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Copper recovery from ore by liquid–liquid extraction using aqueous two-phase system

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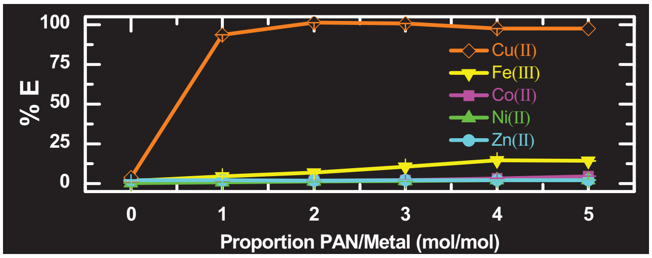
HIGHLIGHTS

- A green method for Cu(II) extraction of ore concentrate was developed.
- Selective separation of Cu(II) and Zn(II), Co(II), Ni(II), Cd(II), Mn(II), Al(III) and Fe(III) was obtained.
- The method is environmental safe, low cost and easy for scale up.
- The liquid–liquid extraction is without use of organic solvent.

GRAPHICAL ABSTRACT



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ABSTRACT

We investigated the extraction behavior of Cu(II) in the aqueous two-phase system (ATPS) formed by ($L35 + MgSO_4 + H_2O$) or ($L35 + (NH_4)_2SO_4 + H_2O$) in the presence of the extracting agent 1-(2-pyridylazo)-2-naphthol (PAN). At pH = 3 and a PAN concentration of 0.285 mmol kg^{-1}, both ATPS lead to the effective separation of Cu(II) from other metallic ions (Zn(II), Co(II), Ni(II) and Fe(III)). High separation factors range between 1000 and 10,000 were obtained for the extraction of Cu(II) and concomitant metallic ions. This ATPS was used for the extraction of Cu(II) from a leached ore concentrate with a extraction percentage of 90.4 ± 1.1%; other metals were mainly located in the bottom phase.

1. Introduction

Copper is widely used because it has several essential properties for different technological applications, such as use in electrical materials and construction, transportation, and industrial machinery parts, which are produced at a higher rate every year. At present, there are two main methods employed worldwide to process copper ore for metal production: pyrometallurgical and hydrometallurgical methods.

The pyrometallurgical method comprises numerous types of shaft and flash technologies, including crushing, grinding, flotation, smelting-refining and electro-refining. The pyrometallurgical method is used for sulfide flotation concentrates, and it is economically feasible for copper rich feeds and large-scale operations [1]. However, this process has several drawbacks, including a high energy consumption and the production of hazardous gases.

Because of an increasing world demand for copper, there is a strong incentive to develop environmentally friendly processes for copper extraction from low-grade ores. Therefore, there is a considerable intensification in the research and development of hydrometallurgical methods. These developments focus on

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by-product and concentrate treatment alternatives to traditional pyrometallurgical methods for the processing of sulfide ores and concentrates, particularly for small-scale production and for the processing of remote metal resources that are not amenable to pyrometallurgy [2]. Hydrometallurgy consists of crushing, leaching, solvent extraction (SE) and electrowinning.

The SE step is very important because it results in the purification and preconcentration of the metal. SE offers a convenient method for the extraction and separation of copper, and SE can be efficiently applied for the recovery of copper from leach liquors and waste solutions using a variety of reagents [3]. SE plants have critical problems that considerably affect the extraction efficiency and selectivity, including crud formation, organic and aqueous phase entrainments, and variable and unpredictable phase separation times in settlers [4]. Furthermore, established SE methods involve organic solvents that are considered hazardous materials because they are detrimental to the environment and harmful to human health [5]. Therefore, it is important to devise novel extraction methods that are cleaner and safer. Hence, the aqueous two-phase system (ATPS) has been introduced as a promising liquid–liquid extraction system for metal separation because it mostly uses water and other nontoxic and nonflammable constituents [6–8].

ATPS is formed under specific thermodynamic conditions when one polymer and one electrolyte are mixed. A phase split results in a polymer-enriched top phase and an electrolyte-enriched bottom phase. Additionally, these systems have a high content of water in both phases [9]. The ATPS has several advantages, including its easy operation, low-cost and the possibility to recycle its components [10]. These systems have been used for the separation, preconcentration, purification and determination of biomolecules [11–14], phenols [15,16], dyes [17] and metallic ions [6–8,18]. Factors such as the pH, the design of the system, the electrolyte composition, the temperature and the extractant concentration strongly affect the partitioning behavior and the separation of analytes [19].

In the described work, we separated copper from other metallic ions using an ATPS formed by a triblock copolymer composed of poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO), $MgSO_4$ and water at 298 K in the presence of 1-(2-pyridylazo)-2-naphthol (PAN) as an extracting agent. The influence of certain parameters on the metal extraction yield was examined, including the amount of the added extracting agent, the pH of the system, the nature of the ATPS electrolyte, as well as the separation factor of the copper compared to several other metallic ions (Cd(II), Fe(III), Al(III), Mn(II), Ni(II), Co(II) and Zn(II)). The extraction method was then applied for the efficient extraction and purification of Cu(II) from the leachate of a copper ore concentrate.

2. Experimental

2.1. Materials and chemicals

All reagents were of analytical grade quality and were used as received without further purification. The triblock copolymer used in this study was poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide), L35, with an average molar mass (M_m) of 1900 g mol^{-1} and 50% ethylene oxide, corresponding to a composition of $(EO)_{11}(PO)_{16}(EO)_{11}$. The triblock copolymer, H_2SO_4 and HNO_3 were obtained from Aldrich (Milwaukee, WI, USA). $MgSO_4{\cdot}7H_2O$, $(NH_4)_2SO_4$, NaOH, $MnSO_4{\cdot}H_2O$, $ZnSO_4$ and $FeCl_3$ were obtained from VETEC (Duque de Caxias, Rio de Janeiro, Brazil). PAN, $HClO_4$, $NH_4Al(SO_4){\cdot}12H_2O$, $CoCl_2$, $CdCl_2{\cdot}H_2O$, $Ni(CH_3COO)_2{\cdot}4H_2O$ and $CuSO_4$ were purchased from MERCK (Darmstadt, Germany).

2.2. Equipment

Deionized water ($R \geq 18\,M\Omega\,cm^{-1}$) was used throughout the experiments. A Milli-Q II water deionizer (Millipore Corporation) was used for the final purification of the distilled water. The pH measurements were performed using a glass electrode connected to a digital pH meter (Digicron Analítica Ltda, Digimed model DM-20). The experiments were performed on an analytical balance (Shimadzu, AY 220) with an uncertainty of ±0.0001 g, and the temperature of the ATPS was adjusted to 25.0 ± 0.1 °C with a temperature-controlled water bath (Microquímica, MQBTC 99-20). A hot plate (Fisatom – 752A) and a centrifuge (Thermo Scientific, Heraeus Megafuge 11R) were also used for the experiments. The metal concentrations were measured with a flame atomic absorption spectrometer (VARIAN AA240). The operations conditions were: wavelength 324.8 nm, resolution 0.5 nm, current lamp 4.0 mA, air–acetylene flame (air and acetylene flux rates 3.50 and 1.50 L min^{-1}, respectively).

2.3. Aqueous two-phase system composition

The aqueous two-phase system formed by L35 + $MgSO_4$ + H_2O was prepared by mixing 2.00 g of a 57.19% (m/m) L35 solution and 2.00 g of a 19.88% (m/m) $MgSO_4$ solution [20]. The aqueous two-phase system formed by L35 + $(NH_4)_2SO_4$ + H_2O system was prepared mixing 2.00 g of a 54.22% (m/m) L35 solution and 2.00 g of a 18.71% (m/m) $(NH_4)_2SO_4$ solution [9].

2.4. Influence of the pH on extraction behavior

The partitioning of each metallic ion in the biphasic system was performed to fix the global metal concentration at 0.0950 mmol kg^{-1}. To study the influence of the pH, a PAN/metal ratio of 3 was used. A concentrated metal solution with a concentration of 0.190 mmol kg^{-1} was prepared in a 19.88% (m/m) $MgSO_4$ solution, and a concentrated PAN solution with a concentration of 0.570 mmol kg^{-1} was prepared in a 57.19% (m/m) L35 solution. When 2.00 g of $MgSO_4$ solution is added to 2.00 g of L35 solution, the metal and PAN final concentration is reduced to a half of initial concentration (0.0950 mmol kg^{-1} for metal and 0.285 mmol kg^{-1} for PAN). The pH of the water used to prepare the $MgSO_4$ and L35 solutions had been previously adjusted. Sulfuric acid was used to adjust the pH = 1.0, 3.0 or 5.0 and NaOH was used to adjust pH = 7.0, 9.0 or 11.0. In a centrifuge tube 2.00 g of the metal solution (0.190 mmol kg^{-1}) and 2.00 g of the PAN solution (0.570 mmol kg^{-1}) were weighed. The tube was manually stirred for 3 min, centrifuged for 15 min at 3000 rpm, and then allowed to settle for 1 h at 25.0 ± 0.1 °C. The top phase was then collected, appropriately diluted, and the metal concentration in the top phase was determined with a flame atomic absorption spectrometer (FAAS). The extraction percentage (%E) of the metallic ions was calculated by Eq. (1).

$$\%E = \frac{(n_{M^{m+}})_{Top}}{(n_{M^{m+}})_{T}} \times 100 \qquad (1)$$

where $(n_{M^{m+}})_{Top}$ is the amount (in mol) of metallic ions in the top phase, and $(n_{M^{m+}})_{T}$ is the total amount of metallic ions in the system.

2.5. Influence of the amount of PAN on extraction behavior

An ATPS at pH = 3.0 was used to study the influence of the amount of PAN. The procedure for this experiment is similar to what was described in Section 2.3, except that the PAN concentration in the L35 solution was varied from 0.190 to 0.950 mmol kg^{-1}.