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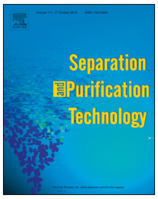

Membrane-assisted enrichment of zinc(II) from and into ammoniacal media through non-dispersive synergistic extraction

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ABSTRACT

The enrichment of zinc(II) in ammoniacal media with non-dispersive synergistic extraction (NDSX) was achieved in a sandwich-supported liquid membrane module, in which a mixed extractant containing 4-ethyl-1-phenyl-1,3-octadione (HA) and trioctylphosphine oxide (TOPO) was used as the carrier. Several parameters of Zn(II) transport, including carrier concentration, diluent type, feed pH, total ammonia concentration, and temperature, were systematically investigated. The results showed that the mixing of TOPO with HA can effectively improve the Zn(II) enrichment from and into ammoniacal solutions. The transport efficiency of zinc increases with increasing carrier concentration and temperature. Moreover, Zn(II) transport is dependent on the total ammonia concentration and solution pH of the feed phase. The nonpolar n-octane is more beneficial to zinc transport than the polar octanol. Five successive transports exhibit excellent membrane stability and the effective uphill transport of zinc from and into ammoniacal media with NDSX.

1. Introduction

Ammoniacal media are favorable for recovering various non-traditional zinc-bearing mineral and waste resources because of its specific coordination features and good leaching selectivity [1–3]. The general process of zinc recovery involves leaching and purification, followed by electrowinning. However, the low concentration of zinc ions in the ammoniacal leachates of these low-grade resources makes it difficult to meet the demands of downstream processes [3]. Thus, the enrichment of zinc ions from ammoniacal liquors through liquid-liquid extraction is a crucial process in the recovery of complex zinc resources [4]. When valuable metal ions in the pregnant organic phase are stripped with mineral acids, the hybrid loop that includes ammoniacal extraction and acidic electrowinning is very complicated for zinc recovery [5]. In particular, ammonia molecules are easily transferred into acidic spent electrolytes by entrainment and/or coextraction, which adversely affects the electrowinning circuit. Therefore, if zinc ions are directly enriched into ammoniacal media, the recovery process of zinc is shortened considerably, which is a standard objective in metallurgical and environmental fields [6,7].

Because of the dispersive feature of solvent extraction, it represents a promising approach and has been successfully applied in metal recovery. However, the enrichment of low-concentration metal ions inevitably consumes a considerable amount of expensive extractants. Alternatively, non-dispersive solvent extraction (NDSX) is an attractive technology used to recover low-concentration metal ions from various raffinates [8,9], in which an organic solvent is confined between two hydrophobic membranes to avoid the dispersive contact of the aqueous and organic phases. Since extraction and stripping are combined into a single step, the membrane-assisted NDSX presents some advantages such as continuous operation, easy scale-up, low extractant inventory, and high selectivity [10]. NDSX can overcome many of the shortcomings associated with solvent extraction, including solvent loss, emulsion formation, entrainment of the organic phase, and the phase separation problem [3]. Moreover, NDSX can offer better average mass transfer flux and membrane stability than both emulsion and supported liquid membranes. By using the NDSX method, Ortiz and coauthors achieved the selective recovery of zinc over iron from spent pickling wastes [11], and separation and concentration of hexavalent chromium from wastewaters [12]. Ambare et al. found that Nd(III) can be quantitatively recovered from nitric acid solutions (99.9%) in 30 min with non-dispersive solvent extraction [13]. In addition, some similar liquid membrane configurations with NDSX have also been used for effective separation of metal ions and present a good metal flux and stability [14–17].

Besides of membrane configuration, the carrier in the membrane phase is crucial for the high flux transport of metal ions. Previous studies showed that extracting zinc ions from ammoniacal solutions is

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difficult because of the formation of stable zinc ammonia species [18]. Conventional zinc extractants, such as D2EHPA, Cyanex272, and Versatic10, are usually applied in acidic systems [19]. Unfortunately, these acidic extractants are inappropriate for zinc extraction from ammoniacal media due to severe emulsification and extractant loss problems. Although β-diketone is an alternative used for zinc recovery from ammoniacal media [18,20], the extraction efficiency is too low to meet industrial demands when used individually, e.g. the commercial extractants Hostarex®DK-16 [21], Henkel®LIX51 [22], and LIX54 [20]. Some studies have revealed that synergistic ligands, such as TBP and TOPO, must be mixed with β-diketones to improve the extraction efficiency of zinc(II) in ammoniacal solutions [5,18]. By combining with synergistic extraction, zinc ions are likely enriched with the NDSX module. However, the stripping of the zinc-loaded organic phase is crucial for continuous operation of NDSX. We previously reported that zinc can be effectively stripped with ammonia solution from the loaded organic phase containing individual β-diketones [23]. The BHP Billition corporation has also successfully recovered nickel from laterite ores through acid leaching-solvent extraction-ammonia stripping [24]. Thus, it is expected that the direct enrichment of zinc from and into ammoniacal media is feasible through ammonia stripping. In order to consider the dynamic transport process of NDSX, it is necessary to understand simultaneously the extraction and ammonia stripping behaviors of zinc, as it is important for the direct enrichment of zinc(II) from and into ammoniacal media through the NDSX strategy.

In the present study, the direct enrichment of zinc(II) in ammonium media with non-dispersive synergistic extraction was investigated in a sandwich membrane module, in which the mixed extractant of β-diketone and TOPO was used as the carrier. The synergistic role of TOPO on both extraction and ammonia stripping of zinc(II) was disclosed. Several parameters of Zn(II) transport, including carrier concentration, diluent type, feed pH, total ammonia concentration, and temperature, were systematically investigated, and membrane stability was evaluated.

2. Experiments

2.1. Chemicals

The 4-ethyl-1-phenyl-1,3-octadione (denoted as HA) was synthesized according to the previous work [25] and the purity was 98%. Trioctylphosphine oxide (denoted as TOPO) with a purity of 99% was supplied by J&K Chemical Ltd. Unless specifically stated, a nonpolar aliphatic solvent (i.e., octane) was used as diluent. For comparison, a nonpolar aromatic solvent (i.e., toluene) and a polar solvent (i.e., octanol) were also used to evaluate the effect of diluent on ion transport. A stock solution of pH 8.5 containing 0.01 mol/L $ZnSO_4$ and 1 mol/L ammonium sulfate was prepared as the feed phase, and an organic solution containing 0.4 mol/L HA and 0.2 mol/L TOPO was used as the membrane phase. An ammoniacal solution of pH 9.5 containing 4 mol/L ammonium sulfate was used as the receiving phase. The initial pH of the aqueous phase was adjusted by using NaOH and H_2SO_4. All the reagents used were of analytical grade and used as received. Ultrapure water obtained from a Milli-Q system (18.2 MΩ cm) was used in the experiments.

2.2. Dispersive solvent extraction

The aqueous phase (10 mL) was equilibrated with an equal volume of organic phase containing 4-ethyl-1-phenyl-1,3-octadione and trioctylphosphine oxide in different diluents by shaking for 10 min. The preliminary tests verified that the time is sufficient to attain the equilibrium. Unless otherwise stated, the experiment temperature was maintained at 30 ± 0.2 °C using a thermostatic water bath. After reaching equilibrium, the phase separation was operated in a separatory funnel. Zinc concentration in the aqueous phases was determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES, Perkin Elmer 5300 DV) before and after extraction. The concentration of zinc in the loaded organic phase was calculated using the mass balance. The extraction efficiency (E%) was defined as the ratio of zinc concentration in organic phase at equilibrium to the initial concentration of zinc in aqueous phase.

2.3. Non-dispersive solvent extraction

The non-dispersive solvent extraction experiments were conducted in a self-designed membrane module with three compartments [16]. In brief, the sandwich membrane module consisted of two hydrophobic porous polyvinylidene fluoride (PVDF, Millipore) films. The porosity, thickness, and average pore size of the PVDF films was 75%, 125 μm, and 0.2 μm, respectively. A 1-mm-thick fluorine rubber gasket was used as a spacer of two membranes to hold the organic phase. The effective membrane area was 12.56 cm^2. The feed and receiving phases (each 100 mL) were separately circulated by peristaltic pump. The flow rate was maintained at 80 $mL{\cdot}min^{-1}$. After the aqueous phases were cycled through the bilateral compartments with a positive pressure differential, the organic solution containing carriers (ca. 0.8 mL) was slowly injected into the middle compartment and then filled the pores of the PVDF films through capillary action. Because a hydrophobic PVDF film is easily wetted by the organic solvent [26], the positive pressure on the side of the aqueous phases can constrain the loss of organic solution from the membrane phase. Unless specifically stated, the feed and receiving phases were maintained at 30 ± 0.2 °C.

At the desired time interval (1 h), equal volumes of the sample were separately collected from the feed and receiving phases for concentration analysis of metal ions, respectively. The pH in the feed phase was monitored using a calibrated Rex-3C digital pH meter. The zinc(II) concentration was measured with the ICP-AES. Zinc(II) concentration in the membrane phase was calculated based on mass balance. The transport behaviors of zinc(II) can be evaluated with three parameters including x_{tf}%, x_{tr}%, and x_{tm}%, which were defined as follows:

$$\text{Extraction efficiency of Zn(II) in feed phase: } x_{tf}\% = \frac{C_{tf}}{C_0} \times 100 \quad (1)$$

$$\text{Stripping efficiency ofZn(II) in receiving phase: } x_{tr}\% = \frac{C_{tr}}{C_0} \times 100 \quad (2)$$

$$\text{Retention of Zn(II) in membrane phase: } x_{tm}\% = \frac{C_0 - C_{tf} - C_{tr}}{C_0} \times 100 \quad (3)$$

where C_0 is the initial Zn(II) concentration in the feed phase; C_{tf} and C_{tr} are the Zn(II) concentration in feed phase and receiving phase at the desired time, respectively.

The transport behavior of Cu(II) in the feed phase, the receiving phase, and the membrane phase were evaluated as follows:

The initial mass flux (J_0, mmol/m^2/h) values of NDSX at the feed solution/membrane interface were calculated using the following equations:

$$\ln\frac{c}{c_0} = -kt \quad (4)$$

$$J_0 = \frac{V}{A} k c_0 \quad (5)$$

where c (mol/L) and c_0 (mol/L) is the concentration of zinc(II) in the feed phase at selected transport time (h) and initial time, respectively, k is the rate constant, V is the volume of the feed phase, and A is the effective membrane area exposed to the feed solution.