



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

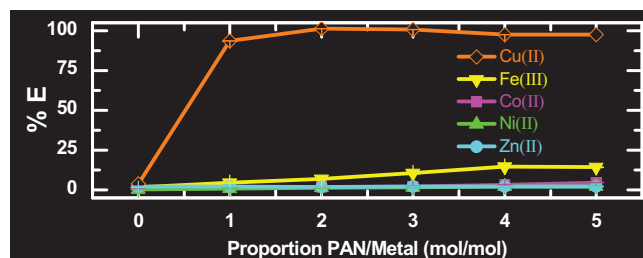
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HIGHLIGHTS

- ▶ 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



ARTICLE INFO

Article history:

Received 14 March 2012
 Received in revised form 13 August 2012
 Accepted 14 August 2012
 Available online 21 August 2012

Keywords:

Green chemistry
 Copper
 Ore
 Liquid–liquid extraction
 Aqueous two-phase system

ABSTRACT

We investigated the extraction behavior of Cu(II) in the aqueous two-phase system (ATPS) formed by (L35 + MgSO₄ + H₂O) or (L35 + (NH₄)₂SO₄ + H₂O) 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.

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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 $(\text{EO})_{11}(\text{PO})_{16}(\text{EO})_{11}$. The triblock copolymer, H_2SO_4 and HNO_3 were obtained from Aldrich (Milwaukee, WI, USA). $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{SO}_4$, NaOH, $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, ZnSO_4 and FeCl_3 were obtained from VETEC (Duque de Caxias, Rio de Janeiro, Brazil). PAN, HClO_4 , $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, CoCl_2 , $\text{CdCl}_2 \cdot \text{H}_2\text{O}$, $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ and CuSO_4 were purchased from MERCK (Darmstadt, Germany).

2.2. Equipment

Deionized water ($R \geq 18 \text{ M}\Omega \text{ cm}^{-1}$) 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 $\pm 0.0001 \text{ g}$, and the temperature of the ATPS was adjusted to $25.0 \pm 0.1 \text{ }^\circ\text{C}$ 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 + $(\text{NH}_4)_2\text{SO}_4$ + 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) $(\text{NH}_4)_2\text{SO}_4$ 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 $0.0950 \text{ mmol kg}^{-1}$. To study the influence of the pH, a PAN/metal ratio of 3 was used. A concentrated metal solution with a concentration of $0.190 \text{ mmol kg}^{-1}$ was prepared in a 19.88% (m/m) MgSO_4 solution, and a concentrated PAN solution with a concentration of $0.570 \text{ mmol kg}^{-1}$ 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 ($0.0950 \text{ mmol kg}^{-1}$ for metal and $0.285 \text{ mmol kg}^{-1}$ 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 ($0.190 \text{ mmol kg}^{-1}$) and 2.00 g of the PAN solution ($0.570 \text{ mmol kg}^{-1}$) 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 $25.0 \pm 0.1 \text{ }^\circ\text{C}$. 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).

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

where $(n_{\text{M}^{m+}})_{\text{Top}}$ is the amount (in mol) of metallic ions in the top phase, and $(n_{\text{M}^{m+}})_{\text{T}}$ 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 $0.950 \text{ mmol kg}^{-1}$.

Table 1
Concentration of predominant metallic ions in the sample ore copper concentrate.

Metal	Concentration
Copper	29.7% (m/m)
Iron	12.0% (m/m)
Nickel	$1.03 \times 10^3 \text{ mg kg}^{-1}$
Zinc	326 mg kg^{-1}
Chromium	134 mg kg^{-1}
Cobalt	98.8 mg kg^{-1}

2.6. Influence of the ATPS component nature on extraction behavior

To study the influence of the ATPS component nature, a PAN concentration of $0.570 \text{ mmol kg}^{-1}$ and a pH of 3.0 were used. The metal solutions were prepared in a MgSO_4 solution or a $(\text{NH}_4)_2\text{SO}_4$ solution depending on the experiment. The subsequent steps were performed according to what was described in Section 2.3.

2.7. Copper ore concentrate

Leaching occurred after incubation at 25°C for 8 h with 1.00 g of the copper (Mineração Caraíba – Jaguarari, Bahia, Brazil) in 5.00 mL of HNO_3 (65%) and 10.0 mL of concentrated HClO_4 . The obtained leachate was filtered and transferred to a 1.00 L flask filled with deionized water. The concentration of the main metals in the resulting solution was then determined with FAAS (Table 1).

2.8. Copper extraction from the ore leachate and stripping experiments

Initially, the pH of the leachate was adjusted to 3.0, resulting in the formation of a precipitate. The precipitate was centrifuged and the concentration of the main metals in the supernatant was determined with a flame atomic absorption spectrometer. The supernatant was used to prepare solutions of L35 and MgSO_4 . The PAN solution ($14.7 \text{ mmol kg}^{-1}$) was prepared in the L35 solution. In a tube 3.00 g of the PAN solution and 3.00 g of the MgSO_4 solution 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 $25.0 \pm 0.1^\circ\text{C}$. After each extraction stage the top phase and bottom phase was collected, appropriately diluted, and the metal concentration in both phases were determined with a flame atomic absorption spectrometer.

For both stripping stages of metal ion, 2.00 g of loaded phase with metal ion (ATPS top phase) was taken and contacted with 2.00 g of ATPS bottom phase added with HNO_3 at different concentration, followed by vigorous shaking to reach equilibrium.

3. Results and discussion

3.1. Influence of the pH on the extraction behavior of metallic ions

The influence of the pH on the extraction behavior of Cu(II), Zn(II), Co(II) and Ni(II) is shown in Fig. 1. These experiments were performed with the ATPS formed from L35 + MgSO_4 + H_2O and with a PAN concentration of $0.285 \text{ mmol kg}^{-1}$.

The results showed that all metals are extracted at a minimum efficiency at a pH of 1.0 because of the strong protonation of the PAN molecule at this pH that hinders its complexation with metals. A high pH favors the ionization of PAN ($\text{p}K_{a1} = 2.9$ and $\text{p}K_{a2} = 11.6$), which facilitates complexation and increases the extraction yield of Zn(II), Co(II) and Ni(II). For Cu(II), the extraction yield initially increases with increasing pH values because of the ionization of PAN [21]; however, for pH values greater than 5.0, the amount of

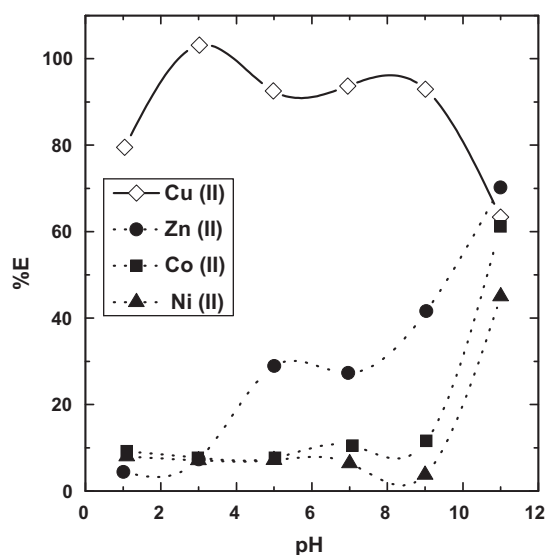


Fig. 1. The effect of the pH of the ATPS on the %E of Cu(II), Zn(II), Co(II) and Ni(II) for the L35 + MgSO_4 + H_2O system with a PAN concentration of $0.285 \text{ mmol kg}^{-1}$.

copper in the top phase decreases. This behavior is because of the increased concentration of hydroxyl groups in the mid-pH range and the subsequent formation of hydroxyl-complexes with Cu(II), reducing the amount of Cu(II) that is available to interact with PAN. This effect is less drastic for the other analyzed metals, without affecting the complexation with PAN.

The maximum extraction yields were $103 \pm 2\%$ for Cu(II) at pH 3.0 and $70.2 \pm 1.5\%$, $61.2 \pm 1.3\%$ and $45.0 \pm 1.2\%$ for Zn(II), Co(II) and Ni(II), respectively, at pH 12. However, most interestingly, at pH 3.0 Cu(II) was completely extracted to the top phase, whereas the other metals were mostly present in the lower phase ($\%E \leq 7.69\%$). This is very important for separation processes that require the separation of Cu(II) from other metallic ions. Therefore, additional studies were performed at this pH.

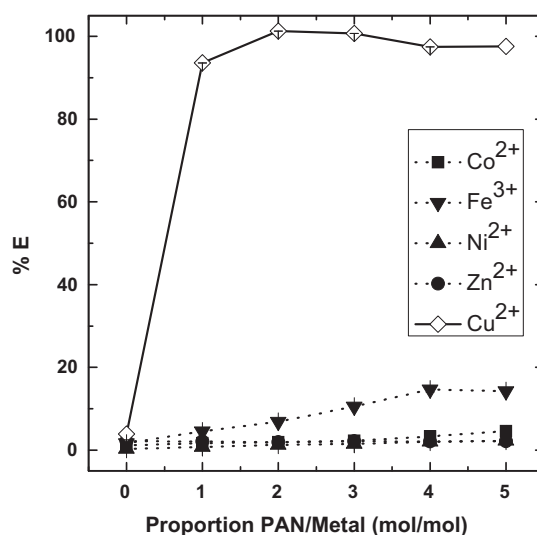
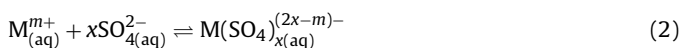


Fig. 2. The effect of the amount of PAN added to the ATPS on the %E of Cu(II), Zn(II), Co(II), Ni(II) and Fe(III) for the L35 + MgSO_4 + H_2O system at pH = 3.

3.2. Influence of the amount of PAN on the extraction behavior of metallic ions

Fig. 2 summarizes the %E of the Cu(II), Co(II), Ni(II), Zn(II) and Fe(III) metallic ions added to the L35 + MgSO₄ + H₂O system at pH = 3.0 as a function of the amount of PAN in the top phase.

In the absence of PAN, the metals are mainly concentrated in the bottom phase (Fig. 2) because there are strong interactions between the sulfate (of the salt in the ATPS that is primarily localized in the bottom phase) and the charged species of the metals (Eq. (2)).



$$K_{M(SO_4)_x^{(2x-m)-}}^{\theta} = \frac{\gamma_{M(SO_4)_x^{(2x-m)-}} \cdot [M(SO_4)_x^{(2x-m)-}]}{\gamma_{M^{m+}} \cdot [M^{m+}] \cdot \gamma_{SO_4^{2-}} \cdot [SO_4^{2-}]^x} \quad (3)$$

In Eq. (3), $K_{M(SO_4)_x^{(2x-m)-}}^{\theta}$ is the standard thermodynamic constant for the formation of the metal–sulfate complex, $\gamma_{M(SO_4)_x^{(2x-m)-}}$ is the activity coefficient of the metal–sulfate complex and $\gamma_{M^{m+}}$ and $\gamma_{SO_4^{2-}}$ are the activity coefficients of the metal and the sulfate, respectively. The stability constant depends on the reaction conditions and the electronic structure of the central metal ion. The metal–sulfate complexes are preferentially formed under standard conditions in the following order: Cu ≅ Zn ≅ Ni ≅ Co < Fe [22]. The metal extraction efficiency is inversely proportional to the formation constant of the complex if only the metal–sulfate interaction is considered.

In general, the addition of organic molecules as complexants results in much larger ion distribution coefficients, but this addition constrains the application of ATPS because the complexant must be water soluble [23]. However, the copolymer ATPS enables the use of the water-insoluble extractant, PAN, because the phase enriched in macromolecules is highly hydrophobic due to the presence of macromolecular aggregated formed by a hydrophobic core and a hydrophilic shells.

The addition of PAN to the ATPS initiates complex formation between PAN and the metals. Fig. 2 shows that the addition of PAN results in an increase in %E for all metals. As the complex between PAN and the metal is formed, the complex moves from the bottom phase to the top phase because it has a specific interaction with the copolymer macromolecules. This PAN–metal complex transfer process results in the formation of additional complexes in the bottom phase via equilibrium displacement. This displacement equilibrium drives the formation of complexes when the concentration of PAN is increased, until a saturation point is reached where additional amounts of PAN do not affect the extraction yield. The extraction of copper in this system is extremely efficient (%E ≅ 100) compared to the extraction of others metals that largely remain in the bottom phase (%E ≤ 45).

3.3. Influence of the ATPS component nature on the extraction behavior of metallic ions

The results of the influence of the ATPS salt nature on the extraction behavior of Cu(II) are shown in Fig. 3. These studies were performed with the ATPS formed by L35 + MgSO₄ + H₂O or L35 + (NH₄)₂SO₄ + H₂O and a PAN concentration of 0.285 mmol kg⁻¹ at pH = 3.0.

Fig. 3 shows that the ATPS formed by L35 + MgSO₄ + H₂O is more efficient for the extraction of Cu(II) at all pH values. The complex between Cu(II) and ammonium (log K = 4.3) [22] has a higher formation constant than the complex between Cu(II) and sulfate (log K = 2.4) [22], thus providing for the ammonium ATPS the least amount of copper for complexation with PAN. Despite its higher efficiency the L35 + MgSO₄ + H₂O ATPS extracted, in the first

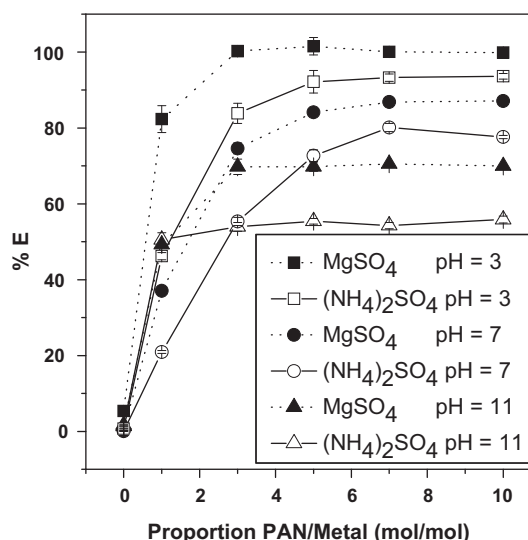


Fig. 3. The effect of ATPS-forming electrolytes (MgSO₄ or (NH₄)₂SO₄) on the %E of Cu(II) for different amounts of PAN at pH = 3.0, 6.0 or 11.0.

extraction stage, only 82% (proportion PAN/metal equal to 1.0). In order to improve the previous results a second extraction stage was carried out for obtaining 100% of extraction. This results demonstrated that with only two extraction process this ATPS is capable to produce a complete transference of Cu(II) from the bottom phase to the top phase.

3.4. Influence of others metals on the extraction behavior of copper

Table 2 lists the separation factors ($S_{M,N}$) for Cu(II) and other metals present concomitantly in the ATPS (L35 + MgSO₄ + H₂O) and a PAN concentration of 0.285 mmol kg⁻¹ at pH = 3 in different proportions. The separation factor expresses the efficiency for the separation of two species, M and N, in liquid–liquid extractions [24], and the value of $S_{M,N}$ can be calculated by Eq. (4):

$$S_{M,N} = \frac{D_M}{D_N} \quad (4)$$

where D_M and D_N are the distribution coefficients of species M and N, respectively. The distribution coefficient of any given species is expressed by Eq. (5):

$$D_M = \frac{\%E}{100 - \%E} \quad (5)$$

$S_{M,N}$ values greater than 10³ indicate an effective separation between two species.

The separation factor of copper is high compared to the other analyzed metallic ions; the separation factors are greater than 10³ for most metal concentrations, even reaching values greater than 10⁴. This system was extremely efficient for the separation of copper from metals concomitant (Fe, Mn, Al, Ni, Co and Zn) present in

Table 2
Separation factors ($S_{Cu,M}$) of copper (Cu) and several metallic ions (metal).

Proportion (metal/Cu)	$S_{Cu,Cd}$	$S_{Cu,Fe}$	$S_{Cu,Al}$	$S_{Cu,Mn}$	$S_{Cu,Ni}$	$S_{Cu,Co}$	$S_{Cu,Zn}$
1	1320	323	–	1600	1470	161	481
10	2560	1980	3720	5270	7040	12,000	872
50	4140	25,300	2230	6100	8400	27,500	979
100	3410	14,900	3020	31,800	11,500	2610	482
500	3100	31,300	19,700	17,200	10,300	–	1290

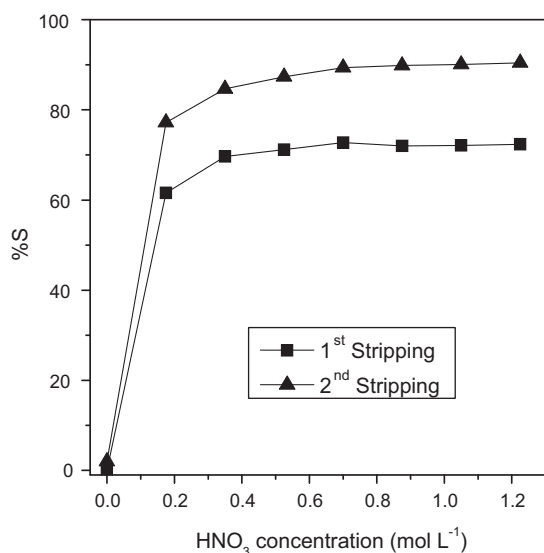


Fig. 4. The stripping of Cu^{2+} using HNO_3 , $[\text{PAN}] = 0.570 \text{ mmol kg}^{-1}$, $[\text{Cu}^{2+}] = 0.190 \text{ mmol kg}^{-1}$.

several different proportions. These contaminants are prevalent in different matrices such as copper ore and electronic scrap.

3.5. Copper extraction from the ore leachate

To determine the efficiency of the extraction system, ATPS was used for the separation and purification of copper from a copper ore leachate. The composition of the metals in the sample was determined (Table 1). The sample was leached, the pH was adjusted to 3.0, the metallic ion concentration in the supernatant was quantified ($[\text{Cu}] = 306 \text{ mg kg}^{-1}$ and $[\text{Fe}] = 54.4 \text{ mg kg}^{-1}$) and the supernatant was used as a solvent for the preparation of the ATPS. The concentration of PAN ($14.7 \text{ mmol kg}^{-1}$) was three times greater than the concentration of copper in this system.

The %E of copper was $90.4 \pm 1.1\%$, demonstrating the efficiency of this extraction technique even with highly concentrated metal samples and in the presence of several contaminating metal species. Iron, the main metal concomitant in this system, was predominantly in the bottom phase and had a low %E of $16.3 \pm 0.5\%$.

3.6. Stripping property

Although $\text{L35} + \text{MgSO}_4 + \text{H}_2\text{O}$ with PAN reveals higher extraction abilities for Cu^{2+} , stripping characteristics are important factors for evaluating its potential application. Stripping of Cu^{2+} was carried out two times using HNO_3 solution at 25°C . To strip the loaded Cu^{2+} , a series of experiments was carried out with varying HNO_3 solution concentration from 0.20 mol L^{-1} to 1.2 mol L^{-1} . The stripping efficiency (%S) is defined as follows:

$$\%S = \frac{[\text{Cu}]_{\text{Bottom}}}{[\text{Cu}]_{\text{Top}}} \quad (6)$$

As shown in Fig. 4, the %S values of Cu^{2+} using $\text{L35} + \text{MgSO}_4 + \text{H}_2\text{O}$ with PAN were 72% and 90% in the first and second stripping stages, respectively.

4. Conclusions

A new and environmentally friendly ATPS technique was developed for liquid–liquid extraction and purification of $\text{Cu}(\text{II})$ from ores pretreated by hydrometallurgical methods. This technique is compatible with the principles of green chemistry and has a good

efficiency and economical viability. The ATPS used in this work consisted of $\text{L35} + \text{MgSO}_4 + \text{H}_2\text{O}$ or $\text{L35} + (\text{NH}_4)_2\text{SO}_4 + \text{H}_2\text{O}$, and PAN was used as the extracting agent. The extraction efficiency of the metal is affected by the pH, the amount of PAN, the nature of the electrolyte and the presence of metal concomitants. The results showed that all $\text{Cu}(\text{II})$ could be extracted to the top phase at $\text{pH} = 3$. At this pH, other metals are mainly present in the lower phase ($\%E \leq 7.69$); thus, it is possible to separate $\text{Cu}(\text{II})$ at this pH. The addition of PAN to the system results in an increased %E for all metals, and a PAN concentration of $0.285 \text{ mmol kg}^{-1}$ resulted in the complete extraction of $\text{Cu}(\text{II})$ to the top phase. The ATPS formed by $\text{L35} + \text{MgSO}_4 + \text{H}_2\text{O}$ showed the highest %E and the highest separation factor values ($S_{\text{Cu,M}} = 1000\text{--}10,000$) for $\text{Cu}(\text{II})$ (compared to other metal concomitants). This system was also used for the extraction of copper from a leached ore concentrate. The %E value of $90.4 \pm 1.1\%$ demonstrated the efficiency of this extraction technique with a highly complex sample with technological applications.

Acknowledgements

The authors acknowledge the Fundação de Amparo a Pesquisa do Estado de Minas Gerais (FAPEMIG), Conselho Nacional de Pesquisa e Desenvolvimento Tecnológico (CNPq) and the Instituto Nacional de Ciências e Tecnologias Avançadas (INCTAA) for financial support. L.R.L. and G.D.R. acknowledge research fellowships from CAPES and CNPq, respectively. The authors also acknowledge the Mineração Caraíba (Jaguarari, Bahia, Brazil) for providing a sample of the copper concentrate.

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