Transport characterisation of a PIM system used for the extraction of Pb(II) using D2EHPA as carrier

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Abstract

The facilitated transport of lead(II) through polymeric inclusion membranes consisting of cellulose triacetate as polymeric support, bis-(2-ethylhexyl)-phosphoric acid (D2EHPA) as carrier, and tris-(2-butoxyethyl)phosphate as plasticiser (TBEP), is investigated. The influence of some of the aqueous and membrane components on the permeability of Pb(II) was studied. The maximum flux obtained with these membranes is 3.5×10^{-6} mol m^{-2} s^{-1}, which is of the same order of magnitude of those reported for supported liquid membranes and is in the upper range of those reported for polymeric inclusion membranes. Aqueous and membranes resistances were determined from a model that describes the transport mechanism across the membranes using the stoichiometric relationship Pb R$_2$2HR and the extraction equilibrium constant value of 6.2×10^{-4} determined independently by solid–liquid extraction. An activation energy of 11 kJ mol^{-1} was also determined for Pb(II) migration, which suggest that the transport of Pb(II) is controlled by a membrane diffusion mechanism. Membrane characterisation was performed using several techniques including atomic force microscopy, scanning electron microscopy coupled with energy-dispersive spectroscopy, and thermal analysis.
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1. Introduction

The removal of toxic ions from waste waters is of great significance due to environmental and economical aspects. The so-called heavy metals have been recovered with separation methods based on solvent extraction (SX), which consume large amounts of organic extractants and solvents. In order to improve some of the drawbacks of solvent extraction processes liquid membranes have been used because of their high transport rates, selectivity factors, and minimisation of the required organic components [1].

Single-stage extraction and back-extraction of a number of species with liquid membranes have been investigated

for about 30 years. Among the different liquid membranes modalities, the supported liquid membranes (SLMs) have been widely used for the separation of a number of species [2]. Whereas their lack of stability, which might prevent upscale applications, has also been reported [3].

Recently, cellulose-based polymeric inclusion membranes (PIMs), first introduced by Sugiura [4], have received increasing attention as an alternative to SLM. Extraction of a number of species has been reported by several groups [5–8]. PIMs have been reported to have better mechanical properties than traditional SLMs and good chemical resistance [9]. The addition of plasticisers is reported to improve the compatibility of the carrier with the polymer, and additionally improve the brittleness and elasticity by creating a polymeric solution [10]. Although PIMs have a higher internal viscosity than SLMs, it has been reported that, for a number of systems, the fluxes across both types of membranes are comparable

[11,12]. In other cases higher fluxes across PIMs have been reported [13,14].

Although the extraction of lead using PIMs with tailor-made carriers [6,15] and commercial carriers [12,16] has been reported previously, to our knowledge there are no experimental reports on the transport of Pb(II) with D2EHPA using SLMs and PIMs. However, Gumí et al. [17] reported the extraction of Pb(II) with D2EHPA using activated composite membranes. These membranes are reported to have an improved stability but present lower recovery rates.
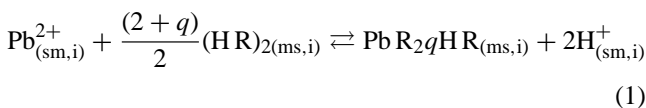
In this work, the influence of some of the aqueous components and membrane components on the transport of Pb(II) from nitrate medium using a PIM system based on cellulose triacetate with a commercial carrier (D2EHPA) is investigated. A model that describes the transport of lead across the membrane is presented. Some of its parameters are fitted to the experimental data obtained in order to determine the maximum flux, the thickness and resistances of the boundary layers. Parameters such as the stoichiometry of the transported complex and the equilibrium constant value are determined in an independent way by previous solid–liquid extraction experiments. The chemical behaviour and the performance of the membrane are compared to other systems. Furthermore, the membranes are characterised in order to obtain information regarding composition and to better understand membrane performance.

2. Transport modelling

In order to have a quantitative description of the transport across the membranes, a model was developed based on a simplified method described elsewhere [18] and the following assumptions:

(1) The interfacial chemical reactions are fast [19].
(2) Concentration gradients across the aqueous boundary layers are linear.
(3) The concentration of species other than metal are the same as in the bulk, since their concentration is used in excess when compared to the metal ion.
(4) The metal concentration at the membrane-receiving interface is negligible since there is a very low partition coefficient and transport across aqueous layers is relatively fast.

The extraction process [20] at the source/membrane interface can be represented by the following reaction:

$$\mathrm{Pb}^{2+}_{(sm,i)} + \frac{(2+q)}{2}(\mathrm{H\,R})_{2(ms,i)} \rightleftarrows \mathrm{Pb\,R}_2 q\mathrm{H\,R}_{(ms,i)} + 2\mathrm{H}^+_{(sm,i)}$$

(1)

with an equilibrium constant, k^q_{ex}:

$$k^q_{ex} = \frac{[\mathrm{Pb\,R}_2 q\mathrm{H\,R}_{(ms,i)}][H^+_{(sm,i)}]^2}{[\mathrm{Pb}^{2+}_{(sm,i)}][(\mathrm{H\,R})_{2(ms,i)}]^{(2+q)/2}}$$

(2)

where H R represents the D2EHPA species and the subscripts m, membrane phase; i, interface; s, source solution.

Hence, the flux of Pb(II) across the membranes can be described applying Fick's first law to the diffusion of metal across the different interfaces. The metal flux at the source/membrane interface, J_a, is defined as

$$J_a = -D_a\frac{\mathrm{d}[M(n)]}{\mathrm{d}x} = \Delta_a^{-1}([M(n)_b] - [M(n)_{s,i}])$$

(3)

$$J_a = -D_a\frac{\mathrm{d}[M(n)]}{\mathrm{d}x} = J_{max} - \Delta_a^{-1}([M(n)_{s,i}])$$

(4)

where the subscript b stands for bulk concentrations. The metal flux at the membrane phase, J_m, is defined by

$$J_m = -D_m\frac{\mathrm{d}[M(n)]}{\mathrm{d}x} = \Delta_m^{-1}([M(n)_{ms,i}] - [M(n)_{mr,i}])$$

$$= \Delta_m^{-1}[M(n)_{ms,i}]$$

(5)

The terms Δ_m and Δ_a represent the resistances across the membrane phase and the aqueous phases, respectively. With $\Delta_m = \delta_m/D_m$ and $\Delta_a = \delta_a/D_a$, δ_m is the thickness of the membrane layer, and δ_a the thickness of the aqueous boundary layer, whereas D_m represents the apparent diffusion coefficient and D_a represents the true aqueous diffusion coefficient.

At steady state, $J_m = J_a = J$, and thus, combining Eqs. (2), (3) and (5), considering the diffusion of mainly one species in the membrane phase, the overall flux J is given by:

$$J = \frac{J_{max}\Delta_a k_{ex}[(\mathrm{H\,R})_{2,ms,i}]^{(2+q)/2}}{\Delta_m[\mathrm{H}^+_{sm,i}]^2 + \Delta_a k_{ex}[(\mathrm{H\,R})_{2,ms,i}]^{(2+q)/2}}$$

(6)

or, if we consider the transport to occur under first-order kinetics, we can express the transport of lead in terms of permeability, this is, the velocity at which the metal is transported as:

$$P = \frac{k_{ex}[(\mathrm{H\,R})_{2,ms,i}]^{(2+q)/2}}{\Delta_m[\mathrm{H}^+_{sm,i}]^2 + \Delta_a k_{ex}[(\mathrm{H\,R})_{2,ms,i}]^{(2+q)/2}}$$

(7)

This equation shows the dependence that permeability has with several parameters, which contain valuable information on the limiting processes of the diffusion and chemical reactions that are actually occurring in the membrane. The aforementioned information is contained in (a) the maximum theoretical flux in the membranes (J_{max}), (b) the aqueous and organic resistances and (c) the complex stoichiometry (depending on q) and extraction constant.

3. Experimental

3.1. Chemicals

Cellulose triacetate (CTA, Aldrich acetyl content 43.6 wt.% Mw = 72–74 kDa) was used as the polymer support for the