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Selective removal of iron(III) from synthetic copper(II) pregnant leach solutions using [bmim][Tf_2N] as diluent and TFA as extracting agent

E. Quijada-Maldonado, J. Romero *, I. Osorio

Laboratory of Membrane Separation Processes (LabProSeM), Department of Chemical Engineering, University of Santiago de Chile, Chile

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ABSTRACT

High concentrations of iron represent a drawback in the hydrometallurgy of copper, since this metal cation could be co-extracted or entrained to the electrowinning step causing difficulties in obtaining pure copper. In this work, a pre-treatment step based on solvent extraction of iron using a hydrophobic imidazolium-based ionic liquid is proposed to overcome this drawback. The ionic liquid [bmim][Tf_2N] was used as the diluent. The β-diketone TFA was used as the extractant. The results show that the combination extractant-ionic liquid is capable to remove iron(III) selectively from a pregnant leach solution (PLS) containing mainly copper(II) and iron(III) at low pH values. Furthermore, the use of this ionic liquid as diluent shows high extraction capacities. Finally, 97% of iron(III) can be stripped from the ionic liquid using a diluted solution of sulfuric acid (2 M).

1. Introduction

Solvent extraction (SX) is an economical and widely used process in hydrometallurgy for the recovery of valuable ions from aqueous solutions after the leaching process. This technology has been used in large scale for the extraction of copper from a pregnant leach solution (PLS) (Free and Moats, 2014; Schlesinger et al., 2011). Basically, in this process the valuable metal ion is transported from an aqueous into an organic phase by means of an extracting reagent or extractant. The organic phase is provided by an organic diluent ranging from hexane to kerosene.

In the hydrometallurgy of copper, the presence of iron is undesirable because in the SX of copper, iron could be co-extracted or entrained to the electrowinning step, leading to difficulties during the purification process. Iron could be removed by means of a selective precipitation forming goethite, jarosite or hematite (Dutrizac, 1987). However, the disposal of insoluble solids represents an environmental drawback. Therefore, the SX of iron has been proposed as pre-treatment before the electrowinning of copper. This would allow recovering the ferric ions to give them a commercial value (Pospiech et al., 2005; Mishra et al., 2011; Li et al., 2011; Sinha et al., 2014; Olivier et al., 2012; Principe and Demopoulos, 2004). The volatile compounds like kerosene used in SX as diluents exhibit several disadvantages such as high volatility and toxicity (Kislik, 2012), which cause evaporation and pollution, respectively. Besides that, these organic solvents are normally used in very large amounts.

Recently, ionic liquids have been proposed as potential replacements of those organic diluents in SX of alkali metals (Shi et al., 2014), transition metals (Sepúlveda et al., 2014; Domanska and Rekawek, 2009; Wei et al., 2003; Lertlapwasin et al., 2010), lanthanides (Nakashima et al., 2005; Yoon et al., 2010) and actinides (Mohapatra et al., 2014; Panja et al., 2012; Shen et al., 2011) due to the excellent properties such as chemical stability, water immiscibility and negligible vapor pressure that would avoid solvent losses providing a total recyclability. This is of great importance in industry because it is well known that ionic liquids are much more expensive than the traditional organic diluents. Nevertheless, the negligible vapor pressure and the high chemical stability would allow recycling the diluent/extractant pair for many times without evaporation losses. Furthermore, previous work found that ionic liquids are advantageous as they exhibit better extractability than the organic diluents (Yoon et al., 2010). This advantage would also allow decreasing the amount of diluent used in the SX process.

From these studies, the ionic liquids 1-butyl-3-methylimidazolium hexafluorophosphate [bmim][PF_6] and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [bmim][Tf_2N] appear as the most promising replacements of the organic diluents due to the commercial availability and hydrophobicity. However, [bmim][Tf_2N] shows several advantages over [bmim][PF_6]: (i) the solubility of [bmim][Tf_2N] in water is less than [bmim][PF_6] (1.6% and 2.3% (w/w), respectively) (Chapeaux et al., 2007; Freire et al., 2007, 2008), (ii) in the presence of water [bmim][PF_6] hydrolyzes to HF (Swatloski et al., 2003).

Thus, the main goal of this work is to achieve an efficient and selective removal of iron from an industrial pregnant leach solution provided by Antofagasta Minerals S.A. and a synthetic solution containing mainly Cu(II)/Fe(III) using the ionic liquid [bmim][Tf_2N] as the diluent and

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* Corresponding author.
E-mail address: julio.romero@usach.cl (J. Romero).

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1,1,1-trifluoro-2,4-pentanedione (TFA) as the extractant. Previously, it was demonstrated that [bmim][Tf_2N] is a suitable diluent to be used in combination with TFA to extract Cu(II) ions (Sepúlveda et al., 2014). In a first step, the effect of TFA concentration on selective removal of iron from the two solutions, PLS and synthetic solution, is analyzed. Secondly, the extraction stoichiometry of Fe(III) and Cu(II) is studied and the removal of both species is analyzed in terms of the effect of the operating variables such as pH and aqueous-organic volumetric ratio (A/O). Finally, the stripping of the iron from the loaded ionic liquid phase with a diluted sulfuric acid solution is carried out.

2. Experimental

2.1. Materials and sample preparation

A pregnant leach solution (PLS) generated at Antofagasta Minerals S.A. mining company located in Antofagasta, Chile, was used for the solvent extraction experiments with 1,1,1-trifluoro-2,4-pentanedione (TFA). The concentrations of Cu(II) and Fe(III) as well as the pH of the PLS are summarized in Table 1. A synthetic solution with the same concentration of metal ions was prepared from Cu(II) sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$) with a purity higher than 98% and Fe(III) sulfate hydrate ($Fe_2(SO_4)_3 \cdot nH_2O$) supplied by Biopack®. The ionic strength of the synthetic solution was reached by adding Potassium nitrate with purity higher than 99% and sodium chloride supplied by Fluka® ($I = 4.4$ M). Reagents were dissolved in double distilled water. Table 1 summarizes the concentration of this synthetic PLS.

The organic phase or so called ionic liquid phase was prepared from 1-butyl-3-methylimidizalium bis(trifluoromethylsulfonyl)imide ([bmim][Tf_2N]) with a purity higher than 98%, which was used as the diluent and 1,1,1-trifluoro-2,4-pentanedione (TFA) with a purity higher than 98% was used as the extractant. Both ionic liquid and extractant were supplied by Sigma-Aldrich® and used without further purification. Fig. 1 shows the structure of the ionic liquid and the extractant used in this work.

The extraction stoichiometry was studied through dedicated experiments, which were carried out using buffer solutions prepared from potassium hydrogen phthalate, hydrochloric acid 37%, acetic acid (purity >99.9%) and sodium acetate.

Table 1
Concentration of main components in PLS and synthetic solution.

Metal species	Concentration (mg/L)	
	PLS	Synthetic solution
Cu(II)[a]	3360	3350
Fe(III)[a]	1570	1570
Mg	>15,000	
Al	>10,000	
Mn	>1000	
Na	>5000	
K	521	
Ca	205	
Zn	107	
Si	48	
Co	32	
Li	14	
Ni	13.7	
Cr	11.1	
Pb	8.2	
Te	3.0	
As	2.0	
Cd	0.54	
Mo	<0.5	
Ag	0.25	
Hg	<0.15	

Initial pH of the PLS and the Synthetic solution was 0.8 and 0.99, respectively.

[a] As sulfates.

A third step considered striping assays, where sulfuric acid with purity higher than 98.1% (J.T. Baker) was used to prepare stripping solutions.

2.2. Experimental procedure

The synthetic solution was prepared using an analytical balance with a precision of ±0.001 g (Denver Instruments Company, model AA200). pH measurements were performed out using a pH meter (Oyster-10® with ATC electrodes).

The solvent extraction experiments were carried out in an open flask where the aqueous and ionic liquid phases were mixed and stirred for 40 min, sufficient time to reach equilibrium. Once these phases were completely separated, the concentration of the metal ions in the aqueous phase was quantified by means of Atomic Absorption Spectrophotometry (AAS) (GBC® Scientific Equipment model SensAA dual beam, equipped with a 4 mA lamp (single element) Photron International®). The concentration of the metal ions in the ionic liquid phase was estimated through the mass balance from the experimental runs using the synthetic solution.

The identification of the solvent extraction stoichiometry of each metal ion was achieved using solutions of copper and iron, which were prepared separately by dissolving the sulfate salt of copper or iron in a buffer solution containing potassium hydrogen phthalate 1.0 M, HCl 0.1 M, acetic acid (glacial) and sodium acetate. After the equilibrium was reached, the pH was measured. It is worth noting that the buffer solution was used only to identify the extraction stoichiometry. This was carried out to avoid the precipitation of iron species with pH changes.

The effect of pH on the solvent extraction was examined using a synthetic aqueous solution containing 0.5 g/Lof Fe(III) and 0.5 g/L of Cu(II). In these experiments, the initial pH of the aqueous solution was adjusted by adding small volumes of 1.0 M H_2SO_4.

Finally, the stripping of the Fe(III) from the loaded ionic liquid phase was carried out. The concentration in this ionic liquid phase was obtained by mass balance. Thus, the phase separated from the previous extraction tests was put in contact with aqueous stripping solution with increasing concentrations of sulfuric acid at volumetric O/A ratio equal to 1.0 and stirred for 40 min. The final concentration of Fe(III) in the aqueous phase was determined.

2.3. Extraction performance and stoichiometry

The extraction performance of the process can be quantified on the basis of the extraction percentage of the metal ion. Eq. (1) defines this parameter:

$$(\%)E = \frac{C_i - C_f}{C_i} * 100 \tag{1}$$

where C_i represents the initial concentration of the metal ion species in the aqueous feed solution and C_f is the concentration of metal ion species in the same phase after the solvent extraction process.

On the other hand, the extraction stoichiometry was investigated for Cu(II) and Fe(III) by determining the extraction (%) as a function of equilibrium pH. There are three possible stoichiometries, which could be classified into cationic (acidic), anionic (basic) or solvating (neutral).

Solvent extraction of Cu(II) using β-diketones as extractant has been previously reported (Przeszlakowski and Wydra, 1982; Fu et al., 2011) where the extraction was related to the formation of neutral complexes (cationic stoichiometry). Further studies show the efficient extraction of Cu(II) ions from aqueous solutions using 1,1,1-trifluoro-2,4-pentanedione (TFA) as extractant and 1-butyl-3-methylimidizalium hexafluorophosphate ([bmim][PF_6]) (Sepúlveda et al., 2014) as the diluent to follow this stoichiometry. This mechanism is possible due to the fact that β-diketones are weak acid molecules, which dissociates into