



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

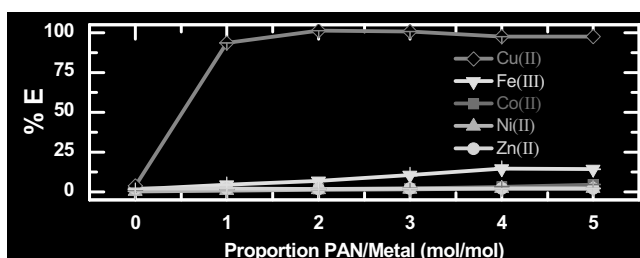
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HIGHLIGHTS

- ▶ 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 + 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 $25.0 \pm 0.1^\circ \text{C}$ 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 $\text{L35} + \text{MgSO}_4 + \text{H}_2\text{O}$ 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 $\text{L35} + (\text{NH}_4)_2\text{SO}_4 + \text{H}_2\text{O}$ 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 $25.0 \pm 0.1^\circ \text{C}$. 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

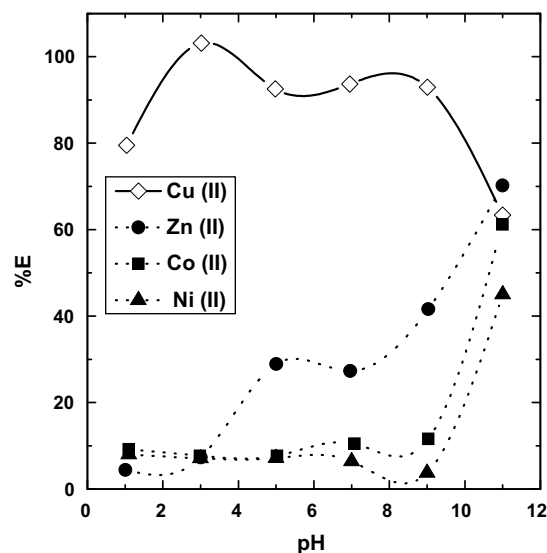


Fig. 1. The effect of the pH of the ATPS on the %E of Cu(II) , Zn(II) , Co(II) and Ni(II) for the L35 + MgSO_4 + H_2O system with a PAN concentration of $0.285 \text{ mmol kg}^{-1}$.

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.

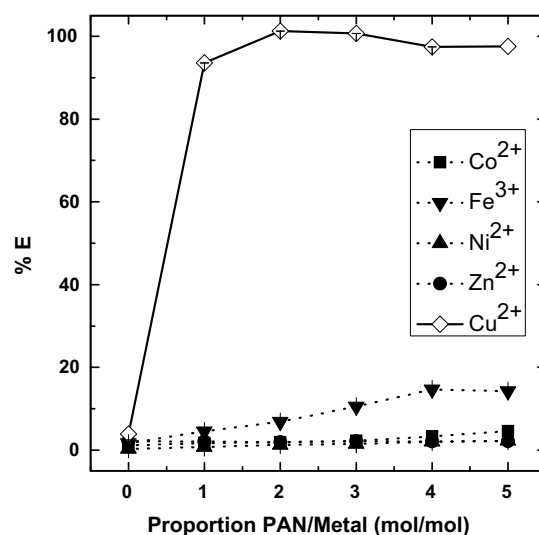
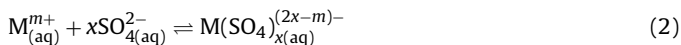


Fig. 2. The effect of the amount of PAN added to the ATPS on the %E of Cu(II) , Zn(II) , Co(II) , Ni(II) and Fe(III) for the L35 + MgSO_4 + H_2O system at pH 3.

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 \cong Zn \cong Ni \cong 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 \cong 100) compared to the extraction of others metals that largely remain in the bottom phase (%E \leq 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

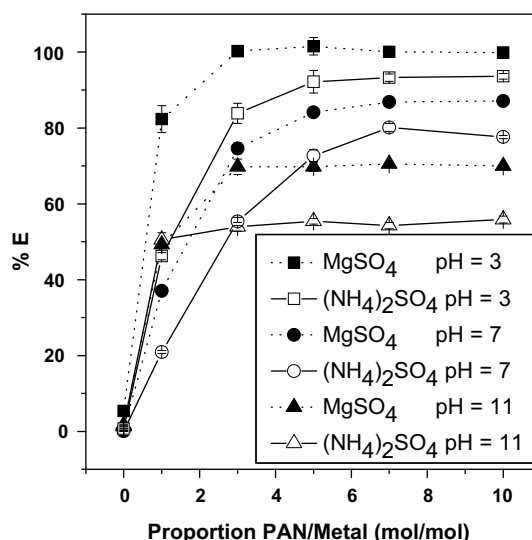


Fig. 3. The effect of ATPS-forming electrolytes (MgSO₄ or (NH₄)₂SO₄) on the %E of Cu(II) for different amounts of PAN at pH = 3.0, 6.0 or 11.0.

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

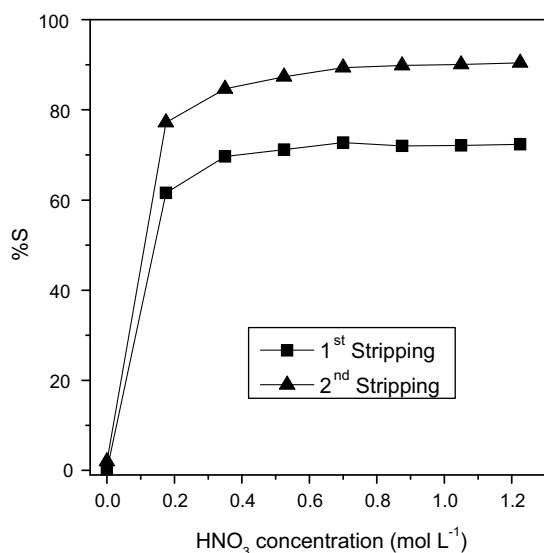


Fig. 4. The stripping of Cu^{2+} using HNO_3 , $[\text{PAN}] = 0.570 \text{ mmol kg}^{-1}$, $[\text{Cu}^{2+}] = 0.190 \text{ mmol kg}^{-1}$.

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 Cu(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 Cu(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 Cu(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 Cu(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 Cu(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.

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Green separation of copper and zinc using triblock copolymer aqueous two-phase systems



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ABSTRACT

The separation of copper and zinc was studied using aqueous two-phase systems (ATPSs) formed by triblock copolymers (L64), electrolyte (MgSO_4 , Li_2SO_4 or $\text{Na}_2\text{C}_4\text{H}_4\text{O}_6$) and water in the presence of 1-(2-pyridylazo)-2-naphthol (PAN) as an extractor. The separation behavior of the metals is affected by the quantity of extractor added, the pH of the system, the nature of the ATPS electrolyte and the system composition. The maximum separation ($S_{\text{Cu,Zn}} = 204$) of Cu and Zn was obtained with the L64 + $\text{Na}_2\text{C}_4\text{H}_4\text{O}_6$ ATPS at pH 3.0, a tie-line length of 41.28% (m/m) and a PAN/metal molar ratio of 3.0. For this ATPS system and at the same thermodynamic condition, the copper stripping percentage reached a maximum value (%S = 83.3%) using H_2SO_4 0.076 mol kg^{-1} .

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1. Introduction

To meet the growing demand for metals such as zinc and copper, an increasing emphasis has been placed on the production of high-purity metals from low-grade ores or waste such as slag, tailings and recycled materials [1]. Current legislation has attempted to regulate the disposal of these substances. The recovery of these metals is economically and environmentally important because of their high cost and their toxicity at high concentrations.

High concentrations of both copper and zinc are present in the effluents/wastes of some metallurgical/plating industries. Cementates of the zinc industry are obtained during the hydrometallurgical zinc-winning process. This process produces waste that contains copper (28.6%) and zinc (22.4%). Waste from the plating industry (the rinse solution) also contains zinc (39–350 mg L^{-1}) and copper (6–535 mg L^{-1}) [2].

Of the techniques available (precipitation, adsorption and solvent extraction) to remove metals from leach solutions, solvent extraction is the most attractive because it not only offers easy and flexible operation with an ability to handle a wide range of concentrations and control over the selectivity of the separation but it is also a clean technique that does not produce sludge [3]. In addition, when solvent extraction is coupled with electroplating, metals can be obtained with purities above 99.9%. Several studies have explored the extraction of copper and/or zinc with various

extractants including LIX 84I [4], Acorga M5640 [5] and Cyanex 272 [6]. However, the solvents used in these liquid–liquid extractions are toxic and flammable [7]. The possibility of forming emulsions is another disadvantage because it increases the time required for phase separation [8]. Therefore, novel extraction methods are needed that are economically viable, clean and environmentally safe. Aqueous two-phase systems (ATPSs) are promising liquid–liquid extraction systems for metal separation because they are composed primarily of water and other components which are neither toxic nor flammable [9,10].

ATPS are produced under specific thermodynamic conditions in which a combination of two aqueous solutions of different macromolecules [11], one macromolecule and one electrolyte [12], or two electrolytes [13] are mixed. In polymer/electrolyte ATPS, the phase separation generally results in a polymer-enriched top phase and an electrolyte-enriched bottom phase. These systems also have higher water content in both phases [14]. Polymer/electrolyte ATPS are easy to use, are low cost with components that can be recycled [14], and have been used for the separation, pre-concentration, purification and determination of biomolecules [15–17], phenols [18,19], dyes [20,21] and metal ions [10].

In 1984, the first paper on the partition of metallic ions using ATPS was published, showing the potential of this technique for metal extraction [22]. In the 1990s, Rogers et al. demonstrated the influence of parameters such as system composition, temperature, polymer nature and electrolyte formation in the partitioning of metal ions [23–25]. With the discovery of triblock-copolymer ATPS, the use of a hydrophobic complexant for metal extraction

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became possible [26]. Triblock copolymers building by two ethylene oxide blocks and one propylene oxide block, with general structure $(EO)_x(PO)_y(EO)_x$, aggregate in an aqueous solution at critical temperatures and concentrations to form micelles with a core dominated by hydrophobic units (poly(propylene oxide), (PO)) that is surrounded by a crown of hydrophilic units (EO) [27]. These cores are able to solubilize the water-insoluble complexing agent and its hydrophobic metal complex.

The separation of copper and zinc was investigated using an ATPS produced by a triblock copolymer of poly (ethylene oxide), PEO, and poly (propylene oxide), PPO, with an electrolyte in water at 298 K. The separation also utilized 1-(2-pyridylazo)-2-naphthol (PAN) as an extracting agent. The influence of the quantity of extracting agent added, the pH of the system, the nature of the ATPS electrolyte and the system composition on the yield of the metal extraction have been examined.

2. Experimental

2.1. Materials and chemicals

All reagents were of analytical grade and were used as received without further purification. The triblock copolymer used was poly (ethylene oxide)-poly (propylene oxide)-poly (ethylene oxide), L64, with an average molar mass (M_m) of 2900 g mol⁻¹ and 40% ethylene oxide, which corresponds to the composition $(EO)_{13}(PO)_{30}(EO)_{13}$. The triblock copolymer was acquired from Aldrich® Chemistry (Milwaukee, WI). $MgSO_4 \cdot 7H_2O$, $Li_2SO_4 \cdot H_2O$, sodium tartrate ($Na_2C_4H_4O_6 \cdot 2H_2O$), H_2SO_4 and NaOH, were obtained from Vetec (Duque de Caxias, Rio de Janeiro, Brazil). The PAN, and $CuSO_4$ were purchased from Merck (Darmstadt, Germany).

Deionized water ($R \geq 18 M\Omega \text{ cm}^{-1}$) was used throughout the experiments. A Milli-Q II water deionizer (Millipore Corporation, Bedford, MA) was used for the final purification of the distilled water. The pH measurements were performed using a glass electrode combined with a digital pH meter ((Wissenschaftlich-Technische Werkstätten, pH 330i/SET)). The experiments were performed on an analytical balance (Shimadzu, AY 220) with an uncertainty of ± 0.0001 g. The temperature of the ATPS was controlled in a temperature-controlled bath (Microquímica, MQBTC 99-20) at 25.0 ± 0.1 °C. A centrifuge (Thermo Scientific, Heraeus Megafuge 11R) was also used in the experiments. The metal concentrations were determined using a flame atomic absorption spectrometer (VARIAN AA240). The instrumental conditions for FAAS measurements are summarized in Table 1.

2.2. Compositions of the aqueous two-phase systems

The aqueous two-phase system formed from L64 and salt was prepared by mixing 2.00 g of an L64 solution and a 2.00 g salt ($MgSO_4$, Li_2SO_4 , or $Na_2C_4H_4O_6$) solution previously prepared in appropriate concentrations. The phase composition of the copolymer and salt in the ATPS was defined according to the equilibrium phases and is shown in Table 2.

Table 1
Instrumental conditions for FAAS measurements.

Element	Wavelength (nm)	Applied current (mA)	Spectral resolution (nm)	Flame composition air/C ₂ H ₂ (L min ⁻¹)
Cu	324.8	4.0	0.5	3.50/1.50
Zn	213.9	5.0	1.0	3.50/1.50

Table 2
System composition and tie-line length (TLL) for the ATPS.

Component	Top phase% (m/m)	Bottom phase% (m/m)	TLL% (m/m)	Ref.
L64	35.15	5.56	29.76	[28]
$MgSO_4$	2.87	6.09		
L64	45.58	5.15	40.73	[28]
$MgSO_4$	2.20	7.18		
L64	41.72	0.41	41.86	[28]
Li_2SO_4	3.27	10.01		
L64	43.03	2.70	41.28	[29]
$Na_2C_4H_4O_6$	4.01	12.86		

2.3. The influence of pH and the quantity of PAN

Each metal ion in the biphasic system was partitioned so that the metal concentration was fixed (0.100 mmol kg⁻¹). However, in the separation study we have used an aqueous mixture of both metals at 50% molar fraction. To study the influence of pH, the molar ratio of PAN to the metal ranged between 0.00 and 10.0. A salt solution ($MgSO_4$, Li_2SO_4 , or $Na_2C_4H_4O_6$) containing 0.200 mmol kg⁻¹ metal and an L64 solution containing between 0.200 and 2.00 mmol kg⁻¹ PAN were prepared. The pH of the water used to prepare the salt and L64 solutions was previously adjusted using H_2SO_4 for acidic pH values (1.0, 3.0 and 5.0) and NaOH for alkaline pH values (9.0 and 11). The metal solution (2.00 g of 0.200 mmol kg⁻¹) and 2.00 g of the appropriate concentrations of the PAN solution were weighed in a centrifuge tube. The tube was manually stirred for 3 min, centrifuged for 10 min at 20,257g and allowed to settle for 20 min at 25.0 ± 0.1 °C in a temperature-controlled bath. Then, the top phase was removed, suitably diluted, and its metal concentration determined using flame atomic absorption spectrometry (FAAS). The extraction percentage (%E) of the metal ions was calculated using the following equation:

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

in which $(n_{M^{m+}})_{UP}$ is the quantity of metal ions in the upper phase (in mol), and $(n_{M^{m+}})_T$ is the total quantity of metal ions in the system.

2.4. The influence of the ATPS nature and the system composition and stripping experiments

The influence of the salt ATPS nature was studied at pH 3.0 for Cu(II) and pH 11 for Zn(II). The metal solutions were prepared in an ATPS salt solution ($MgSO_4$, Li_2SO_4 or $Na_2C_4H_4O_6$) according to the needs of each experiment. The appropriate concentration of salt and copolymer L64 was prepared according to the desired ATPS composition, and the studies were performed according to the method described in Section 2.3.

After metal ion extraction processes from the ATPS bottom phase to the top phase, we conducted a stripping studies of each metal (Cu(II), Zn(II)) ions separated and in a mixtures. For each stripping experiments, 2.00 g of loaded phase with metal ion (ATPS top phase) was taken and contacted with 4.00 g of ATPS bottom phase added with HNO_3 , H_2SO_4 or NH_3 at different concentration, followed by vigorous shaking to reach equilibrium.

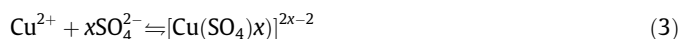
3. Results and discussion

3.1. The effect of the pH and PAN quantities on the metal extraction behavior

The influence of pH on the extraction behavior of Cu(II), expressed as the extraction percentage (%E) as a function the PAN/

Cu molar ratio, is shown in Fig. 1. These studies were performed using the L64 + MgSO₄ + H₂O ATPS.

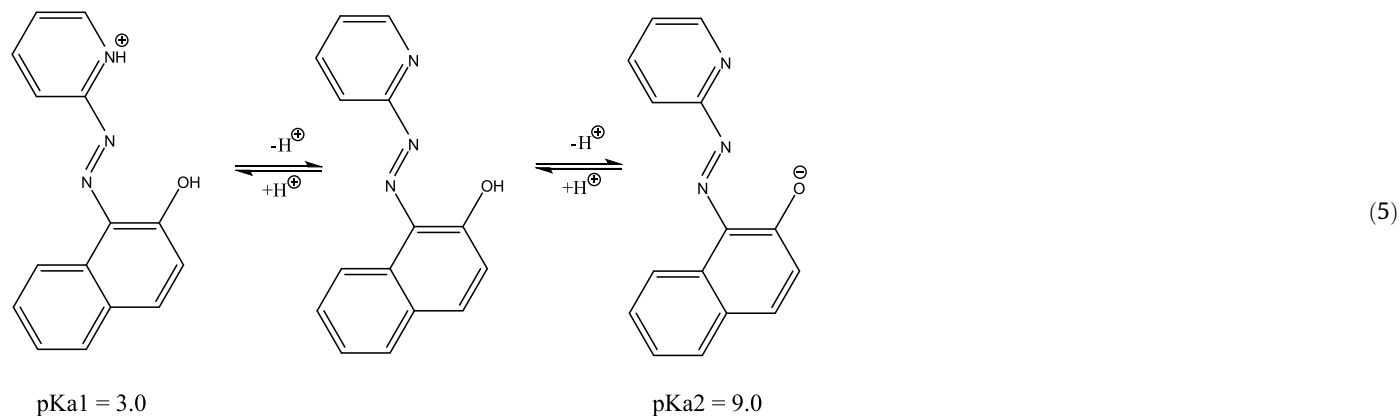
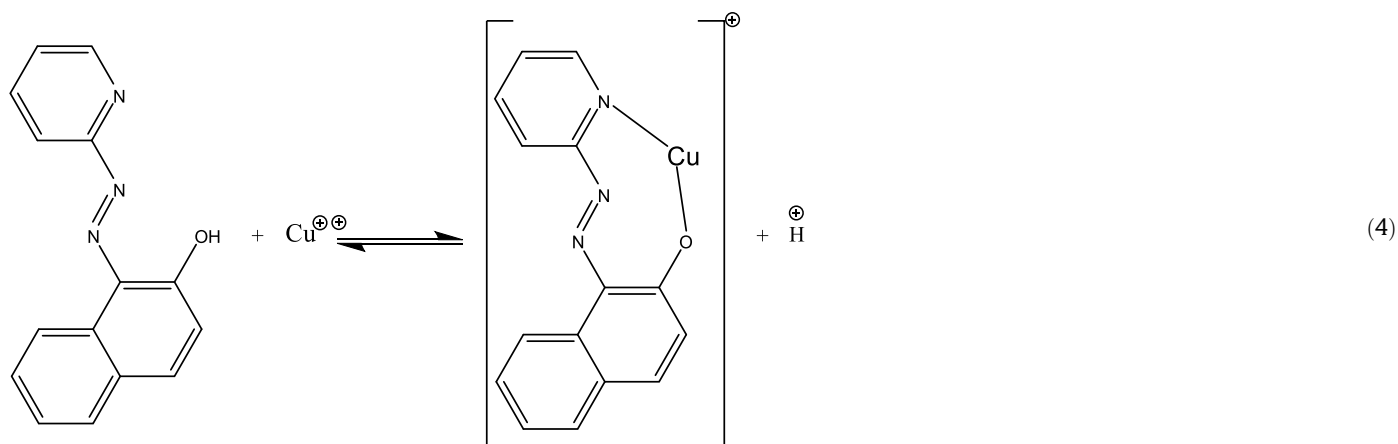
For all pH values, an increase in the PAN quantity leads to an increase in the Cu(II) extraction with curves of similar profile. However, the rate of change in the %E for Cu(II) and the maximum extraction values are dependent on the hydrogen ion concentration. The maximum %E values follow the order: pH 3.0, (91.6 ± 1.6)% > pH 9.0, (78.6 ± 2.7)% ≈ pH 5.0, (76.8 ± 0.1)% > pH 11, (62.0 ± 0.5)% > pH 1.0, (56.6 ± 2.4)%. In the absence of PAN molecules, the Cu(II) %E is independent of the pH and is approximately 17%. Without PAN molecules, the Cu(II) bottom phase concentration is determined by two driving forces: (1) an entropic force in which Cu(II) is concentrated in the bottom phase to increase the entropy system and (2) a specific enthalpic interaction between the Cu(II) ions and the ATPS components to retain the metal in the bottom phase. At any pH and without PAN, the possible Cu(II) equilibria are described by the following equations:



Both copper species concentrate in the bottom phase because they do not interact favorably with the copolymer macromolecule present in the top phase. With the addition of PAN molecules, the Cu(II) %E increases because of the formation of a new Cu(II) species, the Cu–PAN complex (shown in Eq. (4)), at the interface.

The Cu–PAN complex is a water-insoluble cation that moves spontaneously from the ATPS interface to the top phase, solubilizing in the hydrophobic core of the L64 micelles. As more PAN molecules are added to the ATPS system, more PAN–Cu(II) complex is formed at the interface, and more complex is transferred to the top phase, increasing the Cu(II) %E.

The effect of pH on the Cu(II) extraction behavior should be associated with the influence of the [H⁺] concentration on the PAN–Cu(II) complex formation constant, *K_F*. Despite its high value (*K_F* = 1.0 × 10¹²), the Cu–PAN complex formation constant is dependent on the pH because the PAN molecules coexist in three different ionization states dependent on the pH, with p*K_a* values p*K_a*1 = 3.0 and p*K_a*2 = 9.0 [30] (see Eq. (5)).



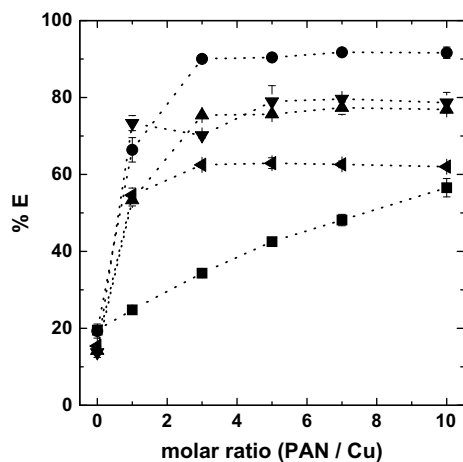


Fig. 1. The effect of pH and [PAN] on the %E of the Cu(II), using L64 + MgSO₄ + H₂O system (TLL = 40.73% (w/w)), where pH = 1.00 (■), pH = 3.00 (●), pH = 5.00 (▲), pH = 9.00 (▼) and pH = 11.0 (◄).

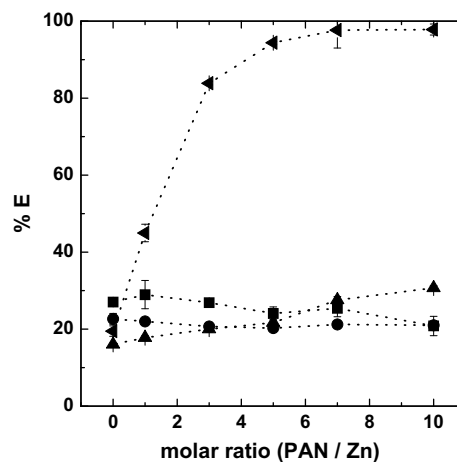


Fig. 4. The effect of pH and [PAN] in the ATPS on the %E of the Zn(II), using L64 + MgSO₄ + H₂O system (TLL = 40.73% (w/w)), where pH = 1.00 (■), pH = 3.00 (●), pH = 5.00 (▲), and pH = 11.0 (◄).

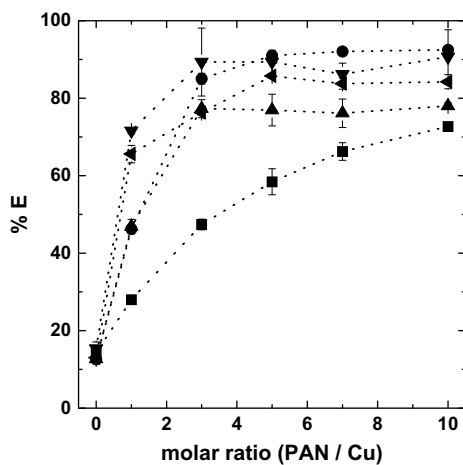


Fig. 2. The effect of pH and [PAN] on the %E of the Cu(II), using L64 + Na₂C₄H₄O₆ + H₂O system (TLL = 41.28% (w/w)), where pH = 1.00 (■), pH = 3.00 (●), pH = 5.00 (▲), pH = 9.00 (▼) and pH = 11.0 (◄).

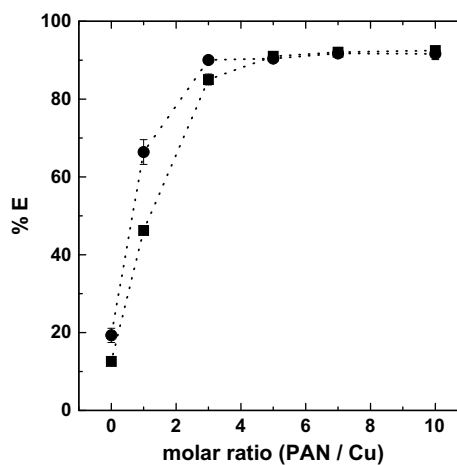


Fig. 5. The effect of nature electrolyte in the ATPS on the %E of the Cu(II), using L64 + Na₂C₄H₄O₆ + H₂O system (TLL = 41.28% (w/w)) (■), or L64 + MgSO₄ + H₂O system (CLA = 40.73% (w/w)) (●).

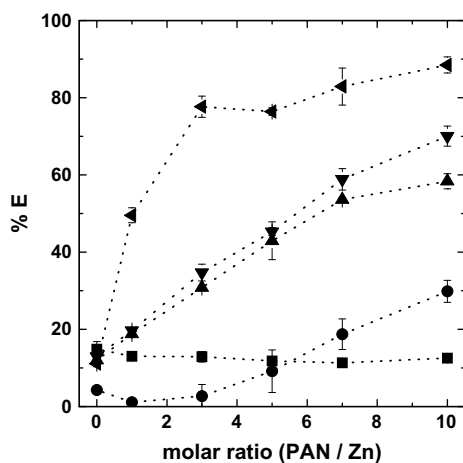


Fig. 3. The effect of pH and [PAN] on the %E of the Zn(II), using L64 + Na₂C₄H₄O₆ + H₂O system (TLL = 41.28% (w/w)), where pH = 1.00 (■), pH = 3.00 (●), pH = 5.00 (▲), pH = 9.00 (▼) and pH = 11.0 (◄).

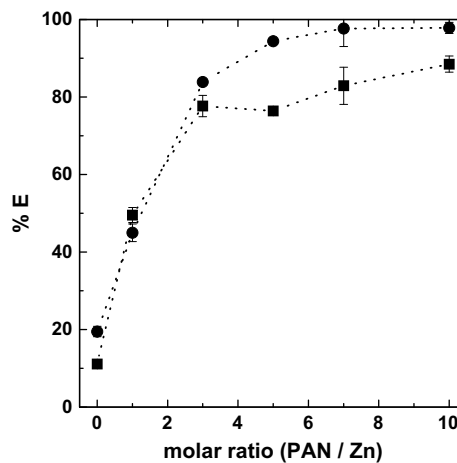


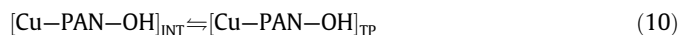
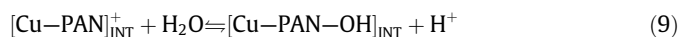
Fig. 6. The effect of nature electrolyte in the ATPS on the %E of the Zn(II), using L64 + Na₂C₄H₄O₆ + H₂O system (TLL = 41.28% (w/w)) (■), or L64 + MgSO₄ + H₂O system (CLA = 40.73% (w/w)) (●).

At pH 1.0, the neutral PAN molecule is at equilibrium with its cationic form, PAN^+ , which is in higher concentration at this pH, causing a decrease in the quantity of the Cu–PAN complex formed because the PAN^+ species does not favorably interact with the Cu(II) ion. With increasing pH, the concentration of PAN molecules begins to increase until it reaches a maximum at pH 9.0. Above pH 9.0, an increase in the pH causes the formation of the PAN anionic species, which does not interact favorably with the Cu(II) cation to form a complex, and the quantity of Cu(II) transferred from the bottom phase to the top phase decreases.

The previously described molecular process is influenced by the nature of the ATPS salts, as shown in Fig. 2. The influence of pH on the extraction behavior of Cu(II) is also shown in Fig. 2. These results derive from studies performed using an $\text{L64} + \text{Na}_2\text{C}_4\text{H}_4\text{O}_6 + \text{H}_2\text{O}$ ATPS with PAN as the complexing agent.

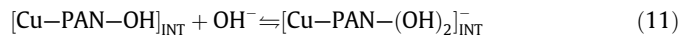
For the $\text{L64} + \text{Na}_2\text{C}_4\text{H}_4\text{O}_6 + \text{H}_2\text{O}$ ATPS, the maximum %E values for Cu(II) followed the order pH 3.0, %E = $(92.5 \pm 0.6)\%$ \approx pH 9.0, %E = $(90.6 \pm 0.9)\%$ > pH 11, %E = $(84.2 \pm 0.6)\%$ > pH 5.0, %E = $(72.9 \pm 0.7)\%$ > pH 1.0, %E = $(72.7 \pm 0.5)\%$.

The dependence of the maximum Cu(II) extraction efficiency on the pH value is influenced by the ATPS electrolyte nature. For both salts, MgSO_4 and $\text{Na}_2\text{C}_4\text{H}_4\text{O}_6$, a higher Cu(II) extraction efficiency by the PAN molecule was obtained at pH 3.0, and a lower extraction efficiency was obtained at pH 1.0. This acidic pH effect can be explained through a discussion of the Cu(II) extraction behavior in the $\text{L64} + \text{MgSO}_4 + \text{H}_2\text{O}$ ATPS. Surprisingly, the Cu(II) cation is extracted in the $\text{L64} + \text{Na}_2\text{C}_4\text{H}_4\text{O}_6 + \text{H}_2\text{O}$ ATPS at pH 9.0 at the same level as it is at pH 3.0. In this ATPS and under the given thermodynamic conditions, the system could produce a new complex of PAN and Cu(II). As suggested by Betteridge et al. [31], at this pH, the Cu–PAN complex forms according to the following equations:



in which the subscripts TP and INT represent the top phase and the interface, respectively. Betteridge et al. [31] suggested that the

[Cu–PAN–OH] complex is more stable than a $\text{Cu}(\text{PAN})_2$ complex. At pH 11, the %E decreases because, at this pH, the following new charged complex can be formed:



For Zn(II) extraction using the $\text{L64} + \text{Na}_2\text{C}_4\text{H}_4\text{O}_6 + \text{H}_2\text{O}$ ATPS, an increase in pH increases the %E. The effect of the pH on the extraction behavior of Zn(II) is shown in Fig. 3. These studies were performed with the $\text{L64} + \text{Na}_2\text{C}_4\text{H}_4\text{O}_6 + \text{H}_2\text{O}$ ATPS using PAN as a complexing agent.

The extraction efficiency of the Zn–PAN complex increases as the pH increases until it reaches a maximum at pH 11, suggesting a Zn/PAN complexation process that differs from that of Cu(II). The Cu–PAN complex follows a 1:1 stoichiometry, while the Zn–(PAN)₂ complex follows a 1:2 stoichiometry. Therefore, Zn–(PAN)₂ complex is a charge-neutral complex capable of solubilizing inside the copolymer micelle. The rate of formation of the Zn–(PAN)₂ complex is likely controlled by the PAN^- species concentration, which is higher at pH 11.

The same result is obtained for the $\text{L64} + \text{MgSO}_4 + \text{H}_2\text{O}$ ATPS as shown in Fig. 4, which depicts the influence of the pH on the extraction behavior of Zn(II) using the $\text{L64} + \text{MgSO}_4 + \text{H}_2\text{O}$ ATPS and PAN as a complexing agent.

For the $\text{L64} + \text{MgSO}_4 + \text{H}_2\text{O}$ ATPS, the maximum Zn(II) %E values followed the order pH 11, %E = (97.8 ± 1.4) > pH 5.0, %E = (30.7 ± 0.6) > pH 3.0, %E = (21.0 ± 0.3) \approx pH 1.0, %E = (20.8 ± 2.5) .

The dependence on the PAN^- concentration only occurs because the formation constant for the Zn–(PAN)₂ complex is high, $K_F = 1 \times 10^{21}$ [32].

3.2. The effect of the ATPS/electrolyte combination on the extraction of metal ions

The effects of the electrolyte on the extractions of Cu(II) and Zn(II) are shown in Figs. 5 and 6, respectively. These studies were performed with the ATPSs formed by $\text{L64} + \text{MgSO}_4 + \text{H}_2\text{O}$, and $\text{L64} + \text{Na}_2\text{C}_4\text{H}_4\text{O}_6 + \text{H}_2\text{O}$ for both Cu(II) and Zn(II) using PAN as the complexing agent and at the pH of maximum extraction.

Fig. 5 indicates that there is no difference between the Cu(II) extraction percentages for the systems formed by $\text{L64} + \text{MgSO}_4 + \text{H}_2\text{O}$ and $\text{L64} + \text{Na}_2\text{C}_4\text{H}_4\text{O}_6 + \text{H}_2\text{O}$. This behavior is due to the similarity in the values of logK for the complexes between the Cu(II) and the anion of the electrolyte in the ATPS (copper–sulfate = 2.4 and copper–tartrate = 2.1). The metal extraction efficiency is

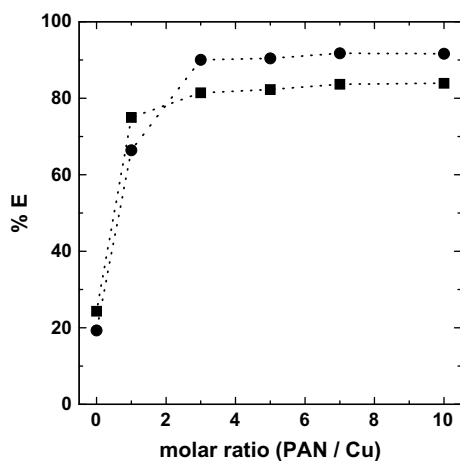


Fig. 7. The effect of TLL in the ATPS on the %E of the Cu(II), using $\text{L64} + \text{MgSO}_4 + \text{H}_2\text{O}$ system (TLL = 29.76% (w/w)) (■), or $\text{L64} + \text{MgSO}_4 + \text{H}_2\text{O}$ system (TLL = 40.73% (w/w)) (●).

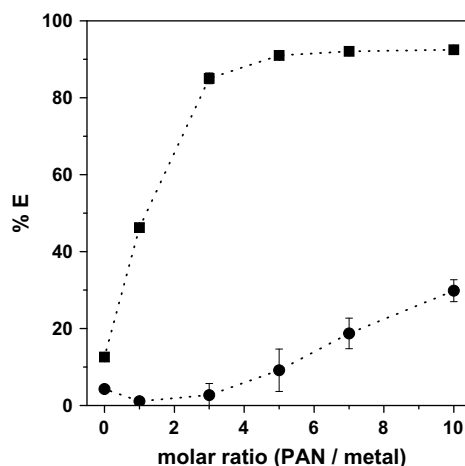


Fig. 8. The effect of [PAN] in the ATPS on the %E of the Cu(II) (■) and Zn(II) (●) at pH = 3.00, using $\text{L64} + \text{Na}_2\text{C}_4\text{H}_4\text{O}_6 + \text{H}_2\text{O}$ system (CLA = 41.28% (w/w)).

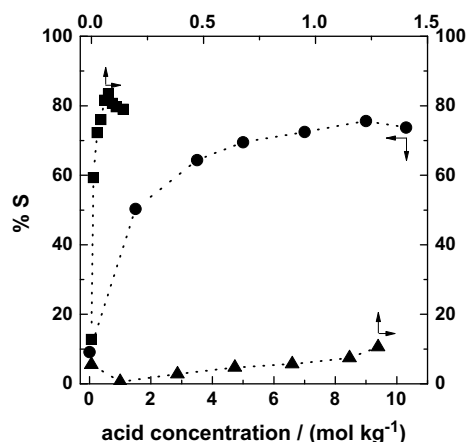


Fig. 9. The stripping of Cu(II) using (●) HNO₃, (■) H₂SO₄ e (▲) NH₃ in the ATPS formed by L64 + Na₂C₄H₄O₆ + H₂O (CLA = 41.28% (w/w)).

inversely proportional to the formation constant for the complex if only the metal–sulfate or metal–tartrate interactions are considered because the metal and the extracting agent are the same.

For Zn(II), the extraction percentage is slightly larger for the L64 + MgSO₄ + H₂O ATPS than for the L64 + Na₂C₄H₄O₆ + H₂O ATPS as shown in Fig. 6. This result is due to the values of log K for the complexes between Zn(II) and the anions of the electrolyte in the ATPS (zinc–sulfate < zinc–tartrate [33]).

3.3. Influence of the ATPS composition on the extraction behavior of metal ions

Differences in the ATPS phase composition are expressed by the tie-line length (TLL). At constant pressure and temperature, the TLL is a thermodynamic parameter of the ATPS that expresses the difference in the intensive thermodynamic functions between the top and bottom phases [34]. The TLL is expressed as the difference between the polymer and salt concentrations present in the different phases and is commonly used as the variable for determining the process of solute partitioning. The difference in the intensive thermodynamic properties is enhanced with an increase in the TLL. The TLL is calculated by the following equation:

$$\text{TLL} = [(C_p^T - C_p^B)^2 + (C_s^T - C_s^B)^2]^{1/2} \quad (12)$$

in which C_p^T and C_p^B are the polymer concentrations in the top and bottom phases, respectively, and C_s^T and C_s^B are the corresponding salt concentrations.

Fig. 7 shows the influence of the TLL on the extraction behavior for Cu(II). These studies were performed with the L64 + MgSO₄ + H₂O ATPS at the two different values of the TLL using PAN as a complexing agent. The results indicate that increasing the TLL value increases the efficiency of the extraction process. The increase in TLL tends to intensify the number of interactions between the metal–PAN complex and the polymer molecules in the top phase, causing more of the complex to partition into the top phase.

3.4. Separation of the Cu(II) and Zn(II) in the ATPS

Fig. 8 shows the Cu(II) and Zn(II) extraction percentages, from a 50% molar fraction mixture of both metal, at several PAN/Metal molar ratios in the L64 + Na₂C₄H₄O₆ + H₂O ATPS at pH 3.00. The results indicate an efficient extraction of the Cu(II), while the Zn(II) remains concentrated in the bottom phase. For a PAN/Metal molar ratio of 3.0, the separation factor ($S_{M,N}$) between the copper and zinc is 204. The separation factor expresses the separation

efficiency of two species, M and N, using liquid–liquid extraction [35] and can be calculated from the following equation:

$$S_{M,N} = \frac{D_M}{D_N} \quad (13)$$

in which D_M is the distribution coefficient of species M, and D_N is the distribution coefficient of the concomitant species, N. The distribution coefficient for any given species is expressed by the following equation:

$$D_M = \frac{\%E}{100 - \%E} \quad (14)$$

At pH 3, this system proved to be extremely efficient at separating the copper and zinc present in many different matrices and wastes.

3.5. Stripping studies

The L64 + Na₂C₄H₄O₆ + H₂O ATPS, at pH 3.00 and using PAN, at PAN/Metal molar ratio of 3.0, as extractor reveals higher extraction abilities for copper and a not efficient extraction for the zinc metal ($\%E_{Cu} = 85.0\%$ and $\%E_{Zn} = 2.7\%$). Due the Zn lower extraction behavior, we study only the copper stripping characteristics because this parameter is an important factor for evaluating the ATPS potential application as copper extractor system. Stripping of copper, i.e., the Cu(II) transfer from the top phase to the bottom phase, was carried out adding to the ATPS HNO₃, H₂SO₄ or NH₃ solution at 25 °C. To strip the loaded copper, a series of experiments was carried out varying ATPS acid concentration and the stripping efficiency (%S) was calculated as follows:

$$\%S = \frac{[Cu]_{\text{Bottom}}}{[Cu]_{\text{Top}}} \quad (15)$$

As shown in Fig. 9, the %S values of copper in the ATPS L64 + Na₂C₄H₄O₆ + H₂O with PAN reached a maximum value (%S = 83.3%) using H₂SO₄ 0.076 mol kg^{−1}. At this stripping conditions no zinc metals was found in the bottom phase, probably because its content on the top phase due the extraction process was very small. In the end of stripping process we have a aqueous solution of copper enriched in electrolytes.

4. Conclusions

A new, environmentally friendly ATPS technique, compatible with the principles of green chemistry, was developed for the liquid–liquid extraction of Cu(II) and Zn(II). A maximum separation ($S_{Cu,Zn} = 204$) of Cu and Zn was obtained when the L64 + Na₂C₄H₄O₆ ATPS was used at pH 3.0 with a tie-line length of 41.28% (w/w) and a PAN/metal molar ratio of 3.0. The proposed separation method demonstrated that ATPS can be applied as a substitute for solvent extraction in hydrometallurgical processes. However this technique should be improved to be possible to apply for the real pregnant leach solution.

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