this organic solution with the aqueous HNO_3 stripping phase, by the reaction:

$$RNH_{2org} + H^+_{st} + X^-_{st} \Longleftrightarrow RNH^+_3X^-_{org} \tag{1}$$

where $X = NO_3^-$; the subscripts "org" and "st" indicated the respective organic and stripping solutions of the pseudo-emulsion phase.

Stock Cr(VI) solutions were prepared by dissolving $K_2Cr_2O_7$ (Merck) in distilled water. All other chemical were of analytical reagent grade.

The solid membrane support used throughout the investigation was Millipore Durapore GVHP 4,700 of 125×10^{-4} cm thick microporous poly(vinylidene difluoride) film with nominal porosity of 75%, effective pore size of 2.2×10^{-5} cm and tortuosity of 1.67. Transport experiments were performed in a permeation cell consisting of two cubic compartments made of methacrylate and separated by the microporous membrane [16]. The membrane effective area was 11.3 cm^2, and the volume of both compartments was 200 ml (each). The feed phase and the organic/stripping pseudo-emulsion phase were mechanically stirred at 20 ± 1˚C using cylindrical glass impellers. Once the membrane support was placed in the cell, the source solution (200 ml) and the organic and stripping phases (100 ml each) were placed in the corresponding chambers and the operation begins. From the initial moment of mixing, an organic/stripping pseudo-emulsion phase was formed. After the operation was stopped (typically 3 h) the organic and the stripping phases were automatically separated (less than 2 min).

Membrane permeabilities were determined by removing samples of the feed solution periodically for analysis. Atomic absorption spectrophotometry (AAS) was used for determine the metal concentration in the feed (or the stripping phase), and data were found to be reproducible within ± 2%.

The overall permeation coefficient (P) was computed using the next equation:

$$\ln\frac{[\mathrm{Cr(VI)}]_t}{[\mathrm{Cr(VI)}]_0} = -\frac{A}{V_{\mathrm{feed}}} \times P \times t \tag{2}$$

where A is the effective membrane area (11.3 cm^2), V_{feed} is the volume of the feed phase (200 ml), $[\mathrm{Cr(VI)}]_t$ and $[\mathrm{Cr(VI)}]_0$ are the chromium concentrations in the feed phase at elapsed time t and time zero, respectively.

The percentage of Cr recovered in the stripping phase was determined using:

$$\%\,R = \frac{[\mathrm{Cr(VI)}]_{\mathrm{stripping}}}{\frac{V_{\mathrm{feed}}}{V_{\mathrm{stripping}}}([\mathrm{Cr(VI)}]_0 - [\mathrm{Cr(VI)}]_t)} \times 100 \tag{3}$$

where $[\mathrm{Cr(VI)}]_{\mathrm{stripping}}$ is the metal concentration in the stripping solution and $V_{\mathrm{stripping}}$ is the volume of the stripping solution (100 ml).

3. Results and discussion

The stoichiometry of the extracted species depends on the Cr(VI) concentration in the source phase. At the lowest Cr(VI) concentrations, $HCrO_4^-$ species is the predominant at pH values between 0–6, whereas as the Cr(VI) concentration increases, $Cr_2O_7^{2-}$ species becomes the predominant one; however, in the range of chromium concentrations investigated in the present work, $HCrO_4^-$ is always the predominant species in the feed solution [12]. Under alkaline conditions (pH > 8), Chromium(VI) exists predominantly as chromate anion.

Thus, under the present experimental conditions, the extraction or transport of Cr(VI) by the ionic liquids PJMTH$^+$NO$_3^-$ (see Eq. (1)) can be represented by the next overall reaction:

$$\mathrm{HCrO}^-_{4\,\mathrm{aq}} + \mathrm{RNH}_3^+\mathrm{X}^-_{\mathrm{org}} \Longleftrightarrow \mathrm{RNH}_3^+\mathrm{HCrO}^-_{4\,\mathrm{org}} + \mathrm{X}^-_{\mathrm{aq}} \tag{4}$$

where X = NO$_3^-$ and the subscripts "aq" and "org" refereed to the feed and organic solutions, respectively.

The ionic liquid reacts with Cr(VI) species to form the corresponding metal-carrier complex in the organic phase, releasing nitrate ions (Eq. (4)) to the feed solution. Thus, the proper metal-extraction reaction can be related to an anion exchange process and in membrane transport terms it is related to a facilitated counter transport mechanism. The driving force for metal transport is the difference in acidity between the feed and strip phases. Metal stripping using HNO_3 solutions takes place as follows:

$$\mathrm{RNH}_3^+\mathrm{HCrO}^-_{4\,\mathrm{org}} + \mathrm{X}^-_{\mathrm{st}} \Longleftrightarrow \mathrm{RNH}_3^+\mathrm{X}^-_{\mathrm{org}} + \mathrm{HCrO}^-_{4\,\mathrm{st}} \tag{5}$$

in this case, the subscript "st" referees to the strip solution.

Taking into account the reactions shown in Eqs. (4) and (5), the facilitated transport mechanism for the Cr (VI) transfer across the membrane is schematically shown in Fig. 1.

3.1. Influence of the stirring speed of the source solution

Stirring speed plays an important role in the mass transfer rate of Cr(VI). In order to achieve the effective permeation of Cr(VI) different experiments were carried out to establish adequate hydrodynamics conditions. The overall mass transfer coefficient of the membrane was studied as a function of the stirring

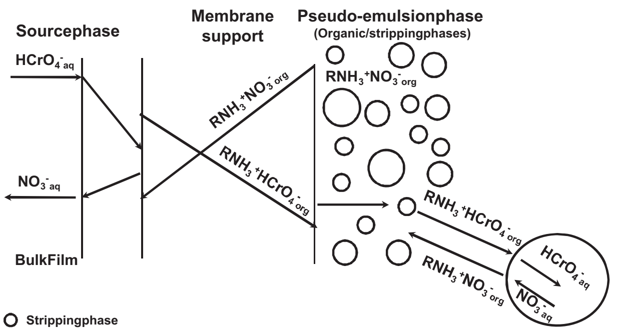

Fig. 1. Schematic profile of Cr(VI) transport in PEMSD operation.

speed (400–1,200 min^{-1}) in the feed solution side. The stirring speed of the organic/stripping (O/S) pseudo-emulsion phase was kept constant at 800 min^{-1}.

Table 1 show the overall mass transfer coefficient obtained when the stirring speed varies from 400 to 1,200 min^{-1}. P values are constant, indicating that the aqueous boundary layer thickness reached a minimum and it was not affected by the stirring speed of the feed phase. The stirring speed of 1,000 min^{-1} in the source phase was kept constant throughout the experiments conducted.

3.2. *Influence of the acid concentration in the feed solution*

The concentration of the acid in the feed solution is a parameter influencing in the extractant efficiencies. It is evident from data presented in Table 2 that the value of the overall permeation coefficient of Cr (VI) decreases with the increase in the acid concentration in the feed solution. At the acid concentration of 1 M, there is not efficient chromium (VI) transport across the membrane. This should be attributable to the similarity in the acidic conditions between the feed and stripping solutions, which makes negligible the effect of the driving force for chromium (VI) transport (see above). Thus, acid concentration in the feed solution is a critical parameter for chromium (VI) extraction.

3.3. *Effect of concentration of the stripping agent*

Different concentrations of HNO_3 were studied as stripping agent. The results were shown in Table 3. The overall permeation coefficient of Cr(VI) increases when it is increased the concentration of HNO_3 in the stripping phase and their values reached a maximum at 1.0 M acid concentration in the stripping solution. The recovery of chromium (%R) in the stripping phase increases with the increase in the concentration of HNO_3 in this solution. The maximum value of chromium stripping was obtained at 3.0 M HNO_3.

Table 1
Influence of the stirring speed on the overall permeation coefficient of Cr(VI)

Stirring speed (min^{-1})	P (cm s^{-1})
400	3.8×10^{-3}
800	3.9×10^{-3}
1,200	4.1×10^{-3}

Feed phase: 200 ml of 0.01 g l^{-1} Cr(VI). Organic/stripping phase: 100 ml of PJMT 10% v/v in cumene and 100 ml of 1.0 M HNO_3.

Table 2
Influence of the acid concentration in the feed solution on the overall permeation coefficient of Cr(VI)

[HNO_3] (M)	P (cm s^{-1})
0.0	3.9×10^{-3}
0.5	1.0×10^{-3}
1.0	No transport

Feed phase: 200 ml of 0.01 g l^{-1} Cr(VI) in various HNO_3. Organic/stripping phase: 100 ml of PJMT 10% v/v in cumene and 100 ml of 1.0 M of HNO_3[a].

Table 3
Influence of the concentration of the stripping agent on the overall permeation coefficient of Cr(VI) and metal recovery in the stripping solution

[HNO_3] (M)	P (cm s^{-1})	R (%)[a]
0.5	3.4×10^{-3}	65
1.0	3.9×10^{-3}	65
3.0	1.8×10^{-3}	80

Feed phase: 200 ml of 0.01 g l^{-1} Cr(VI). Organic/stripping phase: 100 ml of PJMT 10% v/v in cumene and 100 ml of different concentrations of HNO_3. [a]After 3 h.

3.4. *Influence of the metal concentration in the feed phase*

The effect of the Cr(VI) concentration (1.0–0.01 g l^{-1}) on the metal transport is evaluated by using flux values which are defined according to Eq. (6):

$$J = P[\text{Cr(VI)}]_0 \tag{6}$$

where J is the flux, P is the overall permeation coefficient and $[\text{Cr(VI)}]_0$ is the total metal concentration in the initial feed phase.

Table 4 shows the flux (J) and the overall permeation coefficient values for this set of experiments. It is shown that the flux is a strong function of the initial metal concentration in the feed phase, increasing its value when the metal concentration in this phase increases as expected from Eq. (6). The results also indicate that the membrane did not become saturated at either initial chromium concentration since J values are not constant with the initial metal concentrations used in this investigation.

The result obtained shows a decrease in the P value at the highest concentration of Cr(VI), 1.0 g l^{-1}, for the system. This is tentatively attributable to that at higher metal concentrations, the mass transfer of Cr (VI) that crossed the membrane is only described in terms of diffusion of metal species.

Table 4
Influence of the initial metal concentration on the overall permeation coefficient and metal flux

$[Cr]_0$ ($g\,l^{-1}$)	P ($cm\,s^{-1}$)	J ($mol\,cm^{-2}\,s^{-1}$)
0.01	3.9×10^{-3}	7.5×10^{-10}
0.1	3.5×10^{-3}	6.7×10^{-9}
1.0	3.3×10^{-3}	4.1×10^{-8}

Feed phase: 200 ml of solution containing different concentrations of Cr(VI). Organic/stripping phase: 100 ml of PJMT 10% v/v in cumene and 100 ml of 1 M HNO_3.

Table 5
Influence of the PJMT % on the overall permeation coefficient of Cr(VI)

[PJMT] (% v/v)	P ($cm\,s^{-1}$)
10	3.9×10^{-3}
20	3.9×10^{-3}
40	3.9×10^{-3}

Feed phase: 200 ml of 0.01 $g\,l^{-1}$ Cr(VI). Organic/stripping phase: 100 ml of solution containing different concentrations of PJMT in cumene and 100 ml of 1 M HNO_3.

3.5. *Influence of different carrier ($PJMTH^+NO_3^-$) concentrations on the metal transport*

The effect of carrier concentration on the overall permeation coefficient was also investigated in the range 10–40% v/v initial carrier concentration in the organic phase. Results obtained are shown in Table 5, *P* values are constant and thus these are independent of the concentration of the ionic liquid in the organic solution, this being representative of an aqueous diffusion film-controlled permeation process, thus, diffusion in the membrane is negligible if compared with the aqueous diffusion.

In this condition:

$$P = \frac{1}{\Delta_{aq}} = \frac{D_{aq}}{d_{aq}} \tag{7}$$

being Δ_{aq} the transport resistance due to diffusion by the aqueous source boundary layer, D_{aq} the average aqueous diffusion coefficient of the chromium(VI)-containing species and d_{aq} the thickness of the aqueous source boundary layer. Since, $p = 3.9 \times 10^{-3}\,cm\,s^{-1}$, and assuming a value of 10^{-5} $cm^{-2}\,s^{-1}$ for D_{aq} [17], then the value of d_{aq} for the present experimental conditions is 2.6×10^{-3} cm. Furthermore, from experimental results and Eq. (6) the mass transfer coefficient in the aqueous source phase is found to be $3.9 \times 10^{-3}\,cm\,s^{-1}$.

Table 6
Effect of different diluents on the overall permeation coefficient of Cr(VI)

Diluent	P ($cm\,s^{-1}$)
Cumene	3.9×10^{-3}
Toluene	3.6×10^{-3}
n-decane	4.4×10^{-3}
Xylene	3.7×10^{-3}

Feed phase: 200 ml of 0.01 $g\,l^{-1}$ Cr(VI). Organic/stripping phase: 100 ml of PJMT 10% v/v in the different diluents and 100 ml of 1 M HNO_3.

3.6. *Effect of organic diluents*

It is recognized that the organic diluents influences the performance of many liquid membrane systems and thus the metal transport [18,19]. In many cases, the use of organic diluents is mandatory in order to decrease the high viscosity associated with many carriers and also to adequate the range of carrier concentrations used to any particular transport system. From practical purposes, it is desirable to use diluents with the lowest viscosity since the metal-extractant species diffusion coefficient in the organic solution is inversely proportional to the viscosity of such organic solution.

To determine their effect on the present systems, experiments were carried out with different organic diluents. The results obtained are shown in Table 6. For the present system, it can be seen that the change of the diluents influences chromium transport, having n-decane the best transport results. The value of the overall permeation coefficient follows the order: toluene < xylene < cumene < n-decane.

3.7. *Transport of chromium(VI) using different carriers*

The transport of Cr(VI) was also studied using other carriers to compare with result obtained using PJMT. The carriers investigated were Primene 81 R, Hostarex A-324, Cyanex 923, TBP and TDA.

Results are shown in Fig. 2. For the present system it can be seen that the change of the carrier influences chromium transport, having Hostarex A-324 the best transport result. It should be noted, that similarly to amine Primene JMT, in the case of Primene 81R, Hostarex A-324 and tri-n-decylamine the effective carriers are their respective ionic liquids ($RNH_3^+X^-$ for the former and $R_3NH^+X^-$ for the tertiary amines), they are formed upon reaction of the amine with H^+X^- acids from the stripping solution.

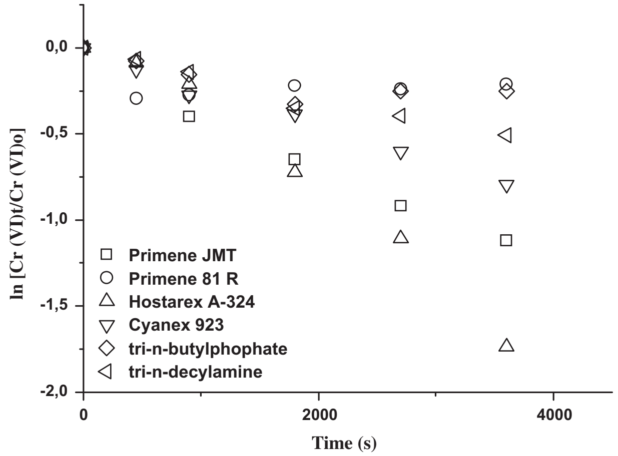

Fig. 2. Effect of various carriers on Cr(VI) transport. Feed phase: 200 ml of 0.01 g l^{-1} Cr(VI). Organic/stripping phase: 100 ml of 10% v/v of the different carrier in cumene and 100 ml of 1 M HNO_3.

3.8. Evaluation of individual resistances to the metal transport

In the present system, it was considered that the local value of the total resistance is the sum of the local values of the individual resistances, namely the resistance due to the aqueous interface in the feed side, the resistance due to the chromium-ionic liquid complex diffusion across the immobilized liquid membrane and the third resistance due to the interface created in the organic-strip solutions interface, that is:

$$R = R_1 + R_2 + R_3 \tag{8}$$

where R, R_1, $R_{2,}$ and R_3 represented the four resistances mentioned previously, respectively.

Therefore, and considering the various experimental data presented in this work (Tables 1–5), in the right-hand side of the above equation, the first term is around 256.4 s cm^{-1} (Eq. (7)) which is equal to the value of the experimentally found overall resistance. This shows that resistance due to the aqueous feed interface is dominant under most of the studied experimental conditions, and first term in Eq. (8), R_1, contributed maximum to the overall resistance.

4. Conclusions

The transport of chromium (VI) from aqueous solution can be effectively carried out, using PEMSD technique and the ionic liquid $PJMTH^+NO_3^-$ in cumene as carrier phase. The metal transport is influenced by a number of variables of the feed phase (stirring speed, acid and metal concentrations) and the organic phase (diluents, carrier type). The best conditions for chromium transport were established as: low acid concentration in the feed phase side, P values are independent of the concentration of the ionic liquid in the membrane phase and it is recommended the use of a 1 M HNO_3 solution as strippant, though best metal recoveries in the strip solution are achieved using 3 M nitric acid as strippant.

The thickness of the aqueous source boundary layer was estimated to be 2.6×10^{-3} cm, and the value of the mass transfer coefficient in this aqueous phase is found to be 3.9×10^{-3} cm s^{-1}. Metal transport is mainly dominant by the resistance due to the aqueous feed interface.

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