Features and Capabilities of New DNPDSE Method

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Abstract

Dissolved Nitrogen Predispersed Solvent Extraction (DNPDSE) is a new method devised for improving the performance of equipment utilized in the solvent extraction (SX) method, especially for dilute solutions. In this method, for mixing the two phases, bubble dispersion of the organic phase (colloidal gas aphrons [CGAs]) is used instead of its drop dispersion in the aqueous phase. Through increased contact area and enhanced buoyancy force of organic phase, this performance mode leads to more satisfactory phase disengagement, less extraction time and more recovery of metal ions in high aqueous/organic (A/O) ratios. The results of experiments conducted on dilute (128 mg Cu/l) and dense (2000 mg Cu/l) synthetic solutions indicated 22% and 2.5% (on average) increased recovery, respectively in the DNPDSE method compared with the SX method. This increase in recovery was only due to the difference between the performance modes of these two methods, and copper ion flotation (IF) by cationic (dodecytrimethyl ammonium bromide) and anionic (sodium dodecylbenzene sulphonate) surfactants was not involved in this promotion. On the other hand, there is the possibility of applying this method combined with the precipitate flotation (PF) and IF methods to produce environmentally-friendly raffinates. Comparison of raffinate pictures from the DNPDSE and PF methods with both ferrous sulfate and aluminum sulfate coagulants indicated increased transparency of raffinate after PF due to elimination of the organic phase from it. Moreover, the flotation of residual copper ions in raffinate using ethyl xanthate resulted in complete removal of copper from it. Finally, the flow sheet representing the combination mode of the three methods (DNPDSE-PF-IF) was presented.

Keywords: Dissolved Nitrogen Predispersed Solvent Extraction (DNPDSE), Colloidal Liquid Aphron (CLA), Colloidal Gas Aphron (CGA), Precipitate Flotation (PF), Ion Flotation (IF).

1–Introduction

Advancements in human societies, in parallel with ever-increasing demands for industrial products, have increased mine productivity, resulting in decreased mineral sources with high-grade and non-complex ores. Studies conducted on correct productivity context from mineral resources indicated that, nowadays, use of low-grade sources and also sources with more difficult technological productivity (like wastewaters) is sited on the agenda of experts. Efforts made in this area have led in the invention and development of new technologies for the recovery of valuable metals of low-grade ores and dilute solutions in mineral processing.

In line with these technological developments, extensive research has been done for promoting the operational power and improving the performance of equipments used in the conventional solvent extraction (SX) method (Gupta, 1990).

The maximum efficiency of this method belongs to dense solutions (Habashi, 1990). However, such reasons as a) difficult conditions of attaining pregnant solutions with proper concentrations and considerable increase in operating costs due to decreased mineral sources with high-grade and b) production of large volumes of dilute solutions containing pollutant and toxic elements such as heavy metals, as a new source of valuable elements, have provided great interests for expansion of research activities in the solvent extraction field of dilute solutions.

Predispersed solvent extraction (PDSE) (Sebba, 1987) froth flotoextraction (Dibrov et al., 1998), solvent extraction with bottom gas injection without moving parts (Sohn and Doungdeethaveeratana, 1998; Doungdeethaveeratana and Sohn, 1998), liquid membranes, nondispersive solvent extraction, microemulsions and reverse micelles (Habashi, 1999) and air-assisted solvent extraction (AASX) (Tarkan and Finch, 2005a and 2006), etc. are examples of research activities in this field, though most of them have not reached industrial applications.

Dissolved Nitrogen Predispersed Solvent Extraction (DNPDSE) is a new method devised in this field, which is a combination of some methods mentioned above. In this method, two phase mixing operation is done through using bubble dispersion of the organic phase, i.e. colloidal gas aphrons (CGAs), instead of its droplet dispersion into the aqueous phase (Tavakoli Mohammadi et al., 2013). The DNPDSE contactor and its schematic diagram are shown in Figure 1.

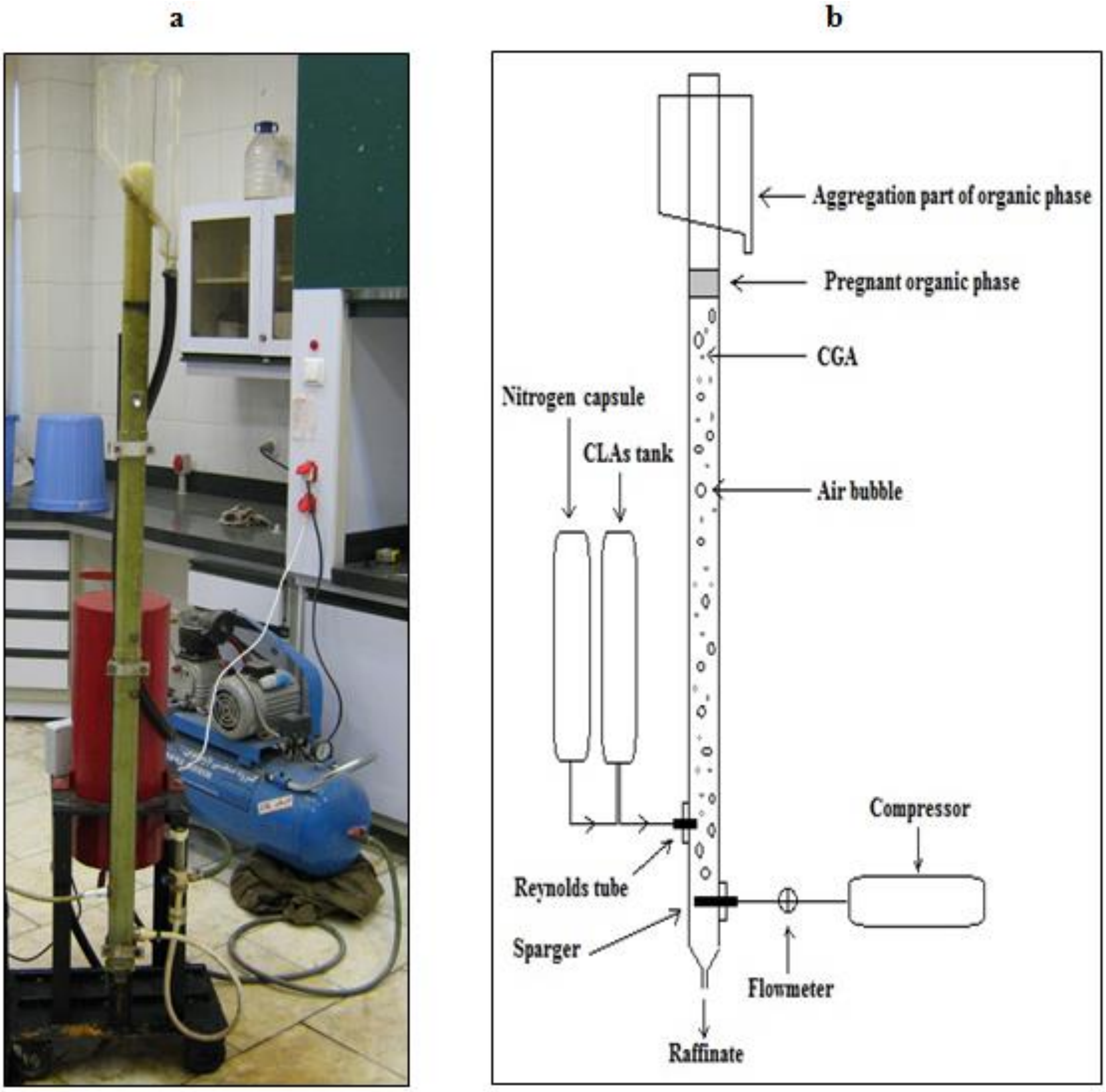


Figure 1) DNPDSE system: a) contactor and b) schematic diagram.

The operation mode of this method has two main specifications:

Larger contact area of bubbles compared with droplets: This feature provides the possibility of using higher aqueous/organic (A/O) ratios due to gaining advantage of the maximum extraction capacity, less time to reach recovery desired and more recovery rates of metal ions from the dilute solution.

Higher buoyancy force of bubbles compared with droplets: This feature can be more effective than the low difference of density between the aqueous and organic phases for satisfactory disengagement of the two phases and the decrease in the organic phase loss due to entrainment (more than 50% of the total organic phase loss) (Tavakoli mohammadi et al., 2013; Young et al., 1999).

These specifications involve the following advantages in addition to achieving the mentioned aims:

-Increased concentration of metal ions in the organic phase due to using high A/O ratios,

-Decreased consumption of organic phase,

-Decreased organic phase loss due to less consumption that can be more important environmentally because of decreased contamination of exit mine wastewaters, in addition to several economic advantages,

-Possibility of using primary pregnant solutions with less concentrations and thus providing the chance of appropriate mixer-settlers replacement with columns for their better advantages over mixer-settlers.

In addition, DNPDSE contactor- for similarity with the columns used in various flotation methods- makes possible the simultaneous implementation of some of the flotation specific methods such as precipitate flotation (PF) and ion flotation (IF) together with this new method. Therefore, suitable conditions were provided for evaluation of the DNPDSE performance mode alone or in combination with various flotation methods to produce environmentally-friendly exit raffinates.

It is expected that this method could be a good replacement for conventional extraction methods used for dense solutions, in addition to fulfilling the intended aims and reducing the problems related to the extraction of dilute solutions.

2–Introduction

2.1- Principles

2.1.1- DNPDSE method principles

The mixing operation of two phases in this method is based on bubble dispersion of the organic phase (colloid gas aphrons [CGAs]) instead of its droplet dispersion in the aqueous phase. In this method, similar to PDSE, to achieve large interface in pregnant solution, the solvent phase is converted into biliquid foam, called polyaphron. Polyaphron is composed of colloidal liquid aphrons (CLAs) aggregation. CLAs are two-layered bubbles consisting of an oil (organic) phase encapsulated in a thin shell of the surfactant solution. Due to their minute size (10-40 µ), they can produce large interfaces.

In the PDSE method, polyaphron should be diluted due to high viscosity and long dispersion time. If the diluted polyaphron is added into the PDSE contactor, it will rise to the pregnant solution surface due to its lower density than the solution. Because of the small size of CLAs, this operation is usually very slow. Hence, increasing of the ascending speed of CLAs to surface is used from CGAs due to hydrophobic property of the soapy shell. CGAs are aggregates of double layer bubbles with small dimensions stabilized by a surfactant) (Save et al., 1999; Sebba, 1987).

In the DNPDSE method, adding new equipment in the PDSE contactor building is done following changes in its operation mode:

1. Conversion of CGAs (in the PDSE method) into common air bubbles to increase the contactor’s performance speed, avoid dilution of the primary solution, and eliminate the need for costly equipment to produce CGAs.

2. Conversion of CLAs (in the PDSE method) into CGAs to significantly increase the contact area, enhance buoyancy force and prevent recovery reduction due to less CGAs dilution requirement.

The first conversion was done with a simple sparger. In fact, instead of applying CGAs produced by expensive equipment and their injecting into the contactor, common air bubbles produced by the compressors and sparger were used.

The second conversion needs a two-step process as follows:

-In the first step, by selecting proper surfactant (silicone oil) for organic phase (i.e. with high foaming property, without improper effect on the extraction and strip processes (Tarkan and Finch, 2005b) and decrease in the temperature of resulting polyaphron (to increase foaminess of oil derivatives (Bolles, 1967), increase of air solubility, and augment the security level), the best foaming conditions are achieved. The aim is to improve the operational conditions of dissolved air flotation (DAF) process. In this process, decreased air/liquid interfacial tension through increasing the amount of foaming, besides providing better conditions for nucleation and bubble formation (increased kinetics), application of lower working pressures becomes possible, which is not only economically beneficial but also important for more security (Feris and Rubio, 1999).

-In the second step, through transfer of the prepared polyaphron into the tank and applying pressure, more gas solubility is enabled based on Henry's Law. According to this Law, maximum molar fraction of a gas dissolved in water (in a fixed temperature) depends on its partial pressure in the gaseous phase according to the below equation:

$$X_G=P_G/H_G \qquad (1)$$

Where, X_G is the mole fraction of gas in water, P_G is the partial pressure of gas in the aqueous phase (atm) and H_G is Henry's constant [atm. $(\text{Mole-fraction})^{-1}$]. This statement simply shows that with increasing of air pressure on the liquid level, more air will be solved in it. Thus, to produce CGAs in this method, polyaphron is placed under high atmosphere pressures (3-6 bars) to dissolve a large amount of gas in it. After air solubilization in CLAs and before the pressurized polyaphron release, a pressure drop is induced by the presence of a constriction or an obstacle on the trajectory of its flow (Rodrigues and Rubio, 2007; Dupre et al., 1998).

In this method, similar to the PDSE method, by choosing the appropriate surfactant for producing air bubbles (a surfactant with a charge opposite to that used to produce CLAs), the operations can be so adjusted that air bubbles break after reaching the surface (because of contrafoams effect) and a continuous solvent layer is attained on the surface (Sebba, 1987). Detailed information about this method have been presented elsewhere (Tavakoli mohammadi et al., 2013).

2.1.2-PF method principles

After performing the extraction operation in the PDSE method proposed by Sebba, there is always extra blur in the resulting raffinate due to the small size of CLAs and CGAs as well as their slow rising speed to surface and maybe dissolving in negligible amounts. In addition, some of these CGAs and CLAs may take colloid form and remain suspended in the solution.3 These suspended particles have mainly negative charges that cause their stability by natural repulsion between the colloid particles due to similar charges. But presence of specific chemicals such as aluminum and ferric sulfates can cause instability and deletion of natural repulsion between these particles through coagulation phenomenon and provide their mutual bond (Sincero and Sincero, 2003; Al-Shamrani et al., 2002). When these coagulants are dissolved in water, they are dissociated according to the below reactions:

$$Al_2(SO_4)_3 \rightarrow 2Al^{3+}+ 3SO_4^{2} \qquad (2)$$

$$Fe_2(SO_4)_3\rightarrow 2Fe^{3+} + 3SO_4^{2-} \qquad (3)$$

Then, considering the solution conditions, various complexes such as $Al(H_2O)_6^{3+}$ for aluminum sulfate, and $FeOH^{2+}$ and $Fe(OH)^{2+}$ for ferric sulfate are formed (Sincero and Sincero, 2003). Due to opposing charges, these complexes are combined with the charged colloid particles of CLAs and CGAs and form specific charged precipitations. Now, if the surfactant, used to form bubbles, has opposite charge to these precipitations, they will aggregate on the surface of gas bubbles and will be transported on the solution surface as foam (Sebba, 1987). In the DNPDSE method, however, owing to the two conversions performed, it is expected that raffinate has less turbidity. Nevertheless, it is possible to use the PF method combined with this method to decrease organic phase loss and improve the transparency of the exit raffinate.

2.1.3- IF method principles

Ion flotation, described for the first time by Sebba in 1950, is a relatively novel separation technology for recovery and elimination of metal ions from dilute aqueous solutions (wastewaters) (Doyle, 2003; Sebba, 1987). In this method, similar to the PF method, to separate valuable ions, a small amount of the surfactant (collector) with opposite charge to the charged ions is added to the solution. Then, using gas spraying into the solution, the charged ions are absorbed in the air-liquid interface area and collected in one foam phase on the surface of solution (Polat, 2007; Doyle, 2003). The main difference of this method with the PF method is the one-to-one stoichiometric relationship between the charged ions and the surfactant that causes increase in its expense compared with the PF method (Sebba, 1987).

The pH of the solution is one of the most important parameters in IF method, because it determines the type and charge of species in the solution and, therefore, type of the required surfactant (anionic or cationic) for the highest recovery (Polat, 2007; Doyle, 2003). For instance, due to the presence of copper ions as Cu^{2+} in extraction pHs (1.2-2.1) with Lix 984N agent, it is expected that copper ions flotation becomes possible in case of application of anionic surfactants- for their opposite charge with those of copper ions. However, in the IF method, it is necessary to have a preferential attraction between the surfactant and the desired ions in relation to other ions (Sebba, 1987).

2.2- Reagents and solutions

Reagent grade $CuSO_4.5H_2O$ (MERCK, Germany) was used to prepare the synthetic aqueous solutions. Characteristics of these solutions are presented in Table 1.

Table 1) Specifications of synthetic aqueous solutions

Solution type / Specification	Dilute	Intermediate	Dense
Concentration (mg $CuSO_4.5H_2O$/L)	500	4000	7813
Concentration (mg Cu/L)	128	1024	2000
The reason to choose the cited concentration	Producing a very dilute solution to demonstrate desirable contactor performance	Producing a solution with an average concentration of dilute and dense solutions of copper (Tarkan et al., 2006)	Producing a solution containing minimum permitted copper grade in the input feed on the circuit of SX (Lazaridis et al., 2004)

The solvent contained 10% v/v chelating type extractant Lix 984N (Cognis) diluted in 90% v/v kerosene containing 0.3 g/l dilute silicon oil (Shin Etsu). Maximum loading of Lix 984N is 5.1 g Cu/l (Lix 984N, 2010). The density of Lix 984N and kerosene is 0.9 and 0.78 g/ml, respectively. 4 g/l sodium dodecyl benzene sulphonate (NaDBS) (Sigma (USA)) and 0.3 g/l dodecyltrimethyl ammonium bromide (DTAB) (Aldrich (USA)) were used as surfactants in the polyaphron and solution aqueous phases, respectively. To adjust the pH at 2.1 (in order to attain high copper extraction), a solution containing 500 mg/L sulfuric acid was used. Furthermore, to keep the pH constant, a buffered solution containing 0.2 M NaOH, 0.04 M acetic acid, 0.04 M phosphoric acid and 0.04 M boric acid was used (Tarkan and Finch, 2005a). To evaluate the occurrence of copper ions flotation during the implementation of the DNPDSE method, DTAB (0.3 g/l) or NaDBS (0.3 g/l) was used in the synthetic aqueous solution. Also, to evaluate the DNPDSE method's combination capability with the PF and IF methods, aluminum sulfate (Fluka, Switzerland) (0.1 g/l) and ferric sulfate (Sigma, USA) (0.1 g/l) coagulants were used in the PF experiments, and ethyl xanthate collector (Sigma, USA) (6.1 g/l) was used in the IF experiment.

2.3- Methods

2.3.1- SX method

In this method, according to the A/O ratios desired, certain volumes of the aqueous and organic phases were mixed using a magnetic agitator (500 rpm) for 15 minutes. Then the content of the agitator was transferred into a separatory funnel for separating the aqueous and organic phases. Time considered for complete separation was 20 minutes. After this time, the aqueous phase was separated and its equilibrium pH was measured. The copper concentration in the aqueous phase was determined by Atomic Absorption Spectrometry (AAS (VARIAN model)). Then its concentration in the organic phase was calculated from the difference between the metal ions concentrations in the aqueous phase before and after the extraction equilibrium.

2.3.2-DNPDSE method

This method consists of two general stages as follows:

2.3.2.1- Polyaphron preparation stage

Since the preparation conditions affect on the size distribution and stability of polyaphron (He et al., 2007; Scarpello and Stuckey, 1999), CLAs were prepared under relatively constant conditions. To this end, to produce 220 ml anionic polyaphron (with PVR=10), 20 ml water was mixed 4 g/l anionic surfactant of NaDBS using a magnetic stirrer (900 rpm) to get gaseous foam (1st stage). PVR is the volumetric ratio of dispersed organic phase to continuous phase. Then the resulting gaseous foam was placed in a container, containing water and ice, to reduce its temperature to about 5°C (2nd stage). Afterwards, 20 ml of extraction agent Lix 984N was mixed with 0.3 g/l of the non-anionic surfactant of silicone oil and its volume was reached to 200 ml by adding kerosene as diluent (3rd stage). The resulting organic phase was also placed in a container, including water and ice, to reduce its temperature to about 5°C (4th stage). After achieving the desired temperature, the organic phase was gradually added (with a flow rate of 1.5 ml/min) into the foamy aqueous phase with mixing (5th stage). At first, the solvent dispersion in the aqueous phase was easily done. However, after adding about two-third of the total solvent, the mixture became viscous and increasing of viscosity was continued to complete dispersion of the solvent. Finally, a white creamy dispersion of CLAs was obtained (6th stage) (Matsushita et al., 1992; Sebba, 1987). The polyaphron obtained was diluted for more contact area in the continuous aqueous solution. For this purpose, polyaphron was gradually added into distilled water with mixing (7th stage). The distilled water’s volume was four times more than the polyaphron volume, considering the dilution ratio of 5, and its temperature was nearly 5°C. By the end of dilution, proper polyaphron for transfer into the column was obtained (8th stage).

2.3.2.2- Simultaneous extraction and separation stage

This stage consists of two general sections as follows:

-Extraction and separation by producing CGAs: In this part, the resulting polyaphron and nitrogen gas, to produce 3.5 bar pressures, were transferred into the tank and enough time was given to them to dissolve (30 minutes). Then the synthetic aqueous solution (1500 ml), containing 0.3 g/l cationic surfactant DTAB, was transferred into the column. Afterwards, according to the A/O ratios desired, the polyaphron phase was injected into the column through the Reynolds tube. The first sampling from the aqueous phase (30 ml) was done from the middle part of the column 6.5 minutes after starting of the operation.

- Extraction and separation by producing air bubbles: In this part, the air bubbles were used to transfer the remaining CGAs onto the surface and for more mixing of the two phases. For this purpose, 7.5 minutes after starting of the operation, by accurate adjustment of the flow meter, the air produced by the compressor with 0.1 l/min flow rate was passed through the sparger. After 15 minutes, 30 ml of the aqueous phase was taken as the second sample to evaluate the effect of the produced bubbles on the extraction process. Finally, the copper concentration in the aqueous samples was determined by Atomic Absorption Spectrometry (AAS, VARIAN model).

2.3.3- IF method in two states for evaluating the effect of its execution mode on copper recovery

In both states of the IF method, with mechanical cell or DNPDSE contactor, intermediate synthetic aqueous solution was used and its pH in the experiments was adjusted equal to 1.2 and 2.1 (at the beginning and at the end of copper extraction range with Lix 984N agent). Then the solution was prepared by adding 0.3 g/l DTAB cationic or NaDBS anionic surfactants for 2 minutes, while being stirred using a mixer.

2.3.3.1- IF with mechanical cell

In this state, a Denver type flotation machine was used. For this purpose, after transferring the prepared solution into the flotation cell, the agitator rotation speed was adjusted to 900 rpm. Then, through air entrance into the cell, foam recovery was manually done with a plastic scraper for 7.5 minutes. Mechanical cell was used for evaluation of the effect of this state on copper recovery and comparison of its results to those obtained in the DNPDSE contactor state.

2.3.3.2- IF with DNPDSE contactor

In this state, after transfer of the prepared solution into the DNPDSE contactor, air injection operation was performed using sparger fitted beneath the column. Afterwards, the foam produced was transferred into the container.

In both states of the IF method, Atomic Absorption Spectrometry (AAS) was used to determine the concentration of metal ions in the aqueous solution remaining in the mechanical cell and DNPDSE contactor, and the concentration of metal ions in the foam phase was determined through needed calculations.

2.3.4- PF method for evaluating its combination capability with the DNPDSE method

To product desired raffinates, two experiments, similar to those in the DNPDSE method, were conducted on the intermediate synthetic aqueous solution. Then output raffinates from the DNPDSE contactor were once again prepared according to Table 2.

Although the proper pH for benefiting from coagulation phenomenon was proposed to be 8 by AL-Shamrani (2002) and 5.5 by Sebba (1987), however, to prevent copper precipitation, probability of its transfer onto the surface by the PF method, and also in order to benefit from the resultant raffinates for the IF method, the selected pH value should be less than that in the initial precipitation of copper.

Table 2) Conditions considered for preparation the raffinate

pH	Additives	
5	Aluminum sulfate or ferric sulfate (coagulants) 100 mg/L (≈ 0.0001 M)	Sodium dodecylbenzene sulphonate (surfactant) 1000 mg/L

In fact, based on the below relations (Monhemius, 1977):

$$[Cu^{2+}]=732.56\ \mathrm{mg/l}=1.1\times10^{-2}\ \mathrm{M} \qquad (4)$$

$$K=[Cu^{2+}]\times[OH^{-}]=4.79\times10^{-20} \qquad (5)$$

$$[OH^{-}]=(4.7\times10^{-20})/0.11 \qquad (6)$$

$$pH=5.3 \qquad (7)$$

the initial precipitation pH for copper in the output raffinates from the DNPDSE contactor was 5.3, so the pH value equal to 5 was utilized for coagulation. This pH is sufficient because of negligible organic phase remnant in the aqueous phase for complete implementation of the PF method. Then the prepared raffinates containing coagulants of aluminum sulfate or ferric sulfate, after transfer to the column, were exposed to the bubbles produced by Sparger for 10 minutes.

2.3.5- IF method for evaluating its combination capability with the DNPDSE method

To conduct the desired experiment, the raffinate from the previous stage, clarified by the coagulant of aluminum sulfate in the PF method, was used. For this purpose, based on the investigations by Lazaridis et al. (2004), O-alkyl dithiocarbonate, known as xanthate, was used as collector. Lazaridis et al. achieved 100 percent recovery per 2000 mg/l of xanthate for a solution containing 240 mg Cu/l. So, regarding the copper concentration in the raffinate (732.56 mg/l), 6100 mg/l xanthate was considered for the IF method. They also showed that the pH range of 2.5-5.5 was not effective on copper ions removal; hence, due to appropriate pH of raffinate (presence of copper as Cu^{2+}), no change was done in its value.

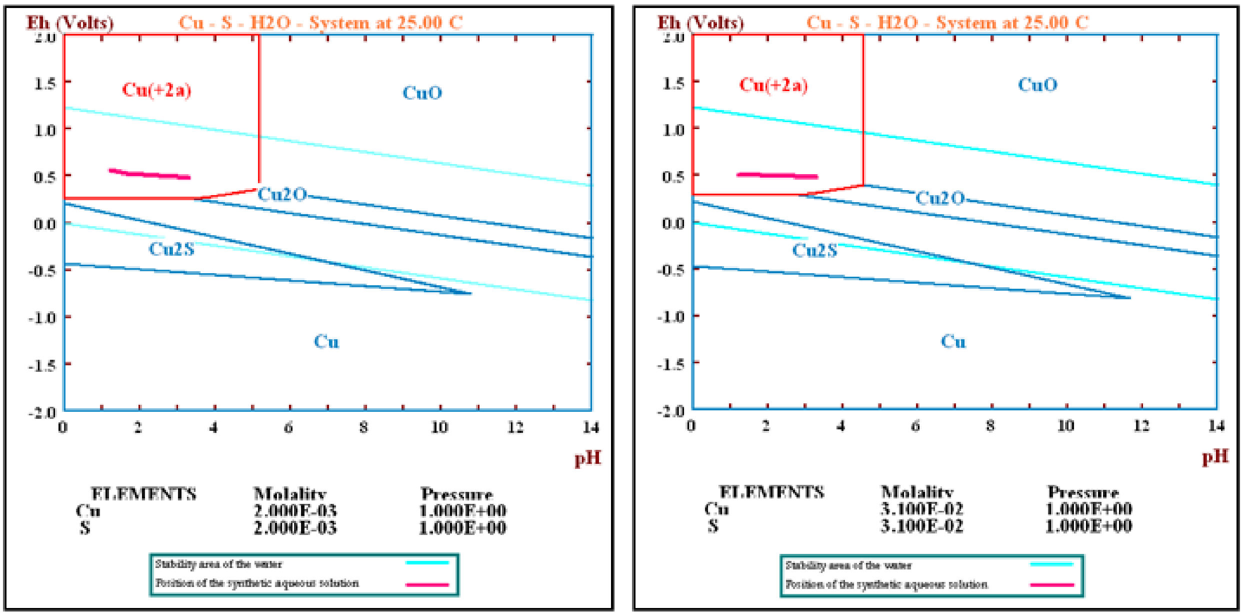
2–Results and discussion

2.1- Evaluation of important copper components in synthetic aqueous solutions

In most of the research experiments conducted to evaluate the performance of different equipments, synthetic aqueous solutions have been used in order to remove the influence of unknown causes and chemical compounds in the solutions and real wastewaters. Hence, to attain results that accurately reflect the extraction performance of the DNPDSE method, here we used synthetic aqueous solutions instead of real ones.

For performing the solvent extraction experiments, the presence of element under study as ion in the solution is necessary. Therefore, it was essential to prove the presence of copper element in the form of Cu^{2+} in synthetic aqueous solutions. Thus the important copper components in these solutions were evaluated by drawing the Eh-pH diagrams by HSC Chemistry 5.11 software. Figure 1 shows the thermodynamic distribution of copper (II) in the synthetic aqueous solutions as a function of Eh-pH. The indicated range in these diagrams (pink line) is the result of connecting the points whose coordinates are Ehs obtained from various pHs of the synthetic aqueous solutions (Table 3).

Comparison of the resulting diagrams shows that the amount of salt used to produce the dilute and dense solutions does not cause a considerable difference in the two diagrams, and the structure of copper ions in both solutions is in the form of Cu^{2+} [in its extraction pH range (1.2-2.4)]. In addition to suitability of synthetic solutions conditions (the presence of elements under study as ions in them), it was necessary that their conditions was uniform to compare the performance of the SX and DNPDSE methods. The results of our investigations in this regard showed no effect of the cationic surfactant DTAB added into the aqueous solution (in the DNPDSE method) on Eh of the solutions and consequently, on the associated diagrams.



a **b**

Figure 1) Eh-pH diagrams of synthetic aqueous solutions: a) dilute solution and b) dense solution.

Table 3) Eh(mv) values for various pHs of dilute and dense synthetic solutions.

pH	1.2	1.5	1.8	2.1	2.4	2.7	3	3.3
Dilute solution	569	545	520	516	506	499	490	483
Dense solution	510	506	503	497	495	492	490	488

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3.2- Reasons for the decrease of the SX method’s efficiency in dilute solutions

As previously mentioned, the maximum efficiency of the SX method belongs to dense solutions (Habashi, 1999). The less efficiency of this method for dilute solutions is for keeping the ratio of A/O equal to 1, which is necessary to achieve satisfactory phase disengagement and decrease the time required to reach desired recovery. However, this offers no concentration enrichment (Tarkan and Finch, 2005a). To elucidate this, the following investigations were performed.

3.2.1- Evaluation of the effect of A/O ratio on phase disengagement

In general, in the SX method:

1-The lower volume phase is usually converted into droplets when mixed with the higher volume phase.

2-If there is more phase volume difference, droplets of the lower volume phase are usually smaller (Ritcey and Ashbrook, 1984; Merigold, 1996).

Hence, it is expected that, through a decrease in organic phase volume, there would be more contact areas by smaller droplets, leading to the absorption of more charges on the solvent. Subsequently, it becomes heavier and, through decreased buoyancy force, ascending of the organic phase droplets for accumulation on the surface becomes more difficult. Conversely, increasing of the organic phase volume, in A/O ratio equal to 1, the amount of extracted ions for the unit of organic phase volume will decease; hence, the droplets of charged organic phase becomes lighter and disengagement becomes easier. In addition, in high A/O ratios, increased ratio of Lix/kerosene aggravates disengagement problems due to increase in the solvent density. For dense solutions, phase disengagement problems do not exist due to economically justified results in the A/O ratio of 1.

Although these points have been approved in the researches carried out by Tarkan and Finch (2005), yet our various tests for approving this effect gave no visible results.

Considering the fact that, for each ton of copper produced by processing a considerable volume of solution, 2 to 4 liters of organic phase are lost (Davenport et al., 2002) and part of this loss is due to such factors as evaporation that do not cause phase disengagement problems, hence, with comparison of the lost volume of organic phase to the primary volume of aqueous phase, it is expected that, in laboratory scale, the problems of phase disengagement are not visible by the naked eye.

Table 4) Evaluation of the effect of A/O ratios on extraction time (pH = 2.1).

Solution type	A/O	Parameters	Times (min)			
			15	10	5	2
Dilute	1	Metal ions concentration in phase aqueous (ppm)	0.15	0.17	0.20	2.40
		Metal ions concentration in phase organic (ppm)	127.85	127.83	127.80	125.60
		Distribution coefficient	852.33	751.94	639.00	52.33
		Recovery (%)	99.88	99.87	99.84	98.13
	20	Metal ions concentration in phase aqueous (ppm)	2.75	3.01	3.60	6.30
		Metal ions concentration in phase organic (ppm)	2505.00	2553.98	2488.00	2434.00
		Distribution coefficient	910.91	848.50	691.11	386.35
		Recovery (%)	97.85	97.65	97.19	95.08
Dense	1	Metal ions concentration in phase aqueous (ppm)	28.32	37.14	51.80	118.38
		Metal ions concentration in phase organic (ppm)	1971.68	1962.86	1948.20	1881.62
		Distribution coefficient	69.62	52.85	37.61	15.86
		Recovery (%)	98.58	98.14	97.41	94.08
	20	Metal ions concentration in phase aqueous (ppm)	1793.64	1797.32	1803.68	1813.92
		Metal ions concentration in phase organic (ppm)	4127.20	4053.60	3926.40	3721.60
		Distribution coefficient	2.30	2.26	2.18	2.05
		Recovery (%)	10.32	10.13	9.82	9.30

3.2.2- Evaluation of the effect of A/O ratio on extraction time

In the SX method, the best conditions for extraction process are reached when the highest recovery is attained with the least mixture time. Accordingly, by conducting the SX experiments, the required times to reach desired recovery in various A/O ratios were evaluated. The results of experiments performed for both the dilute and dense solutions are shown in Table 4.

To assess the results obtained, it was assumed that the extraction operation would be successful whenever the recovery is 98%. Having this in mind, the following results were obtained:

-For dilute solution, the time required to reach recovery desired in the A/O ratio of 1 is less than two minutes, and in the A/O ratio of 20, it is more than 15 minutes. Therefore, in spite of the sufficiency of the amount of organic phase for extraction of metal ions, considering the metal ions concentrations in the organic phase that are much lower than the total loading capacity of the extractant, and also due to more contact area of droplets in higher A/O ratios, the better recovery of metal ions in the A/O ratio of 1 was due to more contact area of the whole organic phase volume and increased collision of the existing metal ions with the extraction agent.

Generally, the following results can be considered for dilute solutions:

**In A/O ratios higher than 1, the extraction time becomes longer. As a result, for the extraction of few metal ions, high power is required.

**In A/O ratio of 1, the extraction time becomes shorter. However, regarding the amount of ions extracted, the amount of organic phase consumed is high.

-For dense solutions, the time required to reach desired recovery in the A/O ratio of 1 is less than 10 minutes while it is not achievable in the A/O ratio of 20. Hence, in real conditions, it is expected that the determining factor for reaching the recovery desired is sufficient capacity of the organic phase for loading the metal ions due to much higher concentrations of these ions in the aqueous phase.

Generally, the following result can be considered for dense solutions:

**Due to very high amounts of metal ions in pregnant solution and the need for sufficient amounts of organic phase to supply the loading capacity of these ions, reaching the recovery desired is possible through using the A/O ratio of 1.

3.3- Comparative survey of recoveries in the SX and DNPDSE methods

In the DNPDSE method, by injecting the organic phase into the column, the water resulting from dilution of polyaphron entered the column as well. Hence, the reduction of the aqueous phase concentration was not only due to the extraction process but also due to the water resulting from the dilution. So, although it was possible to calculate metal ions concentration in the organic phase, it was impossible to draw the extraction isotherm and determine the distribution coefficient due to lack of actual metal ions concentration remaining in the aqueous phase left from the extraction process. It is, however, possible to determine actual recovery for the DNPDSE method due to possibility of calculating the initial concentration of pregnant solution after dilution (according to Appendix). The results of the SX and DNPDSE experiments (at pH=2.1 and different A/O ratios) are presented in Tables A.1 and A.2 of Appendix, respectively, and the resultant comparative diagrams are shown in Figure 2.

The results of comparison of recovery diagrams in the two methods can be expressed as follows:

-The recovery rate in the DNPDSE method, compared with the SX method, was increased, especially for the dilute solution. For instance, the amount of recovery increase for the dilute solution in the A/O ratio of 45 was 22.5% (on average), and for the dense solution in the A/O ratio of 33, it was 2.5% (on average).

- As the dilution amount of aqueous solution is increased by decrease of the A/O ratio, the recovery diagrams in the DNPDSE method have been obtained of more dilute solutions as compared to the SX method, indicating better performance of the DNPDSE method.

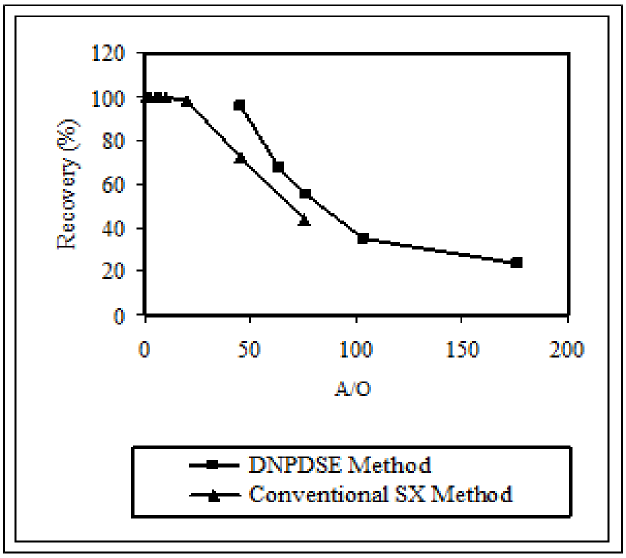

Figure 2) Recovery diagrams of the SX and DNPDSE methods in various A/O ratios.

3.4- Evaluation of the effect of cationic and anionic surfactants on the result of the DNPDSE method

Due to applying anionic (NaDBS) and cationic (DTAB) surfactants in the DNPDSE method and the presence of charged copper ions in the synthetic aqueous solutions, there was a possibility of copper ions flotation during the experiments. Hence, to study the effect of the IF method on the results obtained from the DNPDSE method, the IF experiments were performed in both states of mechanical cell and DNPDSE contactor.

In the IF method, metal ions concentration and the amount of water in the foam phase are of great importance. In fact, the performance of this method will be successful if there is high ratio of metal ions to water in the foam phase. In this method, the weight of water eliminated from the flotation cell (DNPDSE contactor) is similar to the weight of eliminated foam; thus, the measurement of foam's weight directly obtains the water recovery (Lazaridis et al., 2004).

The following results were obtained through comparison of metal ions concentrations in the remnant aqueous and foam phases based on the remnant and recovered aqueous phase percentages presented in Table 5.

- In contrary to what was expected, in both states of the IF method, the metal ions concentration in the foam phase for cationic surfactant DTAB was negligibly increased. Whereas this surfactant is not able to recover copper ions in the IF method due to its similar charge with Cu^{2+}, this increase can be attributed to analytical and experimental errors. Besides, supposing the implementation of the IF method, high volume of recovered water as foam (nearly half of water) prevented the significant increase of metal ions concentration in the foam phase.

-In both states of the IF method, the metal ions concentration in the foam phase for anionic surfactant NaDBS was negligibly decreased. In contrary to what was expected, this surfactant is not able to recover copper ions in the IF method despite of its opposite charge with Cu^{2+}. This result was likely due to lack of NaDBS in the form of negative charged ions in the studied pHs or the absence of bond between the copper and NaDBS charged ions in order to form required complexes to transfer onto the surface. Decrease of the metal ions concentration can be attributed to analytical and experimental errors.

- Due to no participation of the water present in the bottom part of the DNPDSE contactor (the bench of sparger) in the IF experiments, as well as decreased foam discharge with time because of the high height of the contactor, the amount of water recovered in the DNPDSE contactor was less than that in the mechanical cell.

- Comparison of the amounts of water recovered in both states indicated better foaming property of the NaDBS surfactant compared to the DTAB surfactant.

Table 5. Evaluation of copper ions flotation with NaDBS and DTAB surfactants

Parameters	pH	Surfactants	Remnant aqueous	Remnant aqueous	Recovered water	Recovered water	Metal ions concentration	Metal ions concentration

Method			phase (g)	phase (%)	(g)	(%)	in remnant aqueous phase (ppm)	in foam phase (ppm)
IF with DNPDSE contactor	1.2	NaDBS	820.00	54.70	680.00	45.30	1040	1004.71
		DTAB	880.00	58.70	620.00	41.30	1015	1036.77
	2.1	NaDBS	795.00	53.00	705.00	47.00	1033	1014.00
		DTAB	900.00	60.00	600.00	40.00	1021	1028.50
IF with mechanical cell	1.2	NaDBS	565.00	37.70	935.00	62.30	1036	1016.75
		DTAB	745.00	49.70	755.00	50.30	1020	1027.95
	2.1	NaDBS	585.00	39.00	915.00	61.00	1044	1011.00
		DTAB	735.00	49.00	765.00	51.00	1018	1030.00

Besides the mentioned results, it is important to point out that in the DNPDSE method, in addition to the presence of one of the above surfactants in the aqueous solution, the other surfactant with opposite charge was also transferred into the contactor by injecting CGAs and, thereupon, simultaneous presence of the two surfactants with opposite charges obviates the possibility of copper ions flotation, completely.

3.5- Evaluating the combination capability of the DNPDSE method with the PF method

After performing the PF experiments, the pictures obtained from the raffinates of the DNPDSE and PF methods were compared. Since the PF experiments' pictures for both coagulants were the same, here only the pictures of raffinates before and after conducting the PF experiment using aluminum sulfate are shown (Figure 3). The pictures indicate proper performance of the PF method in elimination of organic phase as well as raffinate clarification of the DNPDSE method.

Due to negligible presence of remnant organic phase with negative charge (Al-Shamrani et al., 2002) and considerable amount of coagulant with positive charge (pH=5) (Sincero and Sincero, 2003), positive charged complexes [a combination of aluminum soap (or iron) and aluminum hydroxide (or iron)] are formed by coagulation phenomenon.

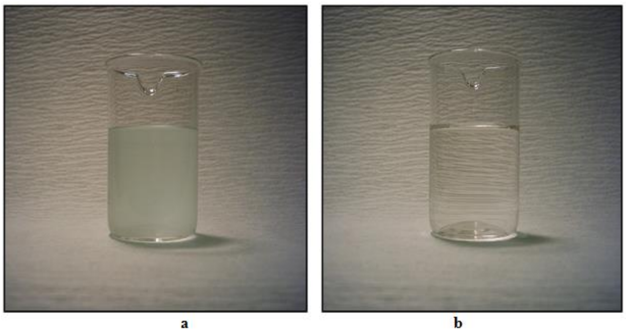
a
b

Figure 3) Comparison of DNPDSE method raffinates: a) before precipitate flotation and b) after precipitate flotation.

The PF method is carried out because of the capability of the bubbles produced by the anionic surfactant of NaDBS to quickly float these complexes (containing all suspended materials in the solution having positive charges) (Sebba, 1987). In this way, there is the possibility of remnant organic phase elimination in the raffinate and its clarification in an efficient manner, which is important both economically and environmentally.

3.6- Evaluating the combination capability of the DNPDSE method with the IF method

As the concentration of copper ions present in the remnant aqueous solution in the DNPDSE contactor after implementation of the IF method was important, a sample from this solution was analyzed. Lack of copper ions detection by Atomic Absorption Spectrometry (AAS) showed complete removal of these ions from the raffinate.

This result was due to the formation of unstable complexes through combination of copper ions with the xanthate anions dissociating to dixanthogen (EtX)2 and cuprous xanthate (CuEtX). These complexes precipitated into the solution as agglomerate and their size was optimized for separation by the IF method. In this way, combination of the IF and DNPDSE methods enables complete copper ions elimination from the raffinate to meet the environmental standards specified for its discharge (in Europe, permitted copper ions amount for discharge is 0.5 mg/l (Lazaridis et al., 2004)). It is important to note that using the IF method may not be economical for this copper concentration due to high stoichiometric consumption of the collector (Doyle, 2003). However, owing to impossibility of performing the DNPDSE method in low A/O ratios due to limit of the column height, and also regarding the aim of the experiment to show advantages of the DNPDSE method when combined with the IF method, this concentration of raffinate was used.

3.7- Presentation of flowsheet

The flowsheet of Figure 4 shows the combination mode of the DNPDSE method with the PF and IF methods.

4- Conclusions

-Evaluating the reasons for the decrease of the efficiency of SX method in dilute solutions showed that:

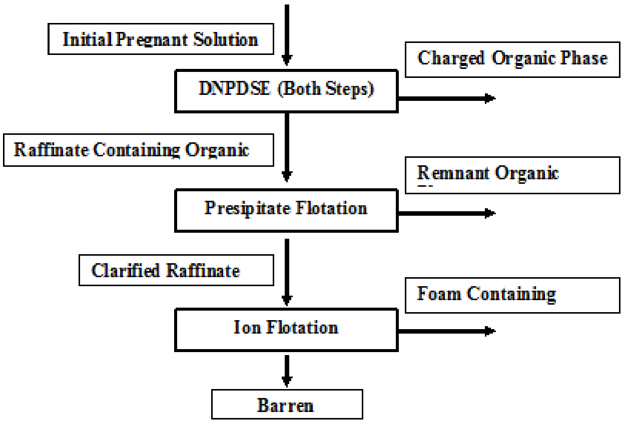

Figure 4) Flow sheet of the DNPDSE-PF-IF methods.

**If A/O ratio is less than 1, the extraction process offers no concentration enrichment because of the transfer of valuable ions from lower volume (aqueous phase) to higher volume (organic phase). In this case, with the increase of the extraction agent, the extraction time may be decreased as well; however, phase disengagement problems still persist.

**If A/O ratio is more than 1, with the decrease of organic phase amount, the concentration of ions existing in the pregnant aqueous solution will increase. On the other hand, phase disengagement is not satisfactory and extraction time gets longer. Nevertheless, it may offer considerable concentration enrichment.

**If A/O ratio is equal to 1, phase disengagement and extraction time are suitable but concentration enrichment is limited.

-Considerable increase in recovery (for instance, 22.5% in the A/O ratio of 45 for dilute solution and 2.5% in the A/O ratio of 33 for dense solution) in the DNPDSE method, as compared to the SX method, indicated its desirable performance for dilute solutions.

- The results of the IF experiments (in both methods) in the initial and final pHs of copper ions extraction range (1.2 and 2.1, respectively) demonstrated negligible effect of this method on the extraction results of the DNPDSE method.

-The use of the PF method in combination with the DNPDSE method enables the removal of remnant organic phase from the raffinate and its proper clarification.

Applying the IF method in combination with the DNPDSE method provides complete copper ions removal from the raffinate to meet the environmental standards for discharge of this element.

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Appendix

Process of calculations in the DNPDSE method

To get acquainted with the process of calculations in the DNPDSE method, an example is given as follows:

Considering one liter of pregnant solution with the initial concentration of 1000 ppm, the concentration of the first and second samples equal to 600 and 585 ppm, respectively, and 35 cm change in the column height (immediately after injection operations), the extraction percent of both stages were calculated as follows:

1. Calculate the total height change; since the height change is dependent on the volume of air dissolved in polyaphron (due to the change of CLAs into CGAs), in addition to the volume of polyaphron injected, first, the height change due to air dissolved was calculated. Therefore, several injection experiments were carried out in different time durations (5-10-15-20 and 25 seconds) and height changes were measured in times 0, 10, 30, 60, 180 and 300 minutes. Average value of all the results at the same times was obtained as near 32% and 25% in height reduction in 3.5 and 2.5 bar pressures, respectively. So, regarding 3.5 bar pressure:

Change the initial height: 35cm

Change the total height (subtracting the height due to the dissolved air):

35 - (35 * 0.32) = 23.8cm

2. Calculate the height change due to CGAs and dilution assuming the use of polyaphron with fivefold dilution:

Height change due to CGAs (subtracting the air dissolved): 23.8 / 5 = 4.76cm

Height change due to dilution: 4.76 * 4 = 19.04cm

3- Calculate the volume of CGAs injected and water added due to dilution considering 11.16 cm^2 as a column's sectional area:

The volume of CGAs injected (subtracting the dissolved air): 4.76 * 11.16 = 53.12 cm^3

The volume of water added due to dilution:

19.04 * 11.16 = 212/49 cm^3

4- Calculate the volume of organic phase injected and the total volume of water added to the pregnant solution assuming PVR=10:

The volume of organic phase injected:

53/12 – (53/12 * 0.1) = 47.81 cm^3

The total volume of water added to the pregnant solution:

212/49 + (53/12 * 0.1) = 217.80 cm^3

5- Calculate the initial concentration of pregnant solution after dilution: As injection of organic phase was caused entry of water resulting from dilution into the column, the initial concentration of the pregnant solution after injection operation was calculated:

1000cm^3 * 1000 ppm = (1000 + 217.80) cm^3* X

X = 821.15 ppm

6- Calculate the theoretical a/o ratio (a/o$_t$):

a/o$_t$= 1000 / 53.12 = 18.83

7- Calculate the real a/o ratio (a/o$_r$):

a/o$_r$ = 1217.49 / 52.73 = 23.09

8- Calculate the metal concentration in the organic phase after the first stage:

821.15 – 600 = 221.15 ppm

221.15 * 23.09 = 5106.3 ppm

9- Calculae the metal concentration in the organic phase after the second stage:

821.15 – 585 = 236.15 ppm

236.15 * 23.09 = 5452.7 ppm

10- Calculate the theoretical extraction percent of the first stage:

[(1000 - 600) / 1000] * 100 = 40%

11- Calculate the theoretical extraction percent of both stages:

[(1000 - 585) / 1000] * 100 = 41.5%

12- Calculate the increase of theoretical extraction percent in the second stage:

41.5 – 40 = 1.5%

13- Calculate the real extraction percent of the first stage:

[(821.15 - 600) / 821.15] * 100 = 26/93%

14- Calculate the real extraction percent of both stages:

[(821.15 - 585) / 821.15] * 100 = 28.76%

15- Calculate the increase of real extraction percent in the second stage:

28.76 – 26.93 = 1.83%

Table A.1) Results of the SX experiments in pH=2.1 and various A/O ratios.

A/O ratio	Metal ions concentration in aqueous phase (X) (ppm)	Metal ions concentration in organic phase (ppm)	Distribution coefficient	Recovery (%) = $((X_{primary} – X_{secondary}) / X_{primary})*100$
1	0.16	127.84	799.00	99.88
3	0.28	383.16	1368.43	99.78
5	0.32	683.40	1995.00	99.75
7	0.46	892.78	1940.83	99.64
10	0.75	1272.50	1696.67	99.41
20	2.77	2504.60	904.19	97.84
45	35.73	4152.15	116.21	72.09
75	72.17	4187.25	58.02	43.62

Table A.2) Conditions and results of the DNPDSE experiments in pH=2.1 and various A/O ratios

Changing initial height (cm)	Initial concentration of pregnant solution after dilution (ppm)	A/O $_{real}$	Metal ions concentration in aqueous phase after the first step (ppm)	Metal ions concentration in aqueous phase after the second step (ppm)	Total real recovery (%)
6.4	124.69	176.18	1932.32	1932.10	23.31
11.1	122.36	103.50	1824.99	1824.57	34.61
15.3	120.36	76.36	1742.72	1742.03	55.21
18.7	118.79	63.36	1649.23	1648.40	67.01
27.1	115.05	45.03	1578.57	1577.51	96.01