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Non-dispersive solvent extraction with strip dispersion (NDSXSD) pertraction of Cd(II) in HCl medium using ionic liquid CYPHOS IL101

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ABSTRACT

The transport of Cd(II) from hydrochloric acid medium in NDSXSD technology is investigated using the ionic liquid CYPHOS IL101 (tetraalkyl)phosphonium salt) dissolved in cumene as carrier phase. The permeation of the metal is investigated as a function of various experimental variables: hydrodynamic conditions, concentration of cadmium(II) and HCl in the feed phase, carrier concentration, support characteristics, etc. In NDSXSD, a pseudo-emulsion is temporarily formed between the organic and stripping solutions. The overall mass transfer coefficient ($K = 4.1 \times 10^{-3}$ cm s^{-1}) and the thickness of the aqueous boundary layer ($d_{aq} = 1.8 \times 10^{-3}$ cm) were calculated from experimental data. Of the different reagents used, 1 M ammonium hydroxide served most efficiently as the stripping agent. Furthermore, the selectivity of CYPHOS IL101-based membrane towards different metals is investigated, whereas the system is compared with other carriers in the liquid membrane phase.

1. Introduction

The removal of toxic cadmium(II) from effluents or waters was and it is nowadays of an utter importance due to the hazardous effects that the intake of this element has on human health [1].

Several technologies are being proposed for the efficient cadmium removal from the various solutions in which cadmium(II) is usually present [2–11].

Liquid membranes, due to their operational characteristics, had gradually become a serious challenge for liquid effluents or wastewaters treatment, and despite the various drawbacks that they presented (i.e. apparent lack of stability under long-term operation). In the case of supported liquid membranes (SLMs) technologies, improvement in their performance resulted in pseudo-emulsion hollow fiber strip dispersion (PEHFSD) and hollow fiber renewal liquid membrane (HFRLM) as advanced SLMs technologies. The characteristics of both technologies are given elsewhere [12,13].

On the other hand, ionic liquids are a generation of fluids, considered as “green solvents”, that due to their specific properties have been proposed, among other applications, for separation processes [14–20].

Coupling liquid membranes technologies and the use of ionic liquids as carriers for metal separations is in its first steps [21,22], thus, to contribute to gain knowledge in these new applications of ionic liquids as carriers in membrane technologies, this work present data on cadmium(II) transport using ionic liquid CYPHOS IL101 as carrier and coupled to the non-dispersive solvent extraction with strip dispersion (NDSXSD) technique. The influence of hydrodynamic conditions and chemical parameters were investigated in order to obtain efficient advanced supported liquid membrane process.

2. Experimental

2.1. Reagents and solutions

Ionic liquid CYPHOS IL101 is a phosphonium salt, which active substance is trihexyl(tetradecyl)phosphonium chloride ($R_3'R''P^+Cl^-$), with molecular weight 519.3, density (25° C) 0.882 g cm^{-3} and viscosity (25° C) 1825 cP. Cumene (Fluka) was employed as diluent in the organic phase to overcome some drawbacks caused by the high viscosity of the extractant [19]. Stock metal solutions were prepared by dissolving the chloride salt (Fluka), except in the case of $K_2Cr_2O_7$ (Merck), in distilled water. All other chemicals used in the present investigation were of AR grade.

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2.2. Membrane support

Polyvinyl-denedifluoride polymeric support used in the investigation was Millipore Durapore GVHP 4700, with porosity (ε) 75%, pore size 0.22 μm and membrane thickness (d_m) 12.5×10^{-3} cm.

2.3. Transport experiments

Transport experiments were carried out in a permeation cell which characteristics are given elsewhere [23].

Once the membrane support was placed in the cell, the source solution (200 mL) and the organic (100 mL) and stripping (100 mL) phases were placed in their corresponding chambers and the operation begins. From the initial moment of mixing, an organic/stripping phases emulsion was formed, and providing adequate stirring speeds in the source phase and in the emulsion phase, the membrane stabilizes similarly to conventional flat-sheet supported liquid membrane operation, i.e. the organic phase wets and it is retained into the micropores of the hydrophobic support by capillarity.

Membrane permeabilities were determined by monitoring metal concentration by AAS in the source (or the stripping) phase as a function of time. The cadmium concentration in the source phase was found to be reproducible within ±2%. From the slope of the straight line obtained by plotting the left hand side of the next equation versus time (t), the overall mass transfer coefficient (K) was estimated:

$$\ln \frac{[\mathrm{Cd(II)}]_t}{[\mathrm{Cd(II)}]_0} = -\frac{A}{V}Kt \qquad (1)$$

where A is the effective membrane area (11.3 cm^2), V (cm^3) is the volume of the feed solution, $[\mathrm{Cd(II)}]_t$ and $[\mathrm{Cd(II)}]_0$ are the metal concentrations in the feed solution at an elapsed time t (s) and time zero, respectively.

The percentage of cadmium recovered in the strip phase was determined using:

$$\%R = \frac{[\mathrm{Cd(II)}]_{s,t}}{(V_{\mathrm{feed}}/V_{\mathrm{strip}})[\mathrm{Cd(II)}]_0 - [\mathrm{Cd(II)}]_t} \times 100 \qquad (2)$$

where $[\mathrm{Cd}]_{s,t}$ represented the metal concentration in the strip solution at an elapsed time, $[\mathrm{Cd}]_0$ and $[\mathrm{Cd}]_t$ has the same meaning as in the above Eq. (1), and V_{feed} and V_{strip} are the volumes of the feed and stripping solutions, respectively.

The separation factor β was estimated accordingly to:

$$\beta = \frac{K_{\mathrm{Cd}}}{K_M} \qquad (3)$$

where K_{Cd} and K_M are the overall mass transfer coefficients for cadmium or a given metal, respectively.

3. Results and discussion

A review in the literature of cadmium extraction results that there are not data about the stoichiometry of the extracted species and extraction constants when CYPHOS IL101 is used as extractant. However, it is possible to discern that, in HCl medium, $\mathrm{CdCl_3}^-$ and $\mathrm{CdCl_4}^{2-}$ are the species presented in the aqueous solution [24,25]. Thus, it is logical to suppose that the extraction or transport of cadmium by CYPHOS IL0101 (an anion exchanger) is represented by:

$$\mathrm{CdCl}^-_{3_{\mathrm{aq}}} + R'_3R''\mathrm{P^+Cl^-_{org}} \Leftrightarrow R'_3R''\mathrm{P^+CdCl}^-_{3_{\mathrm{org}}} + \mathrm{Cl^-_{aq}} \qquad (4)$$

and/or

$$\mathrm{CdCl}^{2-}_{4_{\mathrm{aq}}} + 2R'_3\mathrm{P^+Cl^-_{org}} \Leftrightarrow (R'_3R''\mathrm{P^+})_2\mathrm{CdCl}^{2-}_{4_{\mathrm{org}}} + 2\mathrm{Cl^-_{aq}} \qquad (5)$$

where the subscripts aq and org represented to the aqueous feed and the organic phases, respectively.

Table 1
Cadmium transport at various stirring speeds in the feed phase.

Speed (cm^{-1})	K × (10^3 cm s^{-1})
400	2.4
800	3.2
1000	4.1
1200	4.0

3.1. Influence of the stirring speed of the feed phase

The influence of the stirring speed of the feed phase was studied in order to optimize uniform mixing of aqueous feed phase and to minimise thickness of the aqueous boundary layer with the feed and the pseudo-emulsion conditions being maintained as follows: Cd(II) 0.01 g L^{-1} in 1 mol L^{-1} HCl and 5% (v/v) CYPHOS IL 101 in cumene and water, respectively.

The results obtained are shown in Table 1, the overall mass transfer coefficient (K) becomes virtually independent of the stirring speed in the range 1000–1200 min^{-1}, indicating a decrease in the aqueous boundary layer thickness, and then a minimum value of the thickness is reached in this range. The stirring speed of 1000 min^{-1} in the feed phase was kept constant throughout the experiments conducted.

3.2. Influence of the stripping phase composition on transport of Cd(II)

This study was carried out using feed phases of 0.01 g L^{-1} Cd(II) in 1 mol L^{-1} HCl, whereas the pseudo-emulsion phase was composed by an organic solution of 5% (v/v) CYPHOS IL101 in cumene and the various solutions shown in Table 2 as the stripping phases for Cd(II); from the experimental results it is concluded that metal transport is not influenced by the stripping phase composition ($K = 4.1 \times 10^{-3}$ cm s^{-1}). On the other hand, Table 2 shows the results corresponding to the recovery of the metal in the stripping solution from the above series of experiments. It can be seen that the use of 1 mol L^{-1} $\mathrm{NH_4OH}$ solution as the strip phase allowed the maximum cadmium recovery in this phase. Cadmium stripping from metal-loaded CYPHOS IL101 organic solutions using ammoniacal solutions can be related to the formation of non-extractable cationic ammine complexes $\mathrm{Cd(NH_3)}_n{}^{2+}$, by CYPHOS IL101, in the strip phase, i.e.:

$$\begin{aligned}\mathrm{R_4P^+CdCl}^-_{3_{\mathrm{org}}} + 4\mathrm{NH_4OH_{aq}} &\Leftrightarrow \mathrm{Cd(NH_3)}^{2+}_{4_{\mathrm{aq}}} \\ &+ \mathrm{R_4P^+Cl^-_{org}} + 2\mathrm{Cl^-_{aq}} + 4\mathrm{H_2O}\end{aligned} \qquad (6)$$

with the regeneration of the carrier.

Table 2
Cadmium recovery in the strip solution.

Strip agent	% Cd recovery[a]
Water	3
1 M $\mathrm{H_2SO_4}$	9
2 M $\mathrm{H_2SO_4}$	10
M $\mathrm{NH_4OH}$	55
1 M $\mathrm{NH_4OH}$	83

[a] After 3 h.