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GREEN CHEMISTRY EXTRACTION METHOD FOR RECOVERY OF GOLD IONS FROM CYANIDE WASTEWATERS

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Abstract

In this study, the possibility of Au(III) ions recovery from cyanide solution by extraction in aqueous two-phase systems formed from polyethylene glycol (PEG) and (NH₄)₂SO₄ inorganic salt, in presence of chloride ions as extracting agent, was analyzed in batch systems. Due to the non-toxic character of the components of extraction system, the Au(III) ions extraction in aqueous two-phase systems can be included in the category of “green chemistry” methods. The Au(III) extraction efficiency was examined as a function of several experimental parameters, such as molecular weight of PEG, salt solution pH and chloride ions extractant concentration, in order to find the optimal conditions. The experimental results have shown that the maximum extraction of Au(III) ions (> 89%) is obtained in aqueous two-phase systems prepared by PEG-6000, salt solution with pH of 3.15 and chloride ions concentration higher than 0.1 mol·L⁻¹. These conditions were then used in case of Au(III) extraction from cyanide wastewater, when the experimental data have indicated that the Au(III) ions extraction is more efficient in presence of 0.1 mol Cl⁻·L⁻¹ (> 85%), than in their absence (< 17%). The obtained results indicate that the aqueous two-phase systems have potential for the recovery of Au(III) ions from cyanide wastewaters, both due to its extraction performances, and “green chemistry” characteristics.

Key words: aqueous two-phase system, Au(III) extraction, cyanide wastewater, green chemistry

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1. Introduction

The continuous advances in science and technology have raised new challenges for the researchers from different fields due to the fact that the resources and methods used for the old technologies are not in line with the needs of the new ones (Gnoni et al., 2017). For instance, the development of the electronic industry from the recent years lead to a decrease of the overall life span of devices, which created a higher demand of raw materials (Akcil et al., 2015; Cayumil et al., 2016; Hasegawa et al., 2018). Since the ores are limited and the secondary resources are in a continuous growth, there is a demand in

finding new methods for the recycling of the waste electronics as they are also harmful for the environment and human life if are disposed inappropriately (Cayumil et al., 2016; Hamta and Dehghani, 2017; Mihajlov and Stevanović-Čarapina, 2015; Tuncuk et al., 2012).

Of high interest are the precious metals used in these devices due to their chemical stability, electrical conductivity. Because the quantity of these precious metals resulted from the primary production is smaller than the one found in the secondary resources (Cayumil et al., 2016; Hasegawa et al., 2018), the importance of recovering becomes much more important.

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One of the precious metals that present a special interest is gold. The gold is not used only in the electronics industry, but also in medicine, gilding baths, jewelry. The variety of uses, as well as its high price cost on the market makes the recovery of gold a profitable business.

There are many methods in the current use for recovering Au(III) ions. Active carbon adsorption, ion exchange, precipitation, solvent extraction, etc., are just a few examples that can be successfully used to recover Au(III) ions from secondary sources (wastewater, sediments, waste, etc.) (Al-Said, 2016; Fan et al., 2014; Silvas et al., 2015). Among all, the solvent extraction is considered the most selective and efficient method, which is easy to implement at industrial scale, under different experimental conditions. Unfortunately, the disadvantages associated with the use of toxic and volatile organic solvents that have a major negative impact on the environment and human life, have led to the development of new ecological methods. From environmental perspective, the extraction of metal ions in aqueous two-phase systems gained more ground in the last years.

The aqueous two-phase extraction systems can be obtained either by mixing two aqueous solutions of polymers, or by mixing the solutions of a polymer and an inorganic salt (Benavides et al., 2008). Since the main component of the aqueous two-phase systems is water, this extraction method is considered to be an ecological one. Also, high reproducibility of extraction systems, easy separation of phases, low cost and high availability of components, as well as the fact that they are not toxic for humans or for the environment, are several other economic and environmental benefits of using aqueous two-phase systems in extraction methods (Benavides et al., 2008; Bulgariu and Bulgariu, 2008; Graber et al., 2000).

Depending on the conditions of the extraction (pH, temperature, concentration of the phase forming components, the volume ratio of the two main components, the presence or the absence of the extraction agents), various metal ions (heavy metals or precious metals) were recovered by using this method with high extraction percentages (Birloaga et al., 2013; Bulgariu and Bulgariu, 2013; Hamta and Dehghani, 2017; Zheng et al., 2015). Other components extracted using the aqueous two phase systems were proteins, cells, cell organelles, genetic material, but also organic molecules or organic complexes (Benavides and Rito-Palomares, 2008; Mageste et al., 2009).

In many studies from literature for the recovery of metal ions, the use of polymer-inorganic salt system was found to be a better solution than the polymer-polymer system, due to the flexibility and efficiency of these extraction systems (da Silva and Loh, 2000; Hamta and Dehghani, 2017). This was the reason for that, in this case was chosen an aqueous two-phase system formed by polyethylene glycol (PEG) and $(\text{NH}_4)_2\text{SO}_4$ as inorganic salt. Polyethylene glycol is the most common polymer used in these systems and is

biodegradable, soluble in water, the time necessary for the phase separation is short and it does not form stable emulsions (Murari et al, 2015). In such aqueous two-phase systems, the extraction of metal ions, including gold ions can be quantitative in presence of simple inorganic anions, such as iodide, bromide, chloride or thiosulphate (Akcil et al., 2015; Birloaga et al., 2013; Tuncuk et al., 2012).

But, in many metallic coatings processes, the deposition of gold on various metallic surfaces is made chemically, from aqueous solutions that have high cyanide content. Under these conditions, the wastewater resulted from the gilding baths contain, beside Au(III) ions, large amounts of cyanide ions, which can act as extracting agents in such aqueous two-phase systems. Therefore, recovery of gold ions from such wastewater by extraction in aqueous two-phase systems could be effective under certain experimental conditions, and the simultaneous extraction of cyanide ions together with Au(III) ions may also be an added benefit, in terms of environmental protection.

In this study, the extraction of Au(III) ions in aqueous two-phase systems formed with PEG (40 % (w/w)) and $(\text{NH}_4)_2\text{SO}_4$ (40 % (w/w)), in a mixing ration of 4:5, and in presence of chloride ions as extracting agents, was examined as a function of different experimental parameters. The experiments were performed in batch systems, as a function of molecular weight of PEG, salt solution pH and chloride ions concentrations, in order to establish the optimal conditions for extraction. The obtained optimal conditions were then used for the extraction of Au(III) ions from a cyanide wastewater, resulted from industrial gilding baths.

2. Experimental

2.1. Materials

Polyethylene glycol (PEG) with different molecular weights (2000, 4000 and $6000 \text{ g}\cdot\text{mol}^{-1}$) was purchased from Aldrich and was used as received. In each case, the aqueous solutions of 40 % (w/w) PEG was prepared by dissolving an appropriate quantity of solid polymer in distilled water.

The inorganic salts $(\text{NH}_4)_2\text{SO}_4$, NaCl (purchased from Chemical Company) were of analytical degree and were used without any further purifications. The solution of $(\text{NH}_4)_2\text{SO}_4$ (40 % (w/w)) was also obtained by dissolving an appropriate quantity of solid salt in distilled water. The different pH values of salt solution (1.20, 3.15, 4.65 and 8.50) were obtained by adding small volumes of H_2SO_4 96 % or NH_3 25 % (purchased from Chemical Company) during of solid $(\text{NH}_4)_2\text{SO}_4$ dissolving, and were taken into account in the total solution mass. The extracting agent solution was prepared by dissolving of solid NaCl in 40 % (w/w) $(\text{NH}_4)_2\text{SO}_4$ solution, following by the dilution with 40 % (w/w) $(\text{NH}_4)_2\text{SO}_4$ solution until a concentration of $1.0 \text{ mol}\cdot\text{L}^{-1}$. In this way is prevented the significant change in the composition of the

extraction system to the addition of different volumes of the extracting agent. AuCl₃ solution (1000 mg Au(III)·L⁻¹) was purchased from Fluka and was used as received. The cyanide wastewater was sampled from a local company which uses the gilding baths to manufacture of printed circuits boards. Prior to use in the extraction experiments, the cyanide wastewater sample was filtered on a quantitative filter paper to remove solid impurities.

2.2. Extraction experiments

The extraction experiments were performed in batch systems. In each experiment, the aqueous two-phase systems were prepared by mixing certain volume of PEG (40 % (w/w)) solution and (NH₄)₂SO₄ (40 % (w/w)) solution, in a ratio of 4:5, in 15 mL centrifuge tubes. This value of mixing ration has been established previously as being the optimal (Ghercs and Bulgariu, 2017). The influence of the molecular weight of PEG on the Au(III) extraction efficiency was examined using for the preparation of aqueous two-phase systems, the PEG solutions (40 % (w/w)) obtained by dissolving of polyethylene glycol with different molecular weights (2000, 4000 and 6000 g·mol⁻¹). In the case of the pH effect on extraction efficiency, certain volume of 40 % (w/w) (NH₄)₂SO₄ solution with different pH (1.20, 3.15, 4.65 and 8.50), were used in the preparation of two phase aqueous systems. The pH values of 40 % (w/w) (NH₄)₂SO₄ solutions were measured with a pH/ion-meter (MM 427 type) equipped with a combined glass electrode. 0.5 mL of Au(III) solution (1000 mg·L⁻¹) and 0 – 2.5 mL of NaCl solution (1 mol·L⁻¹) were added, and the final volume of extraction systems was adjusted to 10 mL with distilled water, so that the final volume ratio of the two phases approximately to be 4:5. Each extraction system was centrifuged at 2000 rpm for 10 min and left in stand-by for 24 hours to achieve equilibrium.

Just before analysis, the two phases were separated using Pasteur pipettes and placed into separated tubes. 1.0 – 2.0 mL of superior phase (PEG-rich phase) was measured and used for the spectrophotometrical determination of Au(III) concentration (colour reagent: Rodamine R, Digital Spectrophotometer S 104 D, λ = 500 nm, against blank solution) (Flaschka and Barnard, 1967), using a prepared calibration curve. The Au(III) concentration in the inferior phase (salt-rich phase) was obtained as the difference between the initial Au(III) concentration (c₀, mg·L⁻¹) and the determined Au(III) concentration from the PEG-rich phase.

The distribution coefficient (D_{Au}) and the extraction percent (E_{Au}, %) were calculated from the experimental results using Eqs. (1-2):

$$D_{Au} = \frac{c_{Au}^{PEG}}{c_{Au}^{salt}} \quad (1)$$

$$E_{Au} = \frac{D_{Au}}{D_{Au} + v} \times 100 \quad (2)$$

where: c_{Au}^{PEG} and c_{Au}^{salt} are the Au(III) concentrations in PEG-rich phase and salt-rich phase, and v is the volume ratio of salt-rich phase and PEG-rich phase.

The applicability of the studied aqueous two-phase systems in the recovery of Au(III) ions by extraction was tested using a cyanide wastewater sample with a initial Au(III) ions concentration of 64.62 mg·L⁻¹. In these experiments, in the preparation of the aqueous two-phase systems, the Au(III) ions solution was replaced with the cyanide wastewater, while all other conditions (volume and concentration of components, centrifugation and stand-by time, etc.), were maintained the same as described above.

2.3. Analysis of solidified PEG-rich phases

About 1.0 mL from each PEG-rich phase separated from aqueous two-phase systems was placed on glass slide and allowed to solidify in the air. The solidified PEG-rich phases were then used for recording of FTIR spectra (FTIR Spectrometers BioRad, spectral domain 400 – 4000 cm⁻¹, resolution 4 cm⁻¹, 32 scans, KBr pellet technique) and for optical microscopy studies (Optical microscope Olympus type, polarized light, different orders of magnitude).

3. Results and discussions

According with the studies from literature (Bulgariu and Bulgariu, 2008; Patricio et al., 2011; Rogers et al., 1996), the extraction of metal ions in aqueous two-phase systems can become quantitatively only if the following conditions are met:

- (i) the PEG-rich phase of extraction system has a relatively low content of water,
- (ii) in extraction system, the concentration of the extracting agent is high enough so that the metal ions are transformed into complex anionic species, and then transferred to a PEG-rich phase.

These two conditions are closely related to each other, and for this reason in conducting extraction studies in aqueous two-phase systems, the influence of several experimental parameters on extraction efficiency should be analyzed, before such a method can be used for practical applications.

In case of Au(III) ions, their extraction into such aqueous twp-phase systems is based on the formation of anionic complex species, in accordance with the elementary equilibrium (Eq. 3):



which due to high stability and low-hydration degree will prefer the PEG-rich phase of extraction system (Bulgariu and Bulgariu, 2011).

Starting from these considerations, in this study, the influence of polymer molecular weight, salt solution pH and concentration of chloride extracting agent on the Au(III) extraction efficiency was examined to determine the optimal conditions.

3.1. Influence of PEG molecular weight

The influence of PEG molecular weight on the Au(III) ions extraction efficiency was studied in aqueous two-phase systems formed from PEG with three different molecular weight (i.e. 2000, 4000 and 6000 $\text{g}\cdot\text{mol}^{-1}$). The other experimental conditions were: initial Au(III) ions concentration of $72.12 \text{ mg}\cdot\text{L}^{-1}$, chloride ions concentration of $0.05 \text{ mol}\cdot\text{L}^{-1}$ and salt solution pH of 4.5. The obtained experimental results are presented in Fig. 1. It can be observed from Fig. 1 that the increase of molecular weight of PEG determine the decrease of Au(III) ions concentration in salt-rich phase, concomitant with the increase of the extraction percent.

This variation in extraction efficiency is the result of the decrease in water content of the PEG-rich phases with the increase of molecular weight of PEG. The FTIR spectra of solidified PEG-rich phases (Fig. 2) clearly shown that the amount of water in the PEG-

rich phase is lower as the molecular weight of PEG is higher.

This means that at high molecular weight of PEG, the PEG-rich phases of the extraction systems will have a high hydrophobicity, and the AuCl_4^- anionic species will be extracted more efficiently. It should be noted that a quantitative extraction of Au(III) ions is obtained in all the cases, but the extraction percent increase in the order: PEG-2000 (65.78 %) < PEG-4000 (75.01 %) < PEG-6000 (86.20 %). Therefore, a PEG molecular weight of 6000 $\text{g}\cdot\text{mol}^{-1}$ has been considered the best choice for the extraction of Au(III) ions in the aqueous two-phase systems in the presence of chloride ions as extracting agents.

3.2. Influence of salt solution pH

The influence of salt solution pH was studied in the pH range of 1.05 to 8.50, obtained by adding small volumes of H_2SO_4 (96 %) or NH_3 (25 %) to the phase-forming salt solution ($(\text{NH}_4)_2\text{SO}_4$ 40 % (w/w)), while the other experimental conditions (phase ratio = 5:4, $c_0 = 72.12 \text{ mg Au(III)}\cdot\text{L}^{-1}$, $\text{Cl}^- = 0.05 \text{ mol}\cdot\text{L}^{-1}$ and molecular weight of PEG = 6000), were maintained constant.

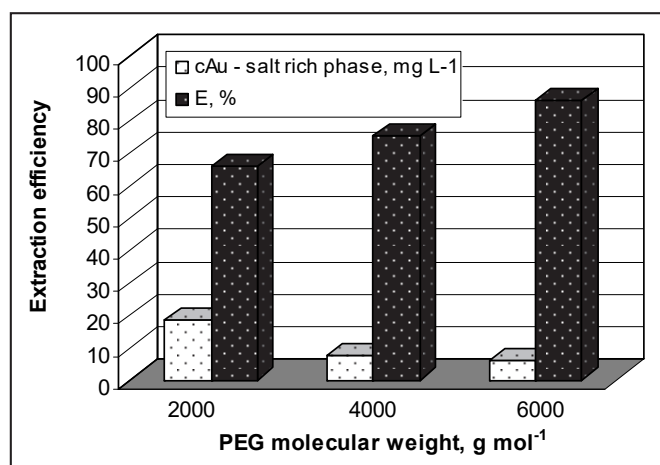


Fig. 1. Influence of molecular weight of PEG on Au(III) ions extraction efficiency (volume ratio: 5:4).

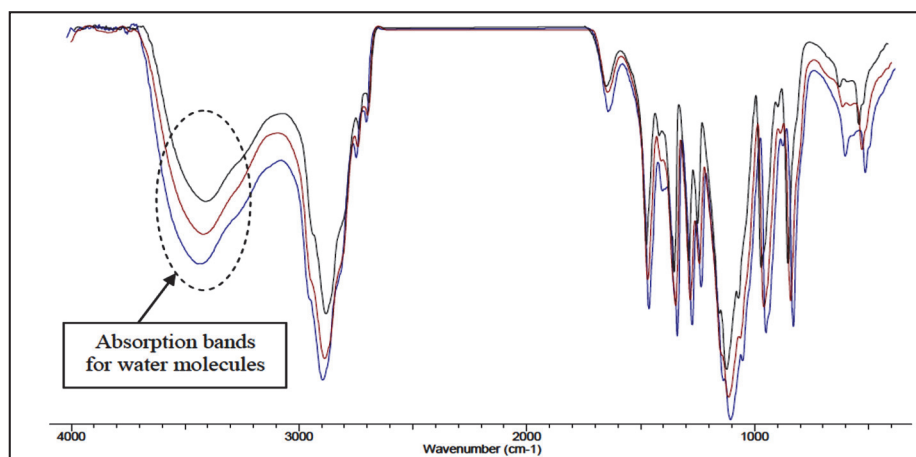


Fig. 2. FTIR spectra of solidified PEG-rich phases at different molecular weight of PEG (black: PEG-6000, red: PEG-4000, blue: PEG-2000)

The experimental results presented in Fig. 3a indicate that increasing in the salt solution pH from 1.05 to 8.50 determines the decrease of Au(III) ions extraction efficiency from 94.30 % to 53.08 %. This variation of the Au(III) extraction percents is the result of two factors, namely: (i) lowering the salt solution pH decreases the amount of water from the PEG-rich phase of the extraction systems and these phases will become more hydrophobic, and therefore more adequate for the extraction of AuCl_4^- species from salt-rich phase, and (ii) in presence of NH_3 molecules (added to reach a pH value of 8.50), beside increasing the amount of water from PEG-rich phase, the speciation form of Au(III) is also changed.

The decrease of water amount from PEG-rich phases with the decrease of salt solution pH can be ease highlighted from FTIR spectra recorded for the solidified PEG-rich phases. The decrease of the transmittance (T %) for the absorption band from $3400\text{--}3450\text{ cm}^{-1}$ (which is attributed to the stretching vibrations of water molecules) with the decreasing of the salt solution pH clearly indicate the increasing of hydrophobic degree of PEG-rich phases. The obtained experimental values are illustrated in Fig. 3b, where for more accuracy the transmittance of PEG-rich phases ($T(\text{phase})$, %) was reported to the transmittance of solidified PEG-6000 (40 % (w/w)) solution ($T(\text{PEG})$, %). Thus, it is observed that the increase in the salt solution pH increases the $T(\text{phase})$ %/ $T(\text{PEG})$ % ratio, which means an increase in the water content in the PEG-rich phases, and therefore their hydrophobic degree decrease, even if not after a linear dependence.

On the other hand, the significant decrease of the Au(III) extraction efficiency at pH of 8.50 is determined both by the increase of water content in the PEG-rich phase, and also by the changing of the

speciation form. In presence of NH_3 molecules, the following equilibrium occurs (Eq. 4):



and the neutral $\text{Au}(\text{NH}_3)_2\text{Cl}$ species (which are more stable than AuCl_3) (Lurie, 1975) will prefer to remain in the salt-rich phase of extraction systems. The simultaneous action of these two factors determines that at salt solution pH of 8.5, the Au(III) extraction percent to decrease to almost half (53.08 %).

On the basis of these experimental observations, a salt solution pH of 3.15 was selected as optimal for the Au(III) ions extraction in aqueous two-phases systems, and was used in the further experiments.

3.3. Influence of initial extracting agent concentration

Another experimental parameter which significant influences the extraction of metal ions in the aqueous two-phase systems is the concentration of extracting agent. This because according with the studies from literature (Rogers et al., 1996; Shibukawa et al., 2000), most of metal ions have a high hydration degree and cannot be extracted into PEG-rich phase of extraction systems, in absence of extracting agent.

In this study the chloride ions were used as extractants for the Au(III) ions extraction in the aqueous two-phase systems, and the influence of their initial concentration on the Au(III) ions extraction efficiency was examined in the concentration range between 0.025 and $0.2\text{ mol}\cdot\text{L}^{-1}$, while the other experimental conditions (phase ration = 5:4, $c_0 = 72.12\text{ mg Au(III)}\cdot\text{L}^{-1}$, pH = 3.15 and molecular weight of PEG = 6000), were maintained constant. The obtained experimental results are presented in Fig. 4.

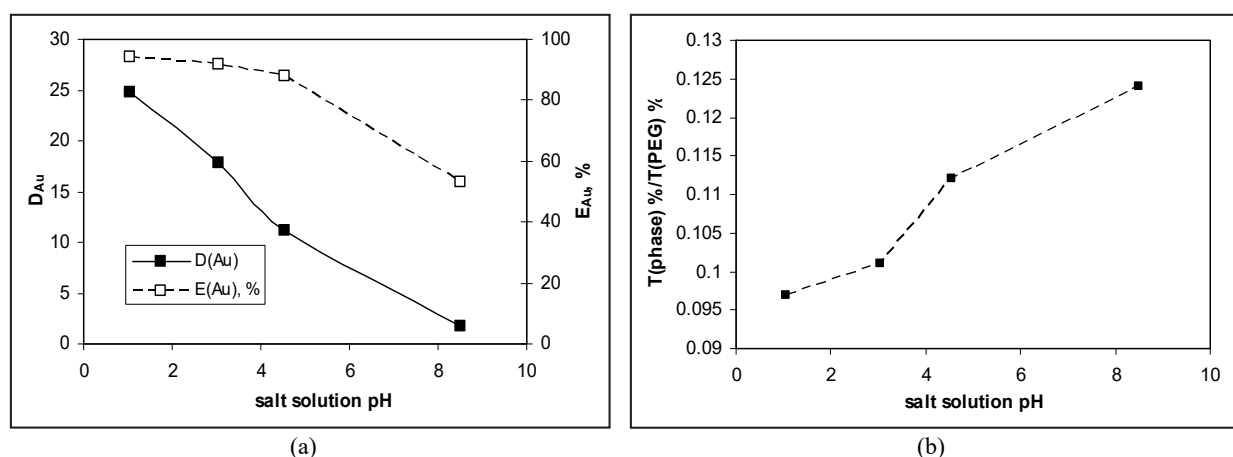


Fig. 3. Influence of salt solution pH on the Au(III) ions extraction efficiency in studied aqueous two-phase system. (a) Extraction percent; (b) Transmittance ration between solidified PEG-rich phases ($T(\text{phase})$) and PEG-6000 ($T(\text{PEG})$), calculated on the basis of FTIR spectra)

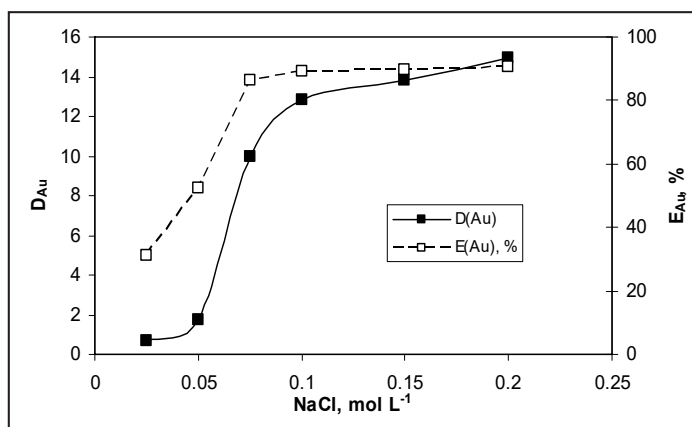


Fig. 4. Influence of initial chloride ions concentration on the Au(III) ions extraction efficiency in aqueous two-phases system

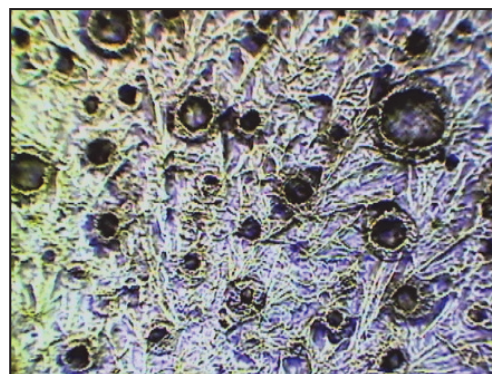
The extraction of Au(III) ions in aqueous two-phase system in presence of the chloride ion as extracting agents is probably based on the formation of anionic AuCl_4^- species, according to Eq. (3). Thus, the neutral AuCl_3 molecules, which are added in the salt-rich phase of extraction system, will pass step by step from solution bulk to interface, where will interact with a new Cl^- ion and will form AuCl_4^- species. These anionic AuCl_4^- species, due to their high stability ($\text{p}K = 21.20$) (Lurie, 1975) and low hydration degree, will be extracted then into PEG-rich phase of extraction systems.

If such mechanism of Au(III) ions extraction in aqueous two-phase system is considered as possible, then it is expected that the efficiency of extraction process to increase with the increase of Cl^- ions concentration. The experimental results presented in Fig. 4 clearly indicate this. As can be observed from Fig. 4, the increase of Cl^- ions concentration from 0.025 to 0.1 $\text{mol}\cdot\text{L}^{-1}$ determine the increase of Au(III) extraction percents from 31.08 to 89.09 %. Further increase of the extracting agent concentration (from 0.1 to 0.2 $\text{mol}\cdot\text{L}^{-1}$) does not significantly change the Au(III) extraction efficiency, the experimental extraction percents varying by no more than one unit (from 89.09 to 90.49 %). Under these conditions, it should be noted that a Cl^- ions concentration of 0.1 $\text{mol}\cdot\text{L}^{-1}$ added in extraction system is enough for the quantitative extraction of 72.12 $\text{mg}\cdot\text{L}^{-1}$ Au(III), in a aqueous PEG(6000)- $(\text{NH}_4)_2\text{SO}_4$ two phase system, where the phases ratio is 5:4 and salt solution pH 3.15.

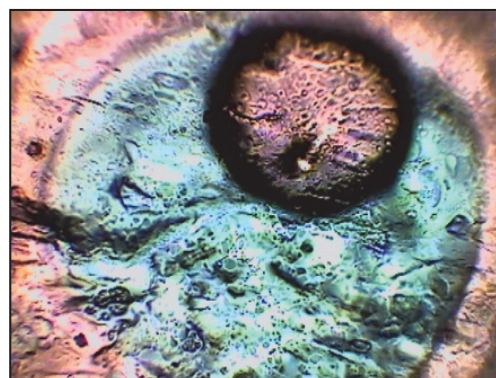
On the other hand, in order to prove the presence of Au(III) species in the PEG-rich phase of extraction system, the microscopic images in natural and polarized light were recorded at different magnitude order, and are illustrated in Fig. 5.

Thus it can be observed that at in the mass of solidified PEG, the extracted Au(III) species are distributed randomly (Fig. 5a), and that inside of a such dark spot (Fig. 5b) it is a clear distinction between zones with solidified PEG (Fig. 5b-red colour) and those which contains Au(III) species (Fig. 5b-blue colour). These observations suggest that in the extraction of Au(III) ion in the aqueous two-phase

system are not involved specific chemical interactions between polymer molecules and Au(III) species. Most likely, the extraction of Au(III) species into PEG-rich phase of extraction system is determined by the chemical stability and hydration degree of the metallic species, and in these conditions the presence of sufficient Cl^- ions is essential to ensure a quantitative extraction. Therefore, a Cl^- ions concentration of 0.1 $\text{mol}\cdot\text{L}^{-1}$ was considered as optimal for the Au(III) ions extraction in mentioned experimental conditions.



(a)



(b)

Fig. 5. Microscopic images of solidified PEG-rich phase obtained at the Au(III) ions extraction in presence of Cl^- ions (0.1 $\text{mol}\cdot\text{L}^{-1}$) at salt solution pH of 3.15., at different orders of magnitude (a) (50x); (b) 250x

3.4. Au(III) extraction from cyanide solution

The applicability of the aqueous two-phase system in the recovery of Au(III) ions by extraction was tested using a cyanide wastewater sample, purchased from a local company. The initial Au(III) ions concentration in cyanide wastewater sample was determined to be $64.62 \text{ mg}\cdot\text{L}^{-1}$, and was adjusted to $650 \text{ mg}\cdot\text{L}^{-1}$ with etalon Au(III) solution. 0.5 and 1.0 mL of cyanide wastewater (which correspond to a initial Au(III) concentration in aqueous two-phase system of 36.11 and $72.23 \text{ mg}\cdot\text{L}^{-1}$, respectively) were used in experiments for the Au(III) ions extractions, in mentioned optimal conditions (phase ratio = 5:4, salt solution pH = 3.15), in absence and in presence of $0.1 \text{ mol}\cdot\text{L}^{-1}$ Cl^- ions extracting agents. The obtained values of extraction percent are presented in Fig. 6.

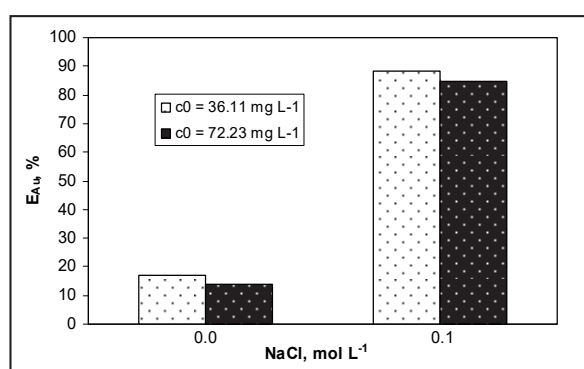


Fig. 6. Extraction efficiency of Au(III) ions from cyanide wastewater, in absence and in presence of $0.1 \text{ mol}\cdot\text{L}^{-1}$ Cl^- ions.

The experimental results presented in Fig. 6 indicate that the Au(III) ions are more efficient extracted from cyanide wastewater in presence of chloride extractants ($> 85 \%$), than in their absence ($< 17 \%$), for both initial Au(III) ions concentration. This is somewhat surprising because due to the high stability of gold cyanide species ($\text{pK}(\text{AuCN}_4^-) = 56$) (Lurie, 1975), it was expected that their extraction to be quantitative and in absence of chloride ions extractants. A possible explanation is that the cyanide concentration from wastewater is not enough to ensure the formation of anionic $\text{Au}(\text{CN})_4^-$ species that will have the high extraction efficiency in such aqueous two-phase systems. Under these conditions, supplementary ligands, such as Cl^- ions, are required so that Au(III) ions to be transformed into anionic species, and then quantitatively transferred into PEG-rich phase of extraction systems. In order to check this hypothesis, additional experimental studies related to the nature of Au(III) extracted species in presence of various cyanide ions concentrations are necessary, and these results will be reported in a further study.

4. Conclusions

In this study the extraction efficiency of Au(III) ions in a aqueous two-phase system formed from

polyethylene glycol (PEG) and $(\text{NH}_4)_2\text{SO}_4$ inorganic salt was examined in batch systems, as a function of several experimental parameters: molecular weight of PEG, salt solution pH and chloride ions extractant concentration. The experimental studies have shown that the maximum extraction of Au(III) ions was obtained when for the preparation of the aqueous two-phase system is used a polyethylene glycol (PEG) with molecular weight of 6000, a salt solution with pH of 3.15 and a Cl^- ions concentration greater than $0.1 \text{ mol}\cdot\text{L}^{-1}$. Under these conditions, the extraction percent of Au(III) ions is higher than 89% , and the extraction can be considered a quantitative one. The applicability of the aqueous two-phase system in the recovery of Au(III) ions by extraction was tested using a cyanide wastewater sample, purchased from a local company. The obtained experimental results have indicate that the Au(III) ions are more efficient extracted from cyanide wastewater in presence of chloride extractants ($> 85 \%$), than in their absence ($< 17 \%$). A possible explanation is that the cyanide concentration from wastewater is not enough to ensure the formation of anionic $\text{Au}(\text{CN})_4^-$ species and therefore supplementary Cl^- ions are required so that Au(III) ions to be transformed into anionic species, and then quantitatively transferred into PEG-rich phase of extraction systems. But, to prove this hypothesis, additional experimental studies are needed. The results presented in this study indicate the potential applicability of aqueous two-phase systems in the Au(III) ions recovery from cyanide wastewaters, both due to its extraction performances, and “green chemistry” characteristics.

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References

- Akcil A., Erust C., Gahan C.S., Ozgun M., Sahin M., Tuncuk A., (2015), Precious metal recovery from waste printed circuit boards using cyanide and non-cyanide lixivants – A review, *Waste management*, **45**, 258-271.
- Al-Said H.M., (2016), The fast recovery of gold(III) ions from aqueous solutions using raw date pits: Kinetic, thermodynamic and equilibrium studies, *Journal of Saudi Chemical Society*, **20**, 615-624.
- Benavides J., Rito-Palomares M., (2008), Practical experiences from the development of aqueous two-phase processes for the recovery of high value biological products, *Journal of Chemical Technology and Biotechnology*, **83**,133-142.
- Benavides J., Aguilar O., Lapizco-Encinas B.H., Rito-Palomares M., (2008), Extraction and purification of bioproducts and nanoparticles using aqueous two-phase systems strategies, *Chemical Engineering Technology*, **31**, 838-845.
- Birloaga I., De Michelis I., Ferella F., Buzatu M., Veglio F., (2013), Study on the influence of various factors in the hydrometallurgical processing of waste printed circuit boards for copper and gold recovery, *Waste Management*, **33**, 935-941.

- Bulgariu L., Bulgariu D., (2008), Extraction of metal ions in aqueous polyethylene glycol–inorganic salt two-phase systems in the presence of inorganic extractants: Correlation between extraction behaviour and stability constants of extracted species, *Journal of Chromatography A*, **1196–1197**, 117-124.
- Bulgariu L., Bulgariu D., (2011), Extraction of gold(III) from chloride media in aqueous polyethylene glycol-based two-phase system, *Separation and Purification Technology*, **80**, 620-625.
- Bulgariu L., Bulgariu D., (2013), Selective extraction of Hg(II), Cd(II) and Zn(II) ions from aqueous media by a green chemistry procedure using aqueous two-phase systems, *Separation and Purification Technology*, **118**, 209-216.
- Cayumil R., Khanna R., Rajarao R., Mukherjee P.S., Sahajwalla V., (2016), Concentration of precious metals during their recovery from electronic waste, *Waste Management*, **57**, 121-130.
- da Silva L.H.M., Loh W., (2000), Calorimetric investigation of the formation of aqueous two-phase systems in ternary mixtures of water, poly(ethylene oxide) and electrolytes (or dextran), *Journal of Physical Chemistry*, **104**, 10069-10073.
- Fan R., Xie F., Guan X., Zhang Q., Luo, Z., (2014), Selective adsorption and recovery of Au(III) from three kinds of acidic systems by persimmon residual based bio-sorbent: A method for gold recycling from e-wastes, *Bioresource Technology*, **163**, 167-171.
- Flaschka A.H., Barnard A.J., (1967), *Chelates in Analytical Chemistry*, Marcel Dekker Inc., New York.
- Gherca M., Bulgariu L., (2017), Studies regarding Au(III) extraction in aqueous two phase systems based on polyethylene glycol with different molecular weights, *Buletinul Institutului Politehnic din Iași*, **63**, 39-48.
- Gnoni M.G., Mossa G., Mummolo G., Tornese F., Verriello R., (2017), Circular economy strategies for electric and electronic equipment: A Fuzzy cognitive map, *Environmental Engineering and Management Journal*, **16**, 1807-1817.
- Graber T.A., Andrews B.A., Asenjo J.A., (2000), Model for the partition of metal ions in aqueous two-phase systems, *Journal of Chromatography B*, **743**, 57-64.
- Hamta A., Dehghani M.R., (2017), Application of polyethylene glycol based aqueous two-phase systems for extraction of heavy metals, *Journal of Molecular Liquids*, **231**, 20-24.
- Hasegawa H., Barua S., Wakabayashi T., Mashio A., Maki T., Furusho Y., Rahman I.M.M., (2018), Selective recovery of gold, palladium, or platinum from acidic waste solution, *Microchemical Journal*, **139**, 174-180.
- Lurie J., (1975), *Handbook of Analytical Chemistry*, Mir Publishers, Moscow.
- Mageste A.B, de Lemos L.R., Ferreira G.M.D., do Carmo Hespagnol da Silva M., da Silva L.H.M., Ferreira Bonomo R.C., Minim L.A., (2009), Aqueous two-phase systems: An efficient, environmentally safe and economically viable method for purification of natural dye carmine, *Journal of Chromatography A*, **1216**, 7623-7629.
- Mihajlov A., Stevanović-Čarapina H., (2015), Rethinking waste management within the resource-efficient concept, *Environmental Engineering and Management Journal*, **14**, 2973-2978.
- Murari G.F., Alves Penido J., Lopes Machado P.A., de Lemos L.R., Lemes N.H.T., Virtuoso L.S., Rodrigues G.D., Mageste A.B., (2015), Phase diagrams of aqueous two-phase systems formed by polyethylene glycol + ammonium sulfate + water: equilibrium data and thermodynamic modeling, *Fluid Phase Equilibria*, **406**, 61-69.
- Patricio P.R., Mesquita M.C., da Silva L.H.M., da Silva M.C.H., (2011), Application of aqueous two-phase systems for the development of a new method of cobalt(II), iron(III) and nickel(II) extraction: a green chemistry approach, *Journal of Hazardous Materials*, **193**, 311-318.
- Rogers R.D., Bond A.H., Bauer C.B., Zhang J., Griffin S.T., (1996), Metal ion separations in polyethylene glycol-based aqueous biphasic systems: correlation of partitioning behaviour with available thermodynamic hydration data, *Journal of Chromatography B*, **680**, 221-229.
- Shibukawa M., Matsuura K., Shinozuka Y., Mizuni S., Oguma K., (2000), Effect of phase forming cations and anions on the partition of ionic solute in aqueous polyethylene glycol-inorganic salt two-phase systems, *Analytical Science*, **16**, 1039-1044.
- Silvas F.P.C., Jimenez-Correa M.M., Caldas M.P.K., de Moraes V.T., Espinosa D.C.R., Tenorio J.A.S., (2015), Printed circuit board recycling: Physical processing and copper extraction by selective leaching, *Waste Management*, **46**, 503-510.
- Tuncuk A., Stazi V., Akcil A., Yazici E.Y., Deveci H., (2012), Aqueous metal recovery techniques from e-scrap: Hydrometallurgy in recycling, *Minerals Engineering*, **25**, 28-37.
- Zheng Y., Tong Y., Wang S., Zhang H., Yang Y., (2015), Mechanism of gold (III) extraction using a novel ionic liquid-based aqueous two phase system without additional extractants, *Separation and Purification Technology*, **154**, 123-127.