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Semi-interpenetrating hybrid membranes containing ADOGEN® 364 for Cd(II) transport from HCl media

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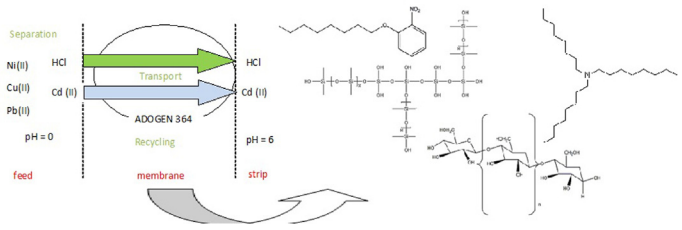
HIGHLIGHTS

- Semi-interpenetrating hybrid membranes are used for quantitative cadmium(II) recovery.
- Optimization of membrane and solutions compositions is performed.
- Membranes present increased stability respect to polymer inclusion membranes.
- Models for cadmium (II) extraction and transport are proposed.
- Excellent selectivity for Cd(II) over Ni(II), Cu(II) and Pb(II) was achieved.

GRAPHICAL ABSTRACT



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ABSTRACT

Cd(II) transport from 1 mol dm^{-3} HCl media was investigated across semi-interpenetrating hybrid membranes (SIHMs) that were prepared by mixing an organic matrix composed of ADOGEN® 364 as an extracting agent, cellulose triacetate as a polymeric support and nitrophenyloctyl ether as a plasticizer with an organic/inorganic network (silane phase, SP) composed of polydimethylsiloxane and a crosslinking agent. The stripping phase used was a 10^{-2} mol dm^{-3} ethanesulfonic acid solution. The effects of tetraorthoethoxysilane, phenyltrimethoxysilane and N′,N′-bis[3-tri(methoxysilyl)propyl]ethylendiamine as crosslinking agents on the transport were studied. H_3PO_4 was used as an acid catalyst during the SP synthesis and optimized for transport performance. Solid–liquid extraction experiments were performed to determine the model that describe the transport of Cd(II) via ADOGEN® 364. The transport was found to be chained-carrier controlled with a percolation threshold of 0.094 mmol g^{-1}. The selective recovery of Cd(II) was studied with respect to Ni(II), Zn(II), Cu(II), and Pb(II) at a 1:1 molar ratio, and the optimized membrane system was applied for the recovery of Cd(II) from a real sample consisting of a Ni/Cd battery with satisfactory results. Finally, stability experiments were performed using the same membrane for 14 cycles. The results obtained showed that SIHMs had excellent stability and selectivity, with permeabilities comparable to those of PIMs.

1. Introduction

The cost of valuable metals continuously increases, despite the toxicity of the metals, due to their wide range of industrial (electrical and mining) and technological applications (metal finishing, batteries, non-ferrous metallurgical manufacturing). As a result of

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their toxic behavior and low abundance, the recovery and recycling of these metal ions is one of the main targets of current industrial policy, particularly in issues related to water management. Cadmium is among the polluting species of interest because of its high toxicity [1–3]. Thus, wastewater treatment for this metal requires serious attention and action.

The methods currently used for water purification are primarily precipitation [1,4,5], ion exchange and adsorption on activated carbon [1,4]. In terms of valuable metal recovery at low concentration levels, liquid–liquid extraction is known to be the best technique [6–8]. The use of membrane technology to replace a purification, recovery or separation step in an existing industrial process may not only reduce the cost and the overall consumption of energy and reagents, but it also represents a more environmentally friendly procedure [4,5,8,9] because of the lack of solvent entrainment phenomena, which allows for the direct treatment of feed solutions containing solids [10]. However, practical applications of membranes remain limited. These include supported liquid membranes (SLMs) and polymeric inclusion membranes (PIMs). A major drawback associated with SLMs is their poor stability, and despite the fact that PIMs retain most of the advantages of SLMs (high diffusion rates, fluxes and selectivity) while exhibiting better stability and, therefore, longer lifetimes, both membrane systems still remain mostly impractical for many large-scale applications. Their degradation is essentially due to the loss of the carriers via dissolution into the aqueous phases [9,11–14]. Consequently, recent developments are focused on new membrane systems with improved lifetimes and stability of the membranes used in industrial applications. To achieve these goals, hybrid inorganic–organic materials have been developed as membranes [9,11–16]. These materials are very attractive for membrane synthesis because they can combine the basic properties of organic and inorganic materials, which results in improved membranes with great potential because they show positive synergistic effects compared with the materials used separately [15–17]. Semi-interpenetrating hybrid membranes (SIHMs), such as those used in the present work, have previously shown excellent transport characteristics for zinc [12] and protons [18]; therefore, their application in the present separation problem is promising.

Among the commercial carriers for cadmium extraction in PIM systems, the performance of Aliquat 336 and organophosphorous reagents, such as di(2,4,4-trimethylpentyl)-phosphinic acid (Cyanex® 272), di(2,4,4-trimethylpentyl)dithiophosphinic acid (Cyanex® 301), bis(2,4,4-trimethyl-pentyl)-monothiophosphinic acid (Cyanex® 302), and di-2-ethylhexylphosphoric acid (D2EHPA), has been reported [19–21]. To the best of our knowledge, no work has been published using ADOGEN 364 as an extracting reagent in a PIM or SIHM system.

In this work, continuing our research on the use of hybrid membranes, we report the influence of some aqueous and membrane components on the transport of Cd(II) from a hydrochloric acid medium using a SIHM system. The SIHMs were prepared by combining an organic matrix composed of cellulose triacetate (CTA) as the polymeric support, nitrophenyloctyl ether (NPOE) as the plasticizer and ADOGEN® 364 as the extractant with an inorganic–organic matrix prepared using poly(dimethylsiloxane) and a crosslinking agent, such as tetraethoxysilane (TEOS), phenyltrimethoxysilane (PTMS) or N′,N′-bis[3-tri(methoxysilyl) propyl]ethylendiamine (BTMSPET). The different crosslinking agents were assayed to determine the effect of this component on the casting of the membrane and on the transport properties. A model that describes the transport of cadmium across the membrane is shown. Certain parameters, such as the stoichiometry of the transported complex and the equilibrium constant, were previously determined independently using solid–liquid extraction experiments. The SIHMs were evaluated in terms of their transport efficiency, stability and selectivity, and their performances were compared with that of a PIM. The selective recovery of Cd(II) was studied with respect to several metal ions (Ni(II), Zn(II), Cu(II), and Pb(II)). Finally, the optimized membrane system was applied for the recovery of Cd(II) from a real sample consisting of a Ni/Cd battery with satisfactory results.

2. Experimental

2.1. Reagents

All chemicals were used as received without further purification. Cellulose triacetate (CTA), nitrophenyloctyl ether (NPOE, 99%), tetraethoxysilane (TEOS, 98%), poly(dimethylsiloxane) hydroxy terminated (PDMS), dichloromethane (CH_2Cl_2, 95%), 2-(N-morpholino) ethanesulfonic acid (MES 99.5%) and hydrochloric acid (37%) were obtained from Aldrich. Phenyltrimethoxysilane (PTMS) was supplied by ABCR and N′,N′-bis[3-tri(methoxysilyl)propyl] ethylendiamine (BTMSPET) by GELEST. ADOGEN® 364, kindly supplied by Witco, is a 50% mixture of C_8 and C_{10} aliphatic substituted tertiary amines with a mean molecular weight of 390 g mol^{-1}, a specific gravity of 0.802 g cm^{-3} and 98% purity.

Solutions prepared by dilution from a cadmium standard (1000 mg L^{-1} in 2% HNO_3, Fisher) were used to calibrate the atomic absorption measurements. The transport solutions were prepared using cadmium nitrate ($Cd(NO_3)_2{\cdot}4H_2O$, 99% Fluka) in HCl.

2.2. Equipment

The metal ion concentrations were determined using FAAS (3100 Perkin Elmer spectrophotometer) under the conditions recommended by the manufacturer. A Burrel 75 mechanical shaker was employed for the solid–liquid extraction experiments. For each membrane, the average thickness was determined by measuring five different points using a digital micrometer (Fowler IP54).

Statgraphics Centurion XVI (StatPoint Technologies, Inc.) was used for the data analysis.

2.3. Procedure

2.3.1. Preparation of PIMs

The PIMs were prepared according to the procedure reported elsewhere [22], i.e., appropriate amounts of CTA (0.0990–0.1100 g), NPOE (0.020–0.035 g) and ADOGEN® 364 (0.0090–0.0900 g) were dissolved in 10 mL of CH_2Cl_2 and stirred for approximately 4 h before pouring the solution into a Teflon Petri dish with a 5-cm diameter. After solvent evaporation at room temperature for 24 h, a film was obtained and removed from the dish. The membranes prepared in this way were transparent films with an average thickness of $4.5 \pm 1.1 \times 10^{-5}$ m.

2.3.2. Preparation of the silane phase (SP)

The silane phase employed as the inorganic–organic fraction was prepared by mixing PDMS (1.900–2.010 g) and the crosslinking agent TEOS (SPT) (1.800–1.900 g), PTMS (SPP) (0.090–1.050 g) or BTMSPET (SPB) (0.800–1.000 g). In some cases, 0.100 mL of an acid catalyst (H_3PO_4) was added.

2.3.3. Preparation of SIHMs

CTA, NPOE and ADOGEN® 364 were dissolved in 10 mL of CH_2Cl_2 and stirred for approximately 1 h before being mixed and stirred together with the silane phase for another 3 h. This solution was poured into a Teflon Petri dish with a 5-cm diameter. After solvent evaporation at room temperature for 24 h, a film was obtained. In addition, a membrane without a crosslinking agent was prepared. The membranes prepared in this way were transparent films