As, Sb, and Fe removal from industrial copper electrolyte by solvent displacement crystallization technique

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Abstract

Presence of impurities in copper electrolyte increases the energy consumption of electro refining process and contaminates the deposited copper on cathode. The concentration of impurities increases over time making it necessary to remove them from the solution. This research introduces a fast, effective, and simple method to refine the industrial electrolyte from arsenic, iron and antimony by solvent displacement crystallization (SDC) technique. In this method when alcohol is added to the electrolyte, the impurities precipitate from the solution as amorphous arsenato antimonite phase. Results show that Fe, Sb, and As are removed from the copper electrolyte by 75.2%, 96.9 % and 99.8% respectively. Electro winning experiments show that the electric energy consumption for electrodeposition of copper is 15.5 % lower when the electrolyte is free of impurities.

Keywords: Copper electrorefining, impurity removal, Solution purification, Isopropyl alcohol, Current efficiency, Energy consumption

1. Introduction

During the electrorefining process of impure copper anodes, impurities that are less noble than copper oxidize and release into the solution. Arsenic (As), Antimony (Sb) and Iron (Fe) are among the most interfering impurities that can decrease the efficiency of electro refining plant by depositing on the cathode surface or passivating of the anode. Thus, the electrolytes must be purified; conventional practice for controlling the impurities concentration consists of withdrawing a certain volume of the solution from the circuit and recovering its copper content by multistage electrolytic deposition in a series of electrowinning cells [1]. The conventional treatment inherently has numerous disadvantages [2, 3, 4, 5, 6, 7, 8, 9, 10] including: (a) the evolution of toxic arsine gas (AsH_3), (b) low quality of the deposited copper due deposition of the contaminants, and (c) the waste of current due to the parasitic reduction-oxidation cycle of iron (where Fe^{3+} reduces to Fe^{2+} at the cathode and Fe^{2+} re-oxidizes at the anode).

Various methods have been proposed to remove impurities from copper electrolyte. Some of these methods such as solvent extraction [3, 11, 12, 13, 14, 15, 16, 17, 18, 19] require the electrolyte dilution from over 200 g/l H_2SO_4 to higher pH values which consequently leads to severe acid loss [20]. Application of adsorbent containing antimony [21] result in low arsenic removal percentages (<20%) even at elevated temperatures for several hours. Activated carbon [2] has also limited desorption efficiency of As and Sb (less than 50%). In addition, ion exchange resins and electrodialysis methods are also investigated in [22, 23, 24, 25, 26].

Solvent Displacement Crystallization (SDC), also known as Anti Solvent crystallization, has attracted attention as an efficient method for precipitation of salts from aqueous solutions [27, 28, 29, 30, 31, 32, 33, 34, 35, 36]. In this method the supersaturation state is achieved by the addition of a water miscible organic solvent (WMOS) to an aqueous solution leading to the salt precipitation of metallic ions [37]. This removes the water ligands from the ions by lowering the thermodynamic activity of water. In fact, when a water miscible organic solvent like isopropyl alcohol is added to an aqueous solution, a competition between the polar

organic molecules and inorganic ions for the water molecules occurs; because of organic solvent higher affinity for water molecules and due to the preferential formation of hydrogen bonds they win the competition and decrease free water for ion hydration, thus leading to solute precipitation [38]. The obtained salts are filtered and subsequently the WMOS can be separated from aqueous solution by low temperature distillation or other techniques. However, most of the organic solvents cannot be recovered and separated from aqueous phase since they form an azeotropic mixture. By separating organic solvents there is no need to the neutralization of the spent acid and it can be reused in the electro refining process. Moldoveanu and Demopoulos [39] used isopropyl alcohol addition for the removal of Ni^{2+} in form of $NiSO_4.6H_2O$ from industrial de-copperized electrolyte. $CuSO_4.5H_2O$ was also produced from sulfate-based solution of Cu^{2+} by ethanol addition [40]. In another study, Moldoveanu and Demopoulos [31] demonstrated that isopropyl alcohol and acetone had good crystallization performance and selected isopropyl alcohol as a solvent of choice. They showed that metal cations can efficiently be removed from H_2SO_4 medium in precipitation sequence of $K^+ > Na^+$ and $Cu^{2+} > Fe^{2+} > Co^{2+} > Ni^{2+} > Zn^{2+} > Mg^{2+}$, however Fe^{3+} did not precipitate well in their SDC experiments. Sato et al [41] used this characteristic for the separation of Nd from Fe^{3+} by adding ethanol to the sulfuric acid solution obtained from Nd-Fe magnet scraps leaching.

Up to now the behavior of As and Sb in SDC process is not studied. However, It is well known that ions with higher charge density and higher hydration enthalpy like As^{5+} can form stronger bond with water molecules [42] and consequently, they will remain in the solution while other ions with lower charge density and hydration enthalpy like Cu^{2+} will precipitate. Thus, SDC can be used to separate these ions from the copper solution. In this research SDC process is employed to purify the copper electrolyte from impurities by adding isopropyl alcohol. In addition, to evaluate the process proficiency, current efficiency and energy consumption of copper electrodeposition from purified and non-purified electrolytes are compared.

3

2. Experimental procedure

2.1. Reagents

In this research, Industrial copper electrolyte with chemical composition mentioned in Table 1 was received from sarcheshmeh copper complex, in Kerman, Iran. Isopropyl alcohol of analytical grade was used as organic solvent for precipitation of ions from copper electrolytes. The 18.2 MΩ deionized water was used for dissolution experiments.

2.2. Anti-solvent crystallization procedure

To study the effect of the organic solvent addition on different ions concentration 40 mL copper electrolyte was poured to a single-neck round-bottom flask with 250 mL capacity and then the organic solvent was added slowly using a manual burette while the liquid mixture was agitated by a magnetic stirrer at a constant speed and ambient temperature. After reaching to a certain organic-aqueous (O/A) volume ratio, the organic solvent addition was stopped and an equilibrium period was allowed. Then, the precipitated powder was separated from the liquid phase by filtration and dissolved in 40 mL of distilled water. Subsequently the resulted solution was first centrifuged at 2000 rpm for a few minutes and then sampled for determination of their ions concentration. All solutions were characterized by inductively coupled plasma emission spectroscopy (ICP-OES, Spectro Arcos), and regarding aqueous-organic mixture, it was first diluted with 5% HCl, and then was characterized by ICP. X-ray diffraction (XRD, Philips X'Pert PW1800 equipped with Cu-kα radiation, λ = 0.15406 nm), X-ray fluorescence (JEOL, JSX-3210), and Fourier transmission infrared spectroscopy (FTIR, Thermo Nicolet Avatar 370) methods were employed to characterize the solid phases. Fig. 1 represents the summary of the experimental procedure of this research.

4

2.3. Copper electrowinning procedure

In order to compare the current efficiency and energy consumption of the purified solution with industrial copper electrolyte, the electrowinning experiments were conducted in experimental cell with the capacity of 250 mL. A platinum wire and two stainless steel cathode with measured dimension of 2 cm × 1.9 cm × 0.1 cm were used as anode and cathodes, respectively. The cathodes were polished with ultrafine abrasive paper, washed with warm 18.2 MΩ deionized water, dried and weighted before the electrowinning experiments. The anode and cathodes were separated by a distance of 3 cm and a saturated calomel electrode (SCE) was used as the reference electrode. The current density was set at 300 A/m^2 using a ZIVE Sp1 potentio/galvanostat equipment and the electrolytes were agitated by a magnetic stirrer at a constant speed at ambient temperature. At the end of each test the cathodes were removed and washed with warm 18.2 MΩ deionized water then immediately dried before weighing it.

3. Results

The schematic of the process used for the purification of copper electrolyte in this research is represented in Fig. 2. As can be seen in Fig. 2, this process comprises of three main sections; SDC process, water dissolving of precipitated salts, and electrowinning. The results of each section is presented in sections 3.1 and 3.2 and is discussed as in section 4.

3.1. SDC process

According to previous researches [31, 38], in the mixture of isopropyl alcohol and H$_2$SO$_4$ solution with the O/A ratio of 4, Cu^{2+} has very slight solubility (around 0.2 g/L), while Ni^{2+} equilibrium solubility is higher (approximately 1 g/L). The concentration of Ni^{2+} in the copper electrolyte used in this work is about 1 g/L, thus in order to be sure of almost complete precipitation of both Cu^{2+} and Ni^{2+}, O/A ratio of 5 was selected. While

5

isopropyl alcohol was being added to copper electrolyte, blue precipitates were formed gradually and the solution color changed from blue to a very light green. The concentration of ions in initial industrial electrolyte and after of the alcohol addition are presented in Table 1.

As can be seen from Table 1, the addition of isopropyl alcohol to copper electrolyte leads to a great decrease in all ions concentration which is a result of two phenomena. One is the formation of precipitates by anti-solvent crystallization due to the behavior of isopropyl alcohol as a water-removing agent [31, 39, 40] and the other one is the dilution of copper electrolyte by the addition of alcohol (the electrolyte is 5 times diluted here). It is clearly obvious that if alcohol is completely separated from aqueous solution before the determination of ions concentration, the latter phenomena will not have any effect on ICP results. However, in this work similar to previous researches [31, 39, 40], isopropyl alcohol was not removed before ICP characterization and consequently the dilution effect on ions concentration has to be considered. Thus the true effect of SDC process can be shown by calculating the ion precipitating percentage as follows:

$$\text{Precipitation (\%)} = \frac{(W_0 - W_f)}{W_0} \times 100 \qquad (1)$$

where W is the initial weight of an ion in the initial Copper electrolyte and W_f is the final weight of an ion in organic solvent-copper electrolyte mixture. The precipitation percentage of the ions calculated by equations 1 is also tabulated in Table 1. Regarding this table, the addition of isopropyl alcohol to copper electrolyte led to almost complete precipitation of Cu, Ni, Ca and Sb while Fe and As mainly remained in the solution. Additionally, the XRD pattern of the precipitate is shown in Fig. 3 which shows that the precipitate is mainly consisted of $(CuSO_4).5H_2O$ confirming that Cu is the major precipitating element.

3.2. Obtaining purified copper rich solution

As mentioned before, the precipitate formed by isopropyl alcohol addition was dominantly $CuSO_4.5H2O$ while deleterious impurities such as As and Fe mainly remained in

6

isopropyl alcohol-aqueous mixture. Therefore, the obtained precipitate is a concentrated feed for the production of copper. As $CuSO_4.5H_2O$ is highly soluble in water, Cu^{2+} rich solution can be acquired by dissolving the obtained precipitate in water. The whole amount of precipitates that had been formed by the addition of 200 mL isopropyl alcohol to 40 mL of copper electrolyte (O/A=5) were dissolved in 40 mL of water at room temperature. The majority of precipitate dissolved easily in few minutes however, a very little amount of it remained undissolved which was subsequently separated by centrifugation and remained as a white powder residue.

Table 2 presents the ions concentration in resulted solution and confirms the purification of copper solution from deleterious impurities. As can be seen, Fe, As and Sb are removed by 75.2%, 99.8% and 96.9%, respectively, at the same time, 98.8% of Cu and 71.6% of nickel were maintained in the solution.

The XRD pattern of the white residue is shown in Fig. 4. This XRD pattern has an amorphous nature with a hill around $2\theta = 30°$ which is similar to arsenato antimonates observed in previous researches [44, 45]. Additionally, the FTIR spectra of white residue is also shown in Fig. 5 and resembles the spectrum of arsenato antimonates investigated in other studies [44, 46, 47]. The main bands can be, respectively, attributed to v_s and v_{as} of O-H (3370.0 and 1629.1 cm^{-1})[48], δ of O-H (1364.4 cm^{-1})[49], δ of As–OH and Sb–OH (1118.8 cm^{-1})[49, 50], v_{as} of As–OX(X = As, Sb) (839.0 cm^{-1})[51], v_{as} of Sb–OH (632.9 cm^{-1}), v_{as} of Sb–OY(Y = As, Sb) (526.7 cm^{-1})[50, 52] and 452.9 cm^{-1} is the twisting vibration absorption spectrum of O-As-O[46].

4. Discussion

The results show that after addition of alcohol to the copper electrolyte, As and Fe mainly remained in the isopropyl alcohol-aqueous mixture because they have strong bond with water molecules. However, it is clear from Table 1, Sb was precipitated completely after adding isopropyl alcohol to the electrolyte. On the other hand, Table 2 indicates that the purified solution is free of Sb and hence Sb is in the undissolved white residue. The XRF characterization of the white residue is represented in Table 3. This table shows that the white residue is rich in antimony and arsenic. Hence, it is clarified that complete removal of

7

antimony is due to the co-precipitation of Sb with a small portion of arsenic which was previously reported in the literature [4, 9, 44, 46, 47, 53, 54]. It was found that the co-precipitation of As and Sb in copper electrolyte is dominant in form of arsenato antimonates, which are white amorphous precipitates with no fixed composition but rich in antimony and arsenic [44, 46, 47].

The Complete precipitation of Cu^{2+}, Ni^{2+}, Ca^{2+} and little removal of Fe^{3+} by organic solvent addition was reported in previous researches [31, 39, 40, 41, 43], while there is no information about the behavior of As and Sb. However, the differences in crystallization behavior among the various ions were generally attributed to the strength of interactions between ions and water dipoles which depends on the hydration enthalpy (ΔH_{hyd}) of ions [31, 55]. ΔH_{hyd} is always negative and consists of enthalpy changes for separating the water molecules (breaking the H bonds) and mixing the separated solute with them (forming the ion-dipole force) [55]. ΔH_{hyd} exhibits trends based on the ion's charge density [55]. According to Coulomb's law, the higher the ion's charge density and the smaller its radius, the closer it gets to the oppositely charged pole of an H_2O molecule and the stronger it bonds with water [42, 55, 56, 57, 58]. Thus, an ion with higher charge density possesses more negative ΔH_{hyd}. Consequently, it would be much more difficult for organic solvent to remove water ligands from the high charge density ions and causing the precipitation of their salts. The radius, charge density and hydration enthalpy of various ions are presented in Table 4. With regard to this table, trivalent, tetravalent and pentavalent ions have higher charge density and more negative hydration enthalpy than monovalent and divalent ions and thus have stronger bonds with water molecules. In copper electrolyte Fe and As mainly present as valency of 3 and 5 respectively, while Sb may be present as trivalent or pentavalent species [3, 9, 11, 53, 59, 60, 61]. Hence, Table 4 reinforces the experimental results and confirms the preferential precipitation of divalent ions such as Cu^{2+} and Ni^{2+}.

As demonstrated before, the obtained purified solution from dissolution step contained high copper and very low amount of deleterious impurities thus, can be recycled back to the electrorefining stage or can be subjected to electrowinning process for copper production. In this section, electrowinning experiments were conducted to confirm the superior

8

performance of purified solution relative to impure industrial copper electrolyte. The results for all of the electrowinning experiments performed are summarized in Table 5.

As can be seen here, copper was electrodeposited with 1.2% and 15.5% lower electrical energy consumption after 3 and 6 hours of electrowinning process. The current efficiency (CE%) is calculated by measuring the weight of cathode before and after the plating test and using the following equation:

$$CE(\%) = \frac{\Delta m}{M_{Theoretical}} \times 100 \qquad (3)$$

Where Δm is the mass difference of cathode before and after experiment (g); $M_{theoretical}$ is the theoretical weight of copper that is supposed to deposit on the cathode and was calculated from the relation:

$$M_{Theoretical} = \frac{It A_{w(Cu)}}{n\,F} \qquad (4)$$

Where I = current (A), = Faraday constant, n = number of electron exchanged, $A_{w(Cu)}$ = copper atomic weight in g/mole, and t = time of electrowinning in seconds. The purified electrolyte contained very lower amount of impurities. Therefore, in the absence of any parasitic reactions, lower current was associated with side reactions and according to the equation (3) and (4) higher mass of copper deposited on the cathode leading to higher current efficiency. Consequently, Higher current efficiency resulted in lower electrical energy consumption (EC) conforming to the equation below:

$$EC = \frac{nFU}{36 CE(\%) A_{w(Cu)}} \qquad (5)$$

Where EC = energy consumption in kWh/Kg, U = the average cell voltage (V), CE(%) =current efficiency, and F denotes the Faraday constant.

The results of the electrowinning experiments show the electrical energy consumption for electrodeposition of copper was 15.5% lower and the current efficiency approached 100% when the electrolyte was refined. This shows the SDC process could be employed as an efficient technique for refining the copper electrolyte. As mentioned in the introduction,

9

isopropyl alcohol cannot be separated from the acid by distillation technique completely. Thus, further investigations are suggested to be done on the recovery of alcohol from acid, finding an appropriate WMOS without an azeotropic mixture by water, and the efficiency of the SDC process for eliminating various impurities in different O/A ratios.

5. Conclusions

In this research Fe, As, and Sb were removed from an industrial copper electrolyte by applying SDC directly on the copper electrolyte without any pretreatment. Results showed that addition of isopropyl alcohol to copper electrolyte leads to almost complete precipitation of copper as $CuSO_4.5H_2O$ while Arsenic and iron mainly remained in the solution due to their higher charge density and hydration enthalpy. However, Sb co-precipitated almost completely with a small portion of Arsenic as an amorphous arsenato antimonite. After dissolving the precipitates in water, the majority of precipitates dissolved easily in few minutes, however the arsenato antimonate was remained undissolved and in this way purified solution of Cu was achieved.

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12

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13

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Figures' captions

Fig. 1. Schematic flow diagram representing the experimental process in this research.

Fig. 2. Schematic flow diagram of the process used for purification of copper electrolyte in this research.

Fig. 3. XRD pattern of the precipitate formed in SDC process.

Fig. 4. XRD pattern of the white residue.
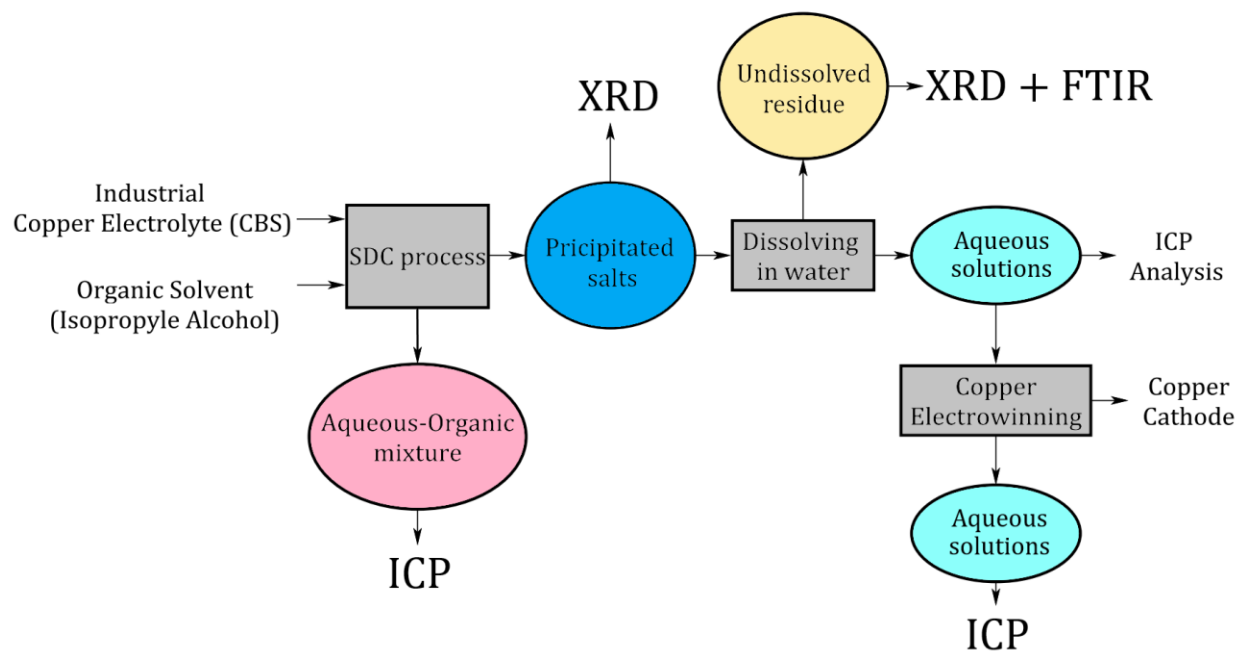
Fig. 5. FTIR spectrum of the white residue.

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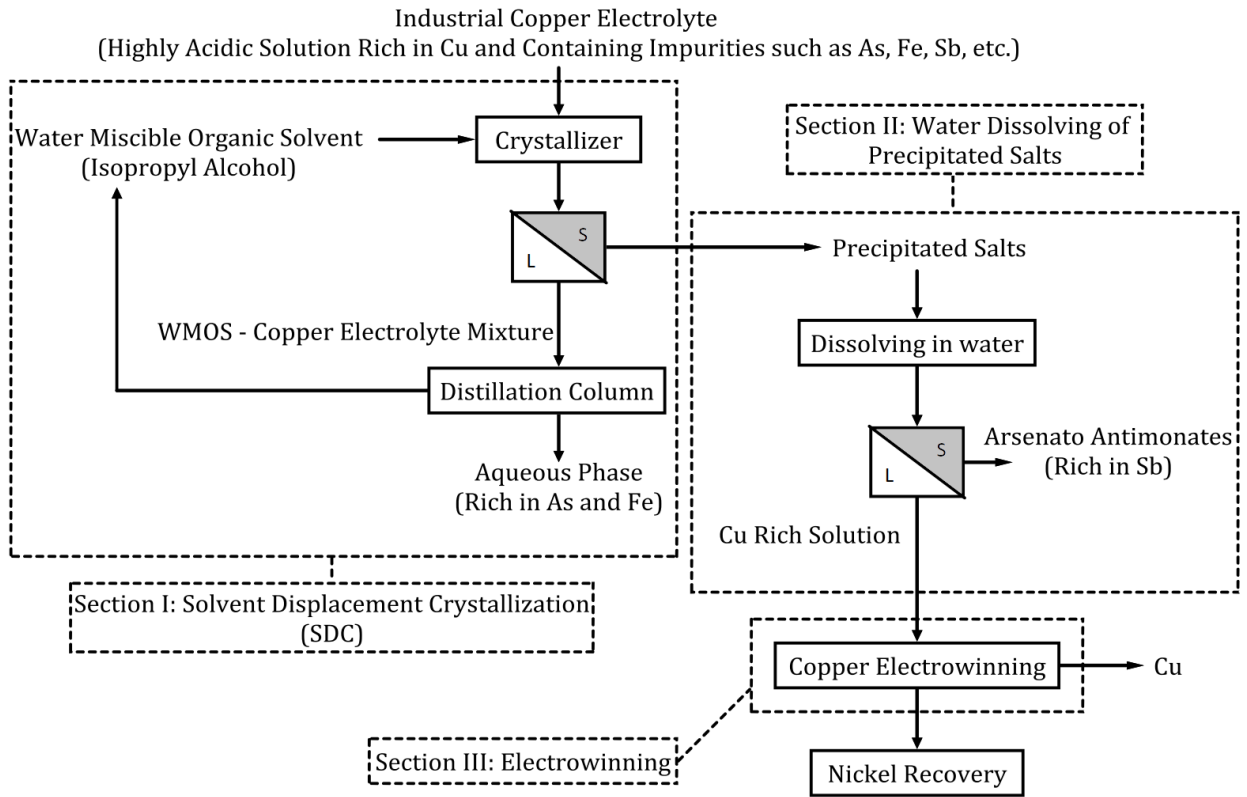
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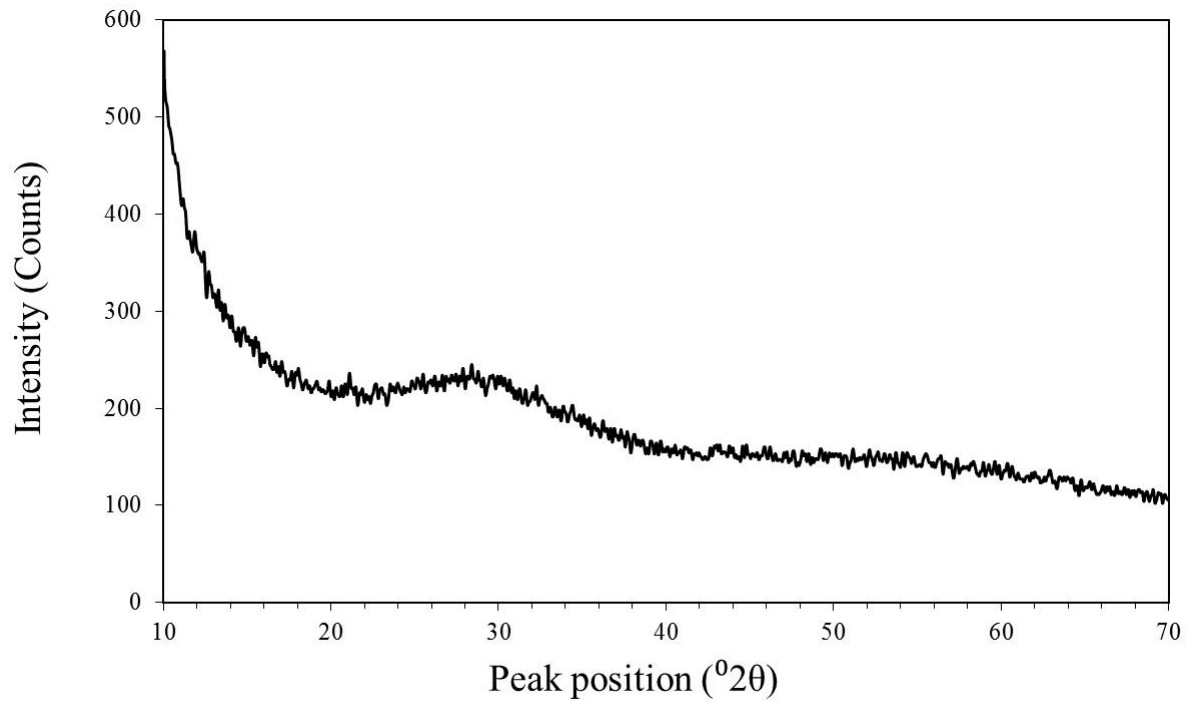
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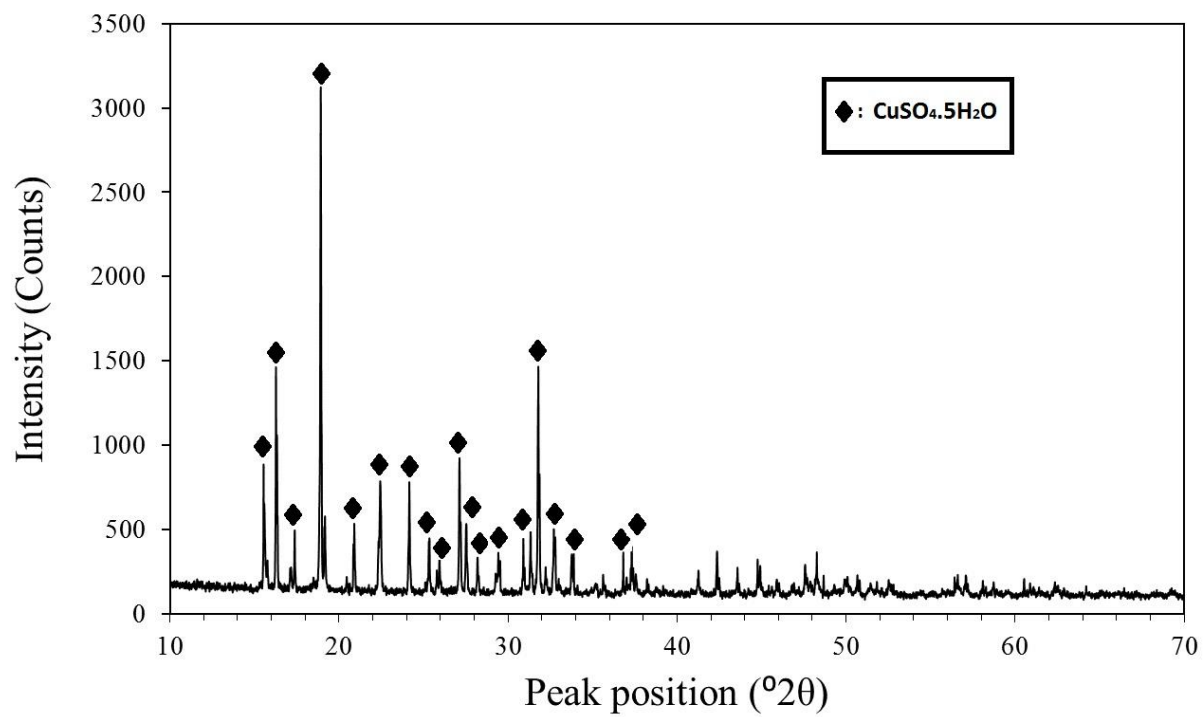Fig. 5. FTIR spectrum of the white residue.
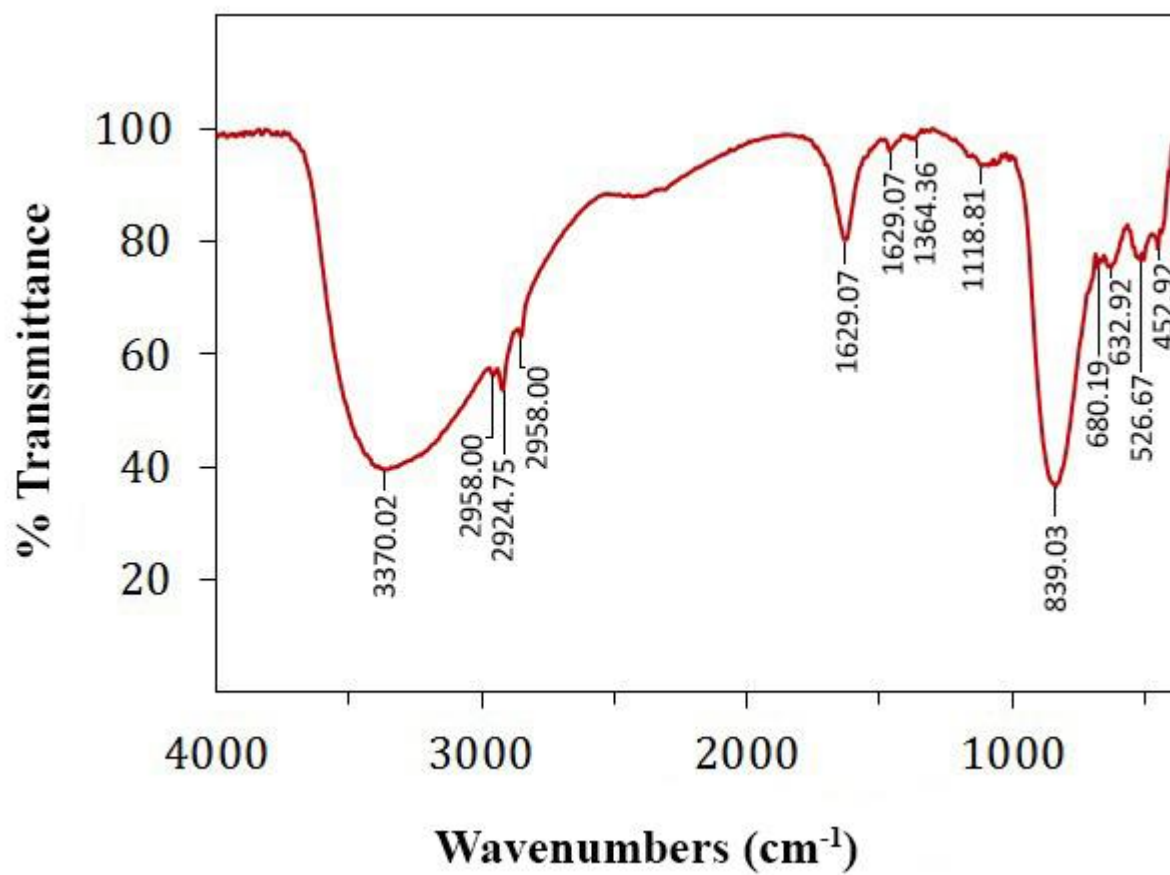
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19

Fig. 5. FTIR spectrum of the white residue.

Table 1

Ions concentration in industrial copper electrolyte and after the addition of isopropyl alcohol (alcohol/ electrolyte = 5, initial electrolyte volume = 40 mL).

	Ions	Cu	Ni	Fe	As	Sb	Bi	Ca
	Industrial Copper electrolyte (ppm)	8587	1130	1105	4789	227	N.D*	189
After addition of alcohol	Electrolyte and alcohol (ppm)**	38	52	137	782	N.D*	N.D*	6
	calculated per 40 mL of electrolyte (ppm)	228	312	822	4692	-	-	36
	Precipitation percent (wt.%)	99.5	72.4	25.6	2	100	-	81

*N.D= Not Detected

** These concentrations are related to the mixture of electrolyte and alcohol.

Table 2

The ions concentration in obtained purified copper solution after dissolving the precipitate in 40 mL of water.

	Cu	Ni	Fe	As	Sb	Bi	Ca
Concentration (ppm)	47991	809	274	11	7	N.D*	151

*N.D: Not Detected

Table 3

The chemical composition of the undissolved (white powder residue) part of obtained precipitate characterized by XRF.

Element	Cu	Ni	Fe	As	Sb	Ca
Wt. %	5.12	0.06	1.98	14.73	50.61	0.09

Table 4

Charge density and hydration enthalpy of various ions [44, 48-49]

Ion	Ionic Radius (pm)	Charge Density* (e/pm^3)		ΔH_{hyd}(kJ/mol)
Z=1				
Na+	1.02	0.224963		-410
K+	1.38	0.090839		-336
Rb+	1.52	0.06798		-315
Z=2				
Ca²⁺	1	0.477465		-1591
Fe²⁺	0.78	1.006138		-1946
Ni²⁺	0.69	1.45343		-2105
Cu²⁺	0.73	1.227362		-2100
Z=3				
Fe³⁺	0.65	2.60791		-4430
Cr³⁺	0.62	3.005091		-4560
As³⁺	0.58	3.670698		-
Sb³⁺	0.76	1.631518		-
Z=4				
Ce⁴⁺	0.87	1.450152		-6300
Zr⁴⁺	0.72	2.558432		-6953
Sn⁴⁺	0.69	2.90686		-7591
Z=5				
As5+	0.46	12.26332		-
Sb5+	0.6	5.526213		-

* Charge density of ions were calculated by dividing the charge of the ion by its volume [e / $(\frac{4}{3}\pi r^3)$] [50].

Table 5

Electro-winning experiments data for industrial and the purified copper electrolyte. All experiments were conducted at current density of 300 (A/m²) at 25°C while electrolytes were agitated by a magnetic stirrer at a constant speed.

Solution	Duration (h)	Average cell Voltage (V)	Current I (A)	Current efficiency ϕ (%)	Side reaction current, $I_s=(1 - \phi/100)\times I$ (A)	Energy consumption (KWh/Kg)
Industrial electrolyte	3	3.71	0.456	85.03	0.068	3.293
Purified electrolyte	3	3.66	0.456	99.98	0	3.252
Industrial electrolyte	6	3.91	0.456	79.11	0.095	4.124
Purified electrolyte	6	3.91	0.456	94.28	0.026	3.483