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Zn(II), Cd(II) and Cu(II) separation through organic–inorganic Hybrid Membranes containing di-(2-ethylhexyl) phosphoric acid or di-(2-ethylhexyl) dithiophosphoric acid as a carrier

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Abstract

A membrane process for metal recovery from aqueous solutions was studied. Metal ions diffused from the feed solution to the stripping phase through an Hybrid Membrane containing di-(2-ethylhexyl) phosphoric acid (D2EHPA) and/or di-(2-ethylhexyl) dithiophosphoric acid (D2EHDTPA) as a carrier. Such membranes were prepared by a sol–gel route including cellulose triacetate and polysiloxanes. Transport behaviour was evaluated for both carriers under similar experimental conditions. The transport experiments reported here concerned transport at different cycles and selectivity towards different metal ions. Using D2EHPA the membrane provided a selective transport of zinc to the stripping compartment of the membrane cell, while copper and cadmium remained in the feed compartment. Whereas, using D2EHDTPA as carrier the transport rate increased and the selectivity profiles were inverted in relation with those of D2EHPA. With a mixture of both extracting agents it was observed an intermediate behaviour in selective transport, being possible to modulate it.

Keywords: D2EHPA; D2EHDTPA; Metal transport; Membrane process; Selectivity

1. Introduction

The application of extraction techniques for removal and recovery of metals is very significant nowadays. Increasing demand of metal production led to the research of more efficient and economical methods of purification required by industry. Membrane Technology has become an important alternative to the normal processes employed for wastewater treatments, separation and recovery of target metals. Selective transport of metal ions has been widely studied with supported liquid membranes (SLM) [1,2].

Their high selectivity, high diffusion rates and the possibility of concentrating ions make them particularly useful. Despite the well-known advantages of SLM, they are not often used for practical separation processes because of their low stability and high degradation rate. These membranes suffer the loss of carrier by dissolution into the aqueous phases and many different studies have been performed to stabilize them [3–5]. Consequently, new membrane systems based on new hybrid materials have arisen with the main objective of improving SLMs physical and chemical characteristics [6]. Organic–inorganic hybrid materials offer some advantages for the preparation of membranes with high selectivity and flux, and also exhibiting a good thermal and chemical resistance. Polymeric membranes have a good film formation; they are not expensive and can be used for any fluid volume treatment. If these membranes are cellulose triacetate based they present a high stability and good mass transport fluxes [7]. Besides, inorganic membranes are very selective and can be used in complex separations [8].

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The main purpose of this kind of membranes is its use in facilitated transport. This transport process takes place through a facilitated mechanism due to the carrier contained inside the membrane. In order to extract metal ions from hydrometallurgical effluents, many different extracting agents have been widely used, i.e. di-(2-ethylhexyl) phosphoric acid (D2EHPA) and di-(2-ethylhexyl) dithiophosphoric acid (D2EHDTPA) [9–11] which are specially appropriated for transition metal ions recovery.

D2EHPA is a carrier that in membrane processes presents a great selectivity towards Zn^{2+}, in relation to other metals such as Cu^{2+}, Ni^{2+}, Ca^{2+}, Mn^{2+}, Fe^{3+}, Al^{3+} and Cd^{2+} as it has been demonstrated in some membrane processes [1].

This carrier has a hydrophobic character and a good solubility in many organic solvents. It often acts as a transport agent following a counter-transport mechanism; in this case, a crossed transport of protons and metallic ions takes place.

In addition, D2EHPA has some suitable characteristics such as high loading capacity of metal charge, good selectivity, high mass transport rates, high chemical stability, low cost and non-volatility [9].

On the other hand D2EHDTPA is an analogous molecule to D2EHPA where two sulfur atoms substitute two oxygen atoms and its acidity is slightly stronger than that of D2EHPA due to the named substitution. Its stability in aqueous solution is low due to the hydrolisation of the thiol group involving molecule decomposition to H_2S and alcohol. It has been shown that D2EHDTPA also presents a crossed transport between protons and metallic ions in a counter-transport system [12,13].

Both carriers were compared under the same experimental conditions and the transport behaviour was studied in each case. Transport experiments reported here concerned mass transfer rates, stability in cycles and selectivity towards different metal ions. Flux values were calculated and compared with other obtained with different membranes systems as Polymeric Inclusion Membrane (PIM) or Activated Composite Membranes (ACM).

Polymeric Inclusion Membrane (PIM) system has several important advantages for the separation aspects compared with SLMs: easy setup, high selectivity, and high durability. PIMs have been modelled and are formed by the precipitation of cellulose triacetate (CTA) to form a thin film [14]. They revealed superior flux values to the SLMs for the cation transport and higher durability [2].

Activated Composite Membranes (ACMs) have demonstrated high selectivity and more stable transport properties within long periods than corresponding SLMs. Membrane preparation was carried out by a known multistep procedure [15]. The final membrane is the result of applying a thin selective layer of polyamide onto a highly porous support membrane. The carrier is introduced in the second polymerisation step. ACMs transport properties have already been applied to study some substances of particular interest.

2. Experimental

2.1. Chemicals

To prepare the membrane, two polysiloxanes were used to obtain the silanes mixture: tetraethyl orthosilicate (TEOS) > 98% (Merck) and dichlorodimethylsilane (DCDMS) > 98% (Merck). The plasticizers tested were 2-nitrophenyl-octyl-ether (NPOE) (Fluka) and tris(2-butoxiethyl)phosphate (TBEP) 94% (Aldrich). Cellulose triacetate (CTA) (Aldrich) was used after dissolution in chloroform 99.9% (Panreac) that was used as solvent to obtain the organic matrix [14,16–18].

The carriers were di(2-ethylhexyl) phosphoric acid (D2EHPA) 97% (Aldrich) and di-(2-ethylhexyl) dithiophosphoric acid (D2EHDTPA) synthesized in our laboratory as explained elsewhere [13].

Zinc acetate hydrate 95% (Merck), copper nitrate trihydrate 99–103% (Panreac), and cadmium sulfate hydrate 99% (Panreac) were used to prepare the solutions involved in the transport experiments.

2.2. Membrane preparation

Hybrid Membranes were prepared at room temperature by mixing a cellulose triacetate matrix (0.04 g), that shows a high compatibility with the organophosphorous extractants and with polysiloxanes (0.03 g), containing different amounts of plasticizer (0.02–0.04 g) and extracting agents (0.08–0.20 g). Note that the amounts in parenthesis correspond to the quantity of each component per membrane. More detailed information will be found elsewhere [19].

The silanes mixture (DCDMS + TEOS) was added to obtain the Hybrid Membrane following a sol–gel route. Both precursors were silicon alkoxides whose hydrolysis leads to the inorganic network in the organic matrix. When all the components were placed together, they were vigorously stirred to mix them homogeneously and the mixture was poured into a Petri dish to carry out the evaporation.

Finally, the prepared membranes were cured in an oven at 80 °C during 20 h. The side of the membrane exposed to the air during the evaporation was the one used to face the solution containing the metal ion in the transport experiences.

2.3. Metal transport procedure

The measurements of ion transport were carried out using a two compartments membrane cell of 200 ml each, with a circular window where the membrane was placed separating the two aqueous phases. The membrane working area was 12 cm^2. The feed and stripping solutions placed in each compartment of the cell were vigorously agitated by mechanical stirrers at 2600 rpm, which is high enough to eliminate aqueous diffusion layers. The stripping phase consisted of 0.5 M HCl in all experiments carried out. To equilibrate the ionic strength with that of the stripping, NaCl 0.5 M was added to