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Exploration of heavy metal ions transmembrane flux enhancement across a supported liquid membrane by appropriate carrier selection

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Abstract

Extraction capabilities of three kinds of carriers, Aliquat 336, Kelex 100 and LIX 54, for cadmium removal have been investigated in supported liquid membrane (SLM) systems. The maximum fluxes obtained using Aliquat 336, Kelex 100 and LIX 54 are 1.12×10^{-9}, 1.5×10^{-10} and 7.9×10^{-11} mol/(cm^2 s), respectively. Theoretical calculation of these three carriers' extraction capabilities for cadmium in SLM systems using the quantum chemical computation method has also been carried out. The single point energy calculation results show that the energy changes in the complex formation process are in the order of Aliquat 336/Cd(II) > Kelex 100/Cd(II) > LIX 54/Cd(II), with energy changes of −657.79, −329.19 and 96.32 kcal/mol, respectively. This indicates the quantum chemical computation supports the experimental results well and can be proposed as an effective tool for carrier selection in the SLM system. FTIR results also agree with the computational results quite well. Investigation on the influence of stirring rate and strippant on the cadmium flux reveals that a stirring rate of 400 rpm and the use of 1 mM EDTA as the strippant constitute the optimal experimental conditions. It was also found that cadmium flux is a function of feed concentration at the low concentration stage and the cadmium flux is enhanced by appropriate addition of certain anion into the feed.

Keywords: Computational approach; Supported liquid membrane; Carrier selection

1. Introduction

The supported liquid membranes (SLMs) technique has received considerable attention over the past few decades because they offer a lot of advantages over conventional separation technologies, such as easy operation, low capital and operating costs, low energy consumption, continuous operation, high selectivity, relatively high fluxes, combination of extraction, stripping and regeneration processes into a single stage, uphill transport against concentration gradients and small amounts of extractants (Sirkar, 1997; Gumi et al., 2003; Kocherginsky et al., 2007; Di Luccio et al., 2000; Cooper et al., 2004). SLM has been demonstrated as an effective tool for the selective separation and recovery of resources from dilute solutions, particularly for the removal and recovery of toxic metals, e.g. cadmium or copper ions, from waste effluents (Ndungu et al., 2005).

Transport of metal species through a supported liquid membrane involves a continuous recycle of the following processes: (1) metal complexation with the carrier; (2) the complex traveling from the feed/membrane interface to the membrane/stripping interface; (3) decomplexation and partition of metal species into the stripping phase; (4) the decomplexed carrier traveling back to the membrane/feed interface where it again complexes with the metal species (Kocherginsky et al., 2007). The steps involving the complexation reactions are very crucial. The structure and nature of organic carriers present in the membrane probably play a decisive role in determining the effectiveness of the extraction step. Therefore, the choice of suitable carriers is vital to obtain a high performance SLM.

In past decades, various carriers for the separation of cadmium, the highly toxic metal ion, using SLM systems have been intensively examined for different experimental conditions (He and Ma, 2000; Urtiaga et al., 2000; He et al., 2000; Wang

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et al., 2000; Schimmel et al., 2001; Nowier et al., 2000; Juang et al., 2004a). However, to our best knowledge, *no work has been done to theoretically predict the extraction power of carriers for Cd(II) in SLM systems*. In this work, a reliable theoretical prediction based on quantum chemical computation has been proposed for the carrier selection based on the extraction process in a SLM system for Cd(II) removal, a typical and practically important example. The computational work can reduce the tedious laboratory experiments significantly and provide guidance when choosing an effective carrier for SLM systems.

The quaternary ammonium salts Aliquat 336, hydroxyquinoline Kelex 100 have been proven to be effective extractants for Cd(II) and β-diketone LIX 54 is also a possible extraction candidate for Cd(II) (Wang et al., 2000; Mellah and Benachour, 2006; Kyuchoukov et al., 1998; Juang et al., 2004b). The quaternary ammonium salts Aliquat 336, hydroxyquinoline Kelex 100 and β-diketone LIX 54 have different functional groups for complexation with Cd(II) (Wang et al., 2000; Mellah and Benachour, 2006; Kyuchoukov et al., 1998; Juang et al., 2004b), resulting different extraction mechanisms with Cd(II). Therefore, they have been specifically chosen as the carrier candidates for Cd(II) removal through the SLM system in this work. Both experimental and computational results reveal Aliquat 336 is the best one. Subsequently, the systematic studies for Aliquat 336/Cd(II), with respects to the Cd(II) flux as a function of carrier concentrations, hydrodynamic conditions, stripping phase compositions, feed concentrations and anion additions in the feed were carried out.

2. Experimental section

The quaternary ammonium salts Aliquat 336, hydroxyquinoline Kelex 100, β-diketone LIX 54 were diluted in kerosene and used as the carriers in the liquid membrane phase. Cadmium (II) solutions were used as the feed phases by dissolving $CdCl_2 \cdot H_2O$ in 1 M HCl or deionized water. Hydrochloric acid, ammonium acetate and ethylenediaminetetraacetic acid (EDTA) were employed as stripping phases in the SLM systems. A Whatman® PTFE membrane filter (UK) was utilized as a membrane support, having a diameter of 4.7 cm and a thickness of 150 μm with ~ 80% porosity and an average pore size of 0.2 μm. We found that an immersion time of 24 h was long enough to get the fully impregnated membrane which was confirmed by showing no further weight gain after longer time immersion. The impregnated membrane after being blotted with a soft paper sheet to remove the extra oil was then placed in a cell holder of the SLM system. The SLM system had two Teflon® chambers holding the feed and strip solutions with volume of 37 ml each and the effective membrane surface area was 8.7 cm^2. Both aqueous phases were mechanically stirred with Teflon® impellers in connection with an overhead mixer.

Metal concentrations in the stripping phase were measured by a Perkin-Elmer Optima 3000 ICP-AES (Norwalk, CT). Membrane fluxes were determined by monitoring metal concentration in the stripping phase as the function of time based on the following equation:

$$J = \frac{dC_s}{dt}\frac{V}{S}, \quad (1)$$

where V is the volume of the stripping phase; S is the effective surface area of the membrane; C_s is the molar concentration of metal in the stripping phase and t is the time elapsed.

Carriers and their complexes formed after reaction with 10 mM $CdCl_2$ in 1 M HCl (for Aliquat 336) or 10 mM $CdCl_2$ only (for the other two carriers) were analyzed by a Bio-Red FTS135 FTIR spectrometer to study the reaction mechanisms of the carriers with cadmium species.

In order to investigate the effect of sulfate and nitrate anions on cadmium flux, various amounts of sodium sulfate or sodium nitrate were added into the feed phase containing cadmium chloride and hydrochloric acid at 10 mM and 1 M, respectively. The concentrations of sulfate and nitrate in the aqueous phase were analyzed by using an ion chromatograph (Metrohm Model 702) equipped with a conductivity detector and a Hamilton PRP-X 100 anion column was used. It was operated at a flow rate of 2 ml/min with an eluent containing 1.7 mM $NaHCO_3$ and 1.8 mM Na_2CO_3.

3. Computational methodology

Calculation and simulation for solving problems in chemical engineering are found to give reliable results (Cao et al., 2006; Sun et al., 2007; Tan et al., 2004), especially quantum chemical computations which are an increasingly important tool in chemical science and engineering. They are good approaches to theoretically select effective SLM carriers by providing the molecular structure–property relations, which is the key to bridge the relation of the carrier structures with their extractabilities. It is well known that for the organometallic compounds such as the cadmium–carrier complexes, density functional theory calculations generally perform well (Ziegler, 1995). Therefore, the reaction processes of Cd(II) with these three carriers were analyzed with the first-principles density functional theory calculations. In the current work, quantum chemical computations were achieved based on the following procedure. Firstly, in order to obtain good initial coordinates for density functional theory optimization, the geometries of the carriers and cadmium–carrier complexes were mechanically minimized with the general Amber force field by using AMBER 8 (Case et al., 2004). Secondly, optimizations of the geometries of the carriers and the cadmium–carrier complexes were achieved with Becke's three-parameter hybrid functional coupled with the Lee–Yang–Parr correlation functional (B3LYP) level of theory at 3-21g basis set. The split-valence basis set 3-21g used here means that the inner shell orbitals are represented by three Gaussians, and the valence orbitals by two Gaussians for the first Slater type orbital (STO) and by one Gaussian for the second STO. Thirdly, the single point energies of the fully optimized geometries of the carriers and the cadmium–carrier complexes were calculated using B3LYP at the 3-21g basis set. All the first-principles density functional theory optimizations