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Leaching of chalcopyrite (CuFeS$_2$) with an imidazolium-based ionic liquid in the presence of chloride

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ABSTRACT

The effects of independent variables such as, temperature, concentration of ionic liquid (1-butyl-3-methyl-imidazolium hydrogen sulphate, [bmim][HSO$_4$]), chloride and sulphuric acid on copper extraction from chalcopyrite (CuFeS$_2$) ore were studied by surface optimization methodology. The Central Composite Face approach and a quadratic model were applied to the experimental design. The optimal copper extraction conditions given by the above methodology were 20% (v/v) of [bmim][HSO$_4$] in water, 100 g L^{-1} chloride, and 90 °C. The concentration of chloride and the temperature together exert a synergistic effect in enhancing chalcopyrite dissolution. Experimental data were fitted by multiple regression analysis to a quadratic equation and analyzed statistically. A model was developed for predicting copper extraction from CuFeS$_2$ ore with variables such as Cl$^-$, [bmim][HSO$_4$], H$_2$SO$_4$ concentrations and temperature in the range studied. The activation energy was calculated to be 60.4 kJ/mol (temperature range 30–90 °C), indicative of chemical control of the reaction and [bmim][HSO$_4$] acts as an acid in the reaction.

1. Introduction

CuFeS$_2$ is the most abundant primary copper sulphide mineral and by far the most refractory towards hydrometallurgical processing (Debernardi and Carlesi, 2013). The slow dissolution of this mineral in sulphate media results in an inefficient industrial process. CuFeS$_2$ dissolution in chloride media results in faster kinetics (Ruiz et al., 2011). Similarly, the leaching of oxides in the presence of high chloride concentration is advantageous because of propitious leaching kinetics due to enhanced proton activity, in addition to the catalytic effect of chloride ions through the formation of metal-ion complexes (Senanayake, 2007). It has been suggested that the use of sodium chloride avoids surface passivation by forming complexes with Cu(I) ions, introduces a second redox couple to the system which improves dissolution rates and/or promotes the formation of a more porous sulphur product (Carneiro and Leão, 2007; Lu et al., 2000). Many studies have been conducted to elucidate the mechanisms of CuFeS$_2$ dissolution in both chloride and sulphate systems, but the results reveal some ambiguities.

Ionic liquids (ILs) are receiving considerable attention due to their potential uses in, for example, synthesis, separations, catalysis, electrochemistry, and extraction and separation of nonferrous metals (Brennecke and Maginn, 2001; Davis, 2004; Tian et al., 2010). The interest in ILs continues unabated because they exhibit different and potentially useful physico-chemical properties. The ILs are liquids across a wide temperature range with negligible vapour pressure, high thermal conductivity, chemical and physical stability, and potentially have multiple applications (Gardas and Coutinho, 2008). The possibility of tailoring the functionality of ionic liquids, offers opportunities for a degree of control over reactivity not possible with traditional molecular solvents (Holbrey and Rogers, 2002).

More specifically, it has been reported that imidazolium-based ILs have lower surface tension than water. Surface tension influences the adsorption of liquids by porous solids and decreases the "solid-solution hydrophobic resistance to electron transfer, thus enabling continuous acid leaching of the solid surface" (Carlesi et al., 2016), therefore promoting the dissolution reaction

compared with aqueous acid solution (Whitehead et al., 2007). The 1-butyl-3-methyl-imidazolium hydrogen sulphate IL ([bmim][HSO$_4$]) has been used in hydrometallurgy either directly as a solvent or in aqueous mixtures for the leaching of gold, silver, copper and base metals from sulphidic ores, with IL recycle, as reported by Whitehead et al. (2004 and 2007). Dong et al. (2009) reported that [bmim][HSO$_4$] acted as an acid in the leaching of CuFeS$_2$ concentrate and that the IL may be more effective than H$_2$SO$_4$ in aqueous solution because its catalysis of the transfer of dissolved oxygen accelerates the oxidative leaching of CuFeS$_2$. Carlesi et al. (2016) proposed that the studied imidazolium-based ILs could be considered as catalysts or leaching additives for CuFeS$_2$ ore leaching, rather than as the leaching agent itself. They reported a synergistic effect when ILs were used together with sulphuric acid. Also, the application of imidazolium-based ILs in solvent extraction as well as some electrochemical processes has been suggested, and these compounds may be able to play an important role in the recovery and purification of high-value metals from water as well as ores, as briefly reviewed by Łuczak et al. (2008).

For this study, the IL [bmim][HSO$_4$] was selected because of its stability, its negligible vapour pressure and the possibility of recycling the IL. Such properties make it a good candidate for a sustainable and environmentally-friendly leaching process. We describe the effect of a mixed [bmim][HSO$_4$] – chloride lixiviant for the extraction of Cu from CuFeS$_2$ ore at atmospheric pressure. Kinetic studies at the pre-determined optimal conditions were also undertaken. The effects of independent variables such as, temperature, concentrations of [bmim][HSO$_4$]), chloride or sulphuric acid on copper extraction from CuFeS$_2$ were studied by the response surface optimization methodology as described by Rautela et al. (1979). A model was developed for predicting Cu extraction from CuFeS$_2$ with variables such as Cl$^-$, [bmim][HSO$_4$] concentrations and temperature.

2. Materials and methods

2.1. Chalcopyrite sample

The CuFeS$_2$ used in this study was obtained from Atómica mine, Antofagasta, Chile. The mineralogical composition was determined using X-ray diffraction (Siemens D500, Total Pattern Analysis Software). The CuFeS$_2$ mineral composition is: 96.6% chalcopyrite; 2.0% albite; and 1.4% covellite. The CuFeS$_2$ sample was ground in a porcelain mortar, oven-dried at 50 °C and then classified by sieving into narrow-range size fractions. The fraction $-65 + 45$ μm was used in this study and its chemical analysis was 34.9% Cu and 28.4% Fe.

2.2. Reagents

The IL selected for study, 1-butyl-3-methylimidazolium hydrogen sulphate, ([bmim][HSO$_4$]), was obtained from Sigma-Aldrich Chemie GmbH. - Germany. The IL density and purity were 1.277 g mL^{-1} and $\geqslant$94.5%, respectively. The IL impurity is $\leqslant$1.0% water and anion traces, chlorides $\leqslant$1.0%. The reagents NaCl and sulphuric acid were analytical grade from Merck.

2.3. Leaching tests

Leaching tests were conducted in glass reactors of 50 mL volume equipped with reflux condensers to minimize water loss through evaporation. The mineral pulp density was 10 g L^{-1}, and the leach solution volume was 20 mL. Mineral suspensions were stirred using a digital magnetic stirrer (760 rpm) with 5

positions (IKA RO5) and the temperature was controlled using an oil-heated circulator (Julabo). The temperature range tested in the experiments was 30–90 °C. The IL concentration (v/v) in aqueous solutions was from 20% to 60%, the IL was dissolved readily in water at all concentrations used. In these tests, the effect of agitation and the optimum stirring speed on Cu extraction were investigated. Stirring speed was tested in the range of 200–760 rpm in tests of 24 h duration at 70 °C and 50 g L^{-1} of chloride.

In addition to the XRD mineralogical analysis, leached residues and the CuFeS$_2$ were analyzed using scanning electron microscope SEM-EDX (JEOL, model: JSM 6360LV). Measurements of pH and oxidation-reduction potential (ORP) of leach solutions were made using a pH-ORP meter (HANNA HI-4222). The solution ORP was measured in a combination ORP electrode cell composed of a platinum working electrode and a saturated Ag/AgCl reference electrode. Cu concentrations in the leach solutions were analyzed using atomic absorption spectroscopy (Varian AA240).

2.4. Experimental design

The effect of independent variables such as: concentration of [bmim][HSO$_4$] chloride, sulphuric acid and temperature were studied by response surface optimization methodology (Montgomery, 2015; Bezerra et al., 2008). The Central Composite Face (CCF) design and a quadratic model were applied to the experimental design for CuFeS$_2$ leaching. Consequently, 27 experimental tests were carried out. For the experimental design, we used Modde version 7.0 software (Umetrics A, B). This approach enabled the effects of these independent variables (IL, Cl$^-$, H$_2$SO$_4$ concentrations and temperature) on the extraction of Cu from the CuFeS$_2$ to be investigated with a minimum number of experimental tests. Experimental data were fitted by multiple linear regression analysis to a quadratic equation and analyzed statistically. The empirical model contains

Table 1
Experimental parameters for Central Composite Face Design.

Variable	Low	Medium	High
[bmim][HSO$_4$] (% v/v)	20	40	60
Chloride (g L^{-1})	0	50	100
Sulphuric acid (M)	0	0.25	0.5
Temperature (°C)	30	60	90
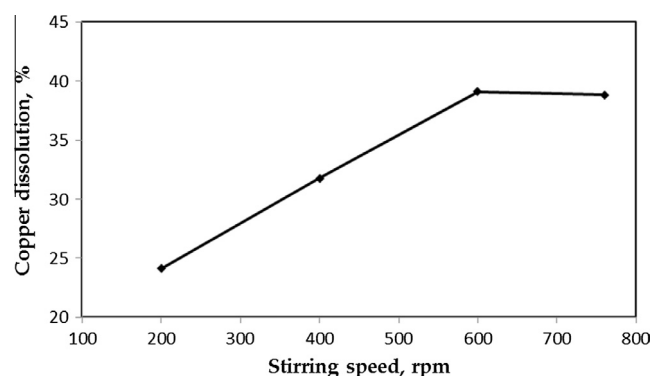
Fig. 1. Copper dissolution from CuFeS$_2$ vs stirring speed. Conditions: 70 °C, 50 g L^{-1} Cl$^-$, 20% (v/v) [bmim][HSO$_4$], pulp density 10 g L^{-1}, 24 h.