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ORIGINAL PAPER

Investigation of an alternative chemical agent to recover valuable metals from anode slime

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Abstract

Anode slime (AS) including high content of precious metals is a by-product obtained after the electro-refining stage in copper production. In this study, it is aimed to recover Cu, Au, and Ag from the AS by using 1-butyl-3-methyl-imidazolium hydrogen sulphate ([Bmim]HSO_4) ionic liquid (IL) as a green solvent. The effects of IL concentration, temperature, reaction time and pulp density on recovery of valuable metals were statistically investigated. A high copper recovery of 87.52% was obtained under optimum condition as in 60% (v/v) [Bmim]HSO_4 at 50 °C after 2 h, pulp density at 40 g/L (1/25 solid/liquid ratio). Also, a remarkable gold recovery as 97.32% has been achieved in 80% (v/v) [Bmim]HSO_4 at 95 °C after 4 h, pulp density at 40 g/L. Temperature and IL concentration were detected as the most effective parameters for copper and gold recovery from AS, respectively. Silver could not be recovered from the AS due to the lower solubility in [Bmim]HSO_4 IL media. According to experimental results, [Bmim]HSO_4 could be offered as an alternative leaching agent, instead of conventional solvents, to recover valuable metals from copper anode slime.

Keywords Anode slime · Recovery · Ionic liquids · 1-Butyl-3-methyl-imidazolium hydrogen sulphate [Bmim]HSO_4 · Leaching

Introduction

Today, most of the copper demand in the world is supplied by the pyrometallurgical treatment of the existing copper ores in the following order; beneficiation, smelting, converting, fire-refining and electro-refining. Also, in order to produce copper, considerable efforts are performed by the treatment of copper alloyed scrap with fire and electro-refining stages. In both cases, copper refinery AS includes valuable metals such as Au, Ag, Cu, Se, Te, etc. (Kılıç et al. 2013). In recent years, numerous reviews have been reported on the treatment processes of AS (Biswas et al. 1998; Hait et al. 2009;Syed 2012; Tokkan et al. 2013; Ranjbar et al. 2014; Lu et al. 2015), which are carried out by pyrometallurgical, hydrometallurgical or both of these chemical processes. Especially, some hydrometallurgical processes such as hot sulphuric acid leaching, alkali fusion-leaching, thiosulfate leaching, decopperization, and oxidative leaching stand out as the main processes to recover the various metals from AS (Yavuz and Ziyadanoğulları 2000; Li et al. 2015; Xu et al. 2016; Wang et al. 2017; Liu et al. 2014). However, the huge amount of acid consumption, low metal recovery efficiency, recycling problem of acid waste and releasing the hazardous gases such as acid vapour, volatile organic compounds and chlorine gas are global difficulties of these methods. For this reason, scientists have focused their efforts to find environmentally sensitive solvents for producing efficiently valuable metals (Hu et al. 2017). Ionic liquids (ILs) are the most promising chemical solvents for metal production in hydrometallurgical routes with excellent properties, such as negligible vapour pressure, non-flammability, thermal stability and high conductivity (Tian et al. 2010; Park et al. 2014).

ILs formed fully of organic cations and inorganic/organic anions have a potential to leach ores and metal oxides greenly due to having ability to dissolve a wide range of inorganic and organic compounds (Hu et al. 2017). The first study on metal extraction using ionic liquid was carried out by Whitehead et al. (2004) with 1-butyl-3-methyl-imidazolium hydrogen sulphate ([Bmim]HSO_4) to take out the precious metals from gold bearing ore. This study was resulted

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85% Au and 60% Ag recoveries for 50 h leaching at room temperature. Whitehead et al. (2007) also performed another study based on imidazolium IL with hydrogen sulphate for 48 h at 50 °C by changing its alkyl chain length. The study showed that IL with short alkyl chain length is more efficient on gold extraction from sulphidic ores. Furthermore, authors emphasized that HSO_4^- anions presented superior effect on gold extraction. An experimental work by Dong et al. (2009) showed that 88% of copper recovery was obtained from chalcopyrite by using pure $[Bmim]HSO_4$ in oxygen ambience at 90 °C. Recently, Hu et al. (2017) used 1-hexyl-3-methylimidazolium hydrogen sulphate ($[Hmim]HSO_4$) in the presence of hydrogen peroxide (H_2O_2) as oxidant. Results of the study showed that 10% (v/v) $[Hmim]HSO_4$ aqueous solution with 25% H_2O_2 was an effective leaching agent for copper extraction with 98.3% from chalcopyrite at 45 °C.

A small number of studies have been conducted by using ILs on the recovery of valuable metals from secondary sources such as electric arc furnace dust, brass waste and printed circuit boards, but most of these studies have been limited to recover Cu, Zn, and Pb from the secondary wastes (Bakkar 2014; Huang et al. 2014; Kılıçarslan et al. 2014). A recent study on recovery of precious metals from AS has been carried out by 1-ethyl-3-methyl-imidazolium hydrogen sulfate ($EmimHSO_4$) IL (Rüşen and Topçu 2017a), and results of this study showed that gold can be recover higher than 89% from AS at optimum leach conditions: 80% IL concentration, 75 °C, 4 h and 1/25 g/mL solid/liquid ratio. Also, authors mentioned that, other metals such as Pb, Sn, Se, Te (except for gold and copper) in anode slime have low dissolution rate in ILs. Therefore, in the present study, we focused to recover main precious metals (Au, Ag and Cu) from AS by a hydrometallurgical route using $[Bmim]HSO_4$ IL as a leaching agent. First of all, chemical, mineralogical and thermal characterization of AS were revealed in detail. Then, the effects of parameters such as IL concentration, temperature, reaction time and pulp density were investigated on copper, gold and silver recovery from anode slime by applying orthogonal array experimental design. Furthermore, the optimum recovery condition for each metal was determined by Taguchi method which is the frequently used method for studies with several variables in recent times (Zarghami et al. 2014, Bayat et al. 2017). Lastly, the most effective parameters on metal recovery from AS were analyzed by analysis of variance (ANOVA) method.

Experimental parts

Materials

The AS used in this study was collected from a copper plant located in Denizli province in Turkey. It was dried at 105 °C for 24 h, and then ground by ball milling (Restch PM-100). After grinding, finer particle with lower than 45 micron was obtained homogeneously.

1-Butyl-3-methyl-imidazolium hydrogen sulphate ($[Bmim]HSO_4$, ≥ 95%) IL (CAS number: 401788-98-5) was chosen as a leaching agent due to its acidic media in aqueous solution and miscibility in water and it was obtained commercially from Sigma-Aldrich.

Optimization method

Taguchi method which keeps experimental cost at minimum level was used in order to determine the optimum recovery conditions for each metal. To investigate optimum conditions for the leaching of anode slime, the effect of some parameter on the process was explored. Based on previous studies (Dong et al. 2009; Kılıçarslan et al. 2014) about leaching works, ionic liquid concentration, reaction temperature, reaction time and solid/liquid ratio were chosen as the four factors to be investigated. According to the Taguchi method, the orthogonal array experimental design L_{16} (4^4), which denotes four parameters, each with four levels, was chosen because it is most suitable for the conditions being investigated (Guo et al. 2010; Dhawan et al. 2011). The possible interactions between factors in the orthogonal matrix were not considered and the order of leaching tests was performed randomly.

In Taguchi method, three different loss functions, viz., larger is the better (S/N_L), smaller is the better (S/N_S) and nominal is the better (S/N_N), are used to measure the performance characteristics and then, the value of loss function is converted to signal to noise (SN) ratio to reduce variability (Safarzadeh et al. 2008; Kumar et al. 2015; Arce et al. 2017). In this study, for optimization of metal recovery, larger is the better has been evaluated by using the following equation:

$$\left(\frac{S}{N}\right)_{\mathrm{L}} = -10\log\left(\frac{1}{n}\sum_{i=1}^{n}\frac{1}{x_i^2}\right), \tag{1}$$

where $(S/N)_{\mathrm{L}}$ is performance statistics, n is number of repetitions done for an experimental combination, and x_i performance value of ith experiment.

The collected data were then analyzed by Minitab 17 software program to evaluate the effect of each parameter on optimization criteria. By using SN analysis, it is possible to determine optimum level of each parameter and optimum set of parameter producing the maximum leaching efficiency. After determining optimum experimental conditions, the performance value corresponding to optimum conditions can be predicted by the following equation (Kim et al. 2009):

$$\left[\frac{S}{N}\right]_{\mathrm{Predicted}} = \left[\frac{S}{N}\right]_{\mathrm{m}} + \sum_{n=1}^{n}\left(\left[\frac{S}{N}\right]_{i} - \left[\frac{S}{N}\right]_{\mathrm{m}}\right), \tag{2}$$

where $(S/N)_m$ is arithmetic mean of performance statistics $(S/N)_L$ for all experiments, $(S/N)_i$ is performance statistic value at optimum level of each investigated parameter.

After estimation of optimum condition, the validity of optimum condition was controlled by confirmation experiments conducted at the optimum conditions.

But Taguchi is insufficient of identifying which factor has influenced the output significantly and how much each factor contributed to the output. Therefore, analysis of variance (ANOVA) in accordance with the Taguchi method was done to determine which investigated parameters are dominant on the leaching performance (Mbuya et al. 2017; Behnajady and Moghaddam 2017). For this reason, the *F* test was used to specify which process parameters had a significant effect on the leach efficiency. Usually, the larger *F* value leads to the greater effect of the leaching efficiency due to the change of the process.

Leaching tests

All leaching tests were carried out in 100 ml Pyrex glass flasks placed on a hot plate with a Teflon-coated magnetic stirrer. The heater was controlled by a thermocouple with sensitivity of ± 0.5 °C. During all the experiments, speed of the magnetic stirrer was fixed at constant value (600 rpm). The leaching tests were performed at constant volume of leaching solution (25 ml) with different pulp densities. Experimental parameters were selected as temperature (25–95 °C), time (0.5–4 h), pulp density (100–40 g/L which corresponds to 1/10–1/25 g/ml solid/liquid ratio) and $[Bmim]HSO_4$ IL concentration (20–80% v/v) prepared by mixing of deionized water. In addition, hot water leaching (HWL) was carried out to specify water-soluble compounds in AS at the following conditions; 95 °C for 120 min with a pulp density of 40 g/L.

After each of the leaching tests, the solid and leach liquor parts were separated by using a vacuum pump. The acidities and conductivities of the initial and final leach solutions were recorded at room temperature by means of an Eh–pH meter. Atomic absorption spectroscopy (AAS, PerkinElmer PinAccle 900T) was used to analyze the Cu, Au and Ag concentrations in the leach solutions.

Anode slime characterization

Chemical characterization of AS was characterized with the fire-assaying method for precious metals (Au and Ag) at General Directorate of Mineral Research and Explorations (MTA). Inductively coupled plasma mass spectrometry (ICP-OES, Agilent ICP-OES 725) and X-Ray Fluorescence Spectrometry (XRF, Rigaku ZSX Primus II) were used for other base metals at. Chemical analysis results of the sample showed that AS was mainly composed of 23.1% Cu, 20.5% Sn, 15.4% Pb, 5.87% Ba, 4.11% S, 0.82% Ni, 0.24% Sb, 0.14% Sr, 0.13% Zn, 0.11% Bi, 21.9 ppm Au, 2204.2 ppm Ag, 413 ppm Se, 83 ppm Te.

Component morphology of AS was detected by X-ray diffraction (XRD, Bruker Advance D8) and scanning electron microscope equipped with energy-dispersive X-ray spectroscopy (SEM–EDX, JSM-6400 electron microscope). Figure 1 and Fig. 2 indicate XRD patterns and SEM–EDX results of AS, respectively. Also, mineralogical analysis was carried out after leaching experiments under optimum conditions for Au and Cu for evaluating the change of morphology of AS.

As shown Fig. 1, $PbSO_4$, SnO_2 and Cu_2O were detected as major components of the AS. Other minor components are determined as $BaSO_4$ and $SbAsO_4$. Besides these compounds, copper was also detected in CuS form and low amount of silver was determined by SEM–EDX analysis. According to the SEM images (Fig. 2), which show at different magnifications for selected points, anode slime particles have more complex morphology with different shapes especially spherical and rod (twiggy). EDX analysis shows that all of the SnO_2 particles appear as rod form in the AS with different sizes. In addition, $PbSO_4$ and Cu_2O phases were detected by EDX analysis. SEM–EDX analysis results support the XRD and chemical analysis results of the anode slime.

Simultaneous Thermogravimetric (TG) and Differential Thermal Analysis (DTA) of the sample were measured by Tetra TG/DTA 6300 in oxygen and argon environments to determine the thermal properties of the anode slime by heating at 30–1100 °C with a heating rate of 25 °C/min. TG and DTA curves of AS were given in Fig. 3.

First of all, when compared to both curves (Fig. 3a, b), it is obviously concluded that all mass gains in the curve obtained in oxygen atmosphere are caused by oxidation of different components in AS for all temperatures between 350 and 700 °C.

According to the thermal analysis in oxygen ambience (Fig. 3a), the TG curve can be divided into three main parts; (a) initial mass loss (up to 400 °C), (b) mass gain part (400–700 °C), (c) final mass loss (from 700 to 1100 °C).

(a) The mass losses at low temperatures in Fig. 3a stem from removing moisture, chemical bonded water and volatiles content of the anode slime, which corresponds to nearly 1.5%. The mass losses continuing up to 400 °C is probably due to evaporation of free selenium and removal SO_2 gas emerged by oxidation of CuS compound present in anode slime (Shah and Khalafalla 1971, Hait et al. 1998).

(b) After 400 °C, the mass gain may be caused by interaction of the elements available in the metallic form in the anode slime with an oxidizing atmosphere. From the chemical analysis it is known that copper (with possible Cu^o, CuS, Cu_2O or Cu_2Se forms in the AS) exists in the highest amount (23.1%) and it can be oxidized at lower temperatures. Most

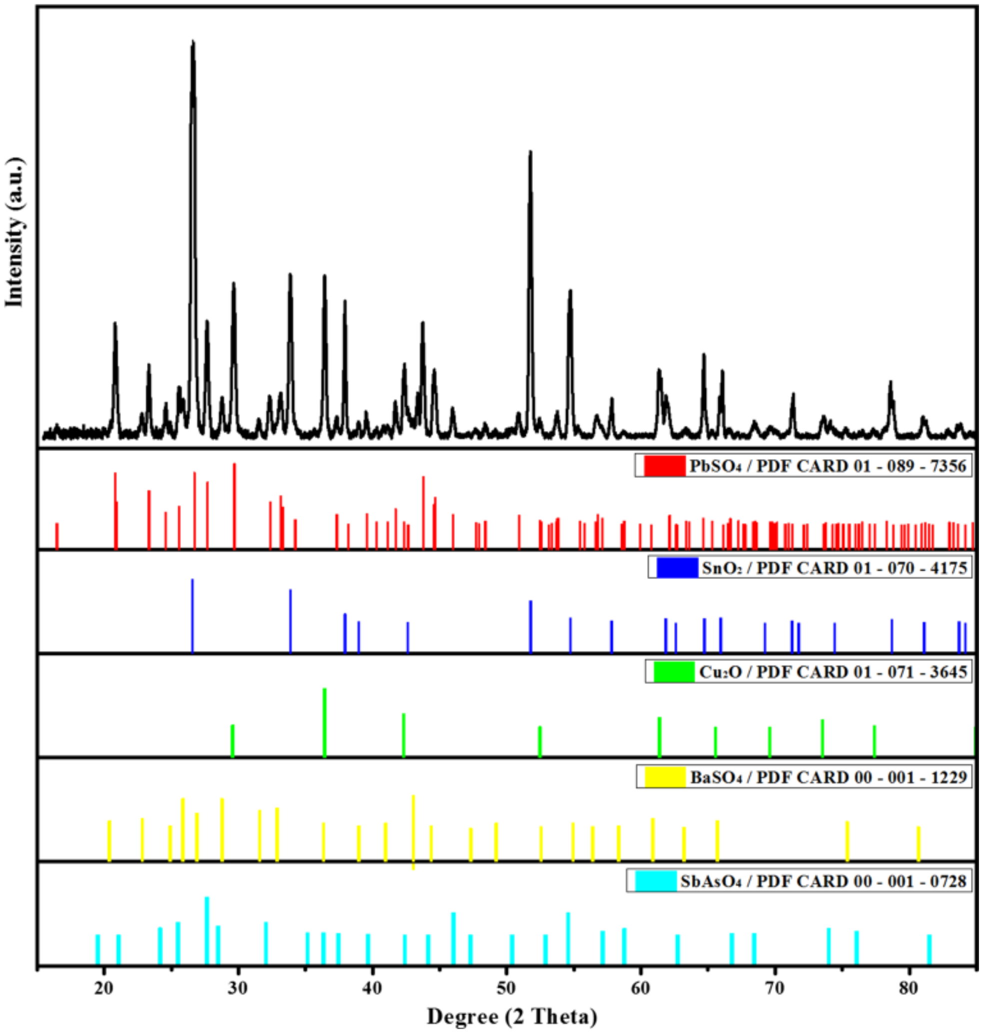


Fig. 1 XRD patterns of anode slime

of the copper in the AS was detected as Cu_2O form by XRD analysis. According to the Won et al. (2006), Cu_2O can be oxidized to form CuO in the range of 400–600 °C as Rx. 3. Also, authors stated that oxidation of Cu_2O decreases with increasing temperature. Besides this, the mass gain occurring in temperature interval 550–600 °C may be attributed to oxidation of Cu_2Se compound in the sample (Rx. 4) (Dunn and Muzenda 2001; Won et al. 2006):

$$Cu_2O + {}^1\!/_2O_2 \rightarrow 2CuO\ (400\text{–}600°C) \tag{3}$$

$$Cu_2Se + 2O_2 \rightarrow Cu_2SeO_4(550\text{–}600°C). \tag{4}$$

According to these reactions, approximately %2 mass gain in the AS is expected. But, the mass gain corresponding to 1.5% indicates that the components could not be fully oxidized at the specified temperatures.

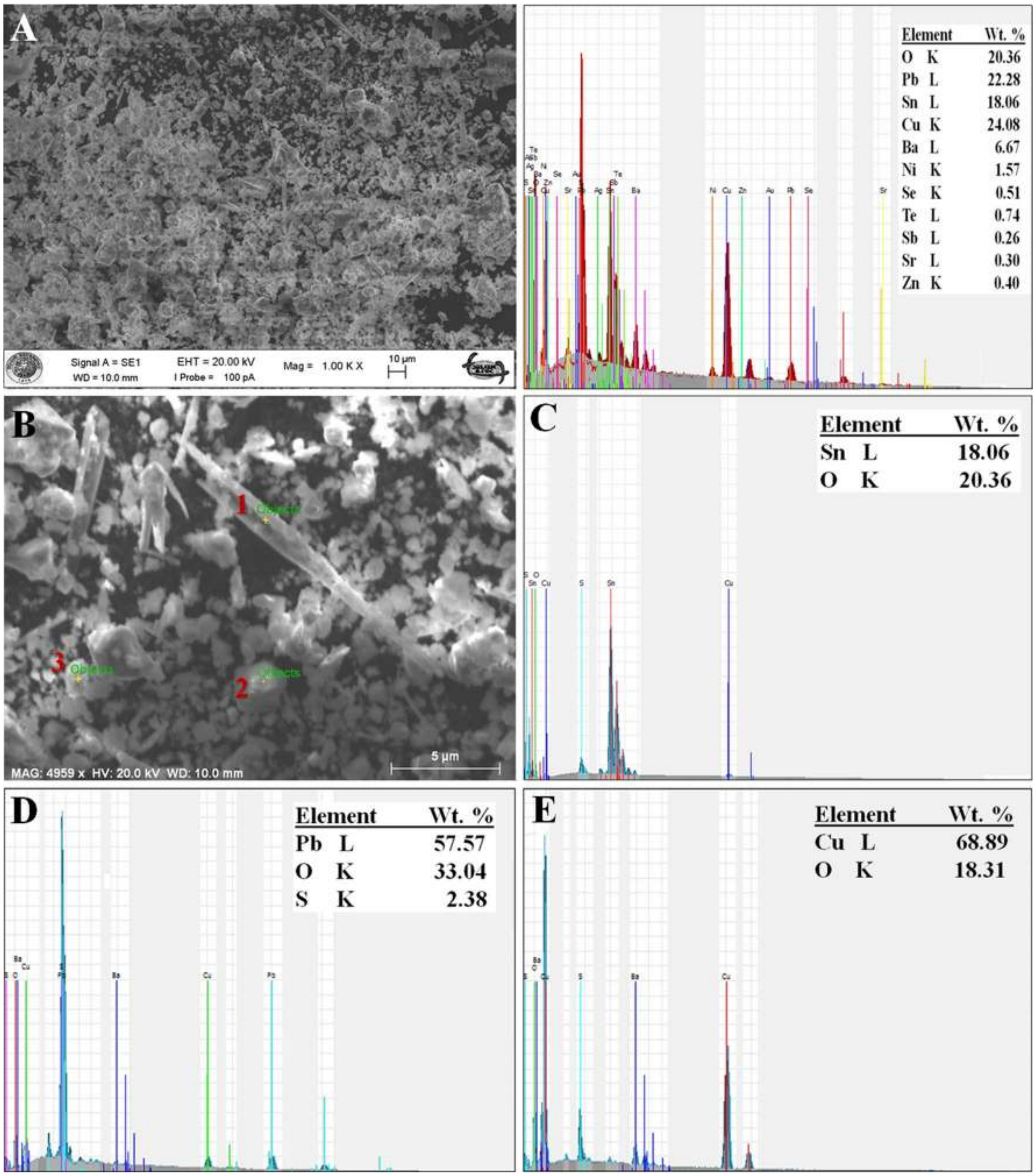
At the DTA curve, endothermic peak between 400 and 450 °C without significant mass change proved the phase transformation or phase formation in the anode slime. Taskinen et al. (2014) described the phase transformation at these temperatures as the conversion of Cu_2O to $CuSO_4$ in the presence of SO_2 and O_2 gases by the following reaction (Rx. 5):

$$Cu_2O + 2SO_2 + 3/2O_2 \rightarrow 2CuSO_4(420\text{–}550°C). \tag{5}$$

(c) It is thought that the last mass losses and endothermic peaks observed at about 700 and 1100 °C represent the decomposition of sulphated structures such as $CuSO_4$, $PbSO_4$ and $BaSO_4$ by following chemical reactions (Rxs. 6–8). DTA curve reveals that $CuSO_4$ decomposition takes place in the range of 700–740 °C (Minić 2005). Dissociation of lead sulphate starts at 705 °C and fully desulphurization is completed up to 980 °C (Abdel–Rehim 2006). Further temperature increment causes intensive decomposition of $BaSO_4$ with the appearance of endothermic peak at higher than 1000 °C (Prameena et al. 2013):

$$PbSO_4(s) \rightarrow PbO(s) + SO_3(g) \tag{6}$$

$$BaSO_4(s) \rightarrow BaO(s) + SO_2(g) + {}^1\!/_2\,O_2(g) \tag{7}$$



Element	Wt. %
O K	20.36
Pb L	22.28
Sn L	18.06
Cu K	24.08
Ba L	6.67
Ni K	1.57
Se K	0.51
Te L	0.74
Sb L	0.26
Sr L	0.30
Zn K	0.40

Element	Wt. %
Sn L	18.06
O K	20.36

Element	Wt. %
Pb L	57.57
O K	33.04
S K	2.38

Element	Wt. %
Cu L	68.89
O K	18.31

Fig. 2 **a** SEM image of anode slime with EDX result of all surface area, **b** SEM image of the selected area with higher magnification, **c** EDX results of the #1 (rod bar), **d** EDX result of the #2, **e** EDX results of the #3

$$CuSO_4(s) \rightarrow CuO(s) + SO_2(g) + \tfrac{1}{2}O_2(g). \qquad (8)$$

On the other hand, as seen in Fig. 3b, the TGA curve decreases continuously during the entire analysis in argon ambience, which indicates removal of moisture and chemical-bonded water (up to 450 °C), the evaporation of elements and volatile components in AS at different temperatures (from 450 to 750 °C), and decomposition of sulfated compounds ($PbSO_4$, $BaSO_4$, etc.) from 750 to 1100 °C according to Rx. 6–8.

Results and discussion

Leaching results

To optimize the leach conditions on recoveries of valuable metals (Cu, Au and Ag) from AS in IL system, four parameters each at four levels were investigated by using L_{16} (4^4) orthogonal array experimental design. The HWL of anode slime showed that there is no water-soluble form of Cu, Au and Ag compounds in the AS. In the present study,

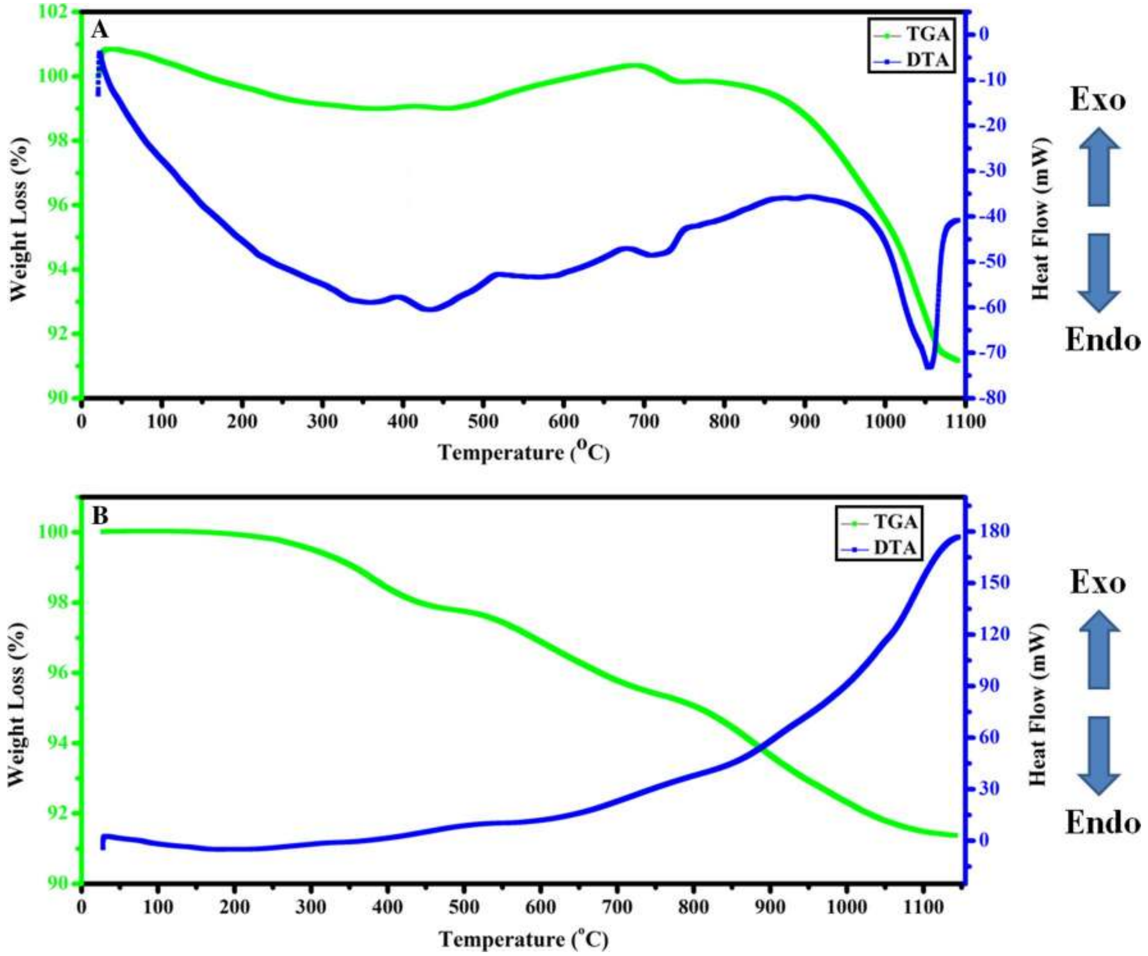


Fig. 3 Thermal curves of anode slime **a** in oxygen ambience and **b** argon ambience

the highest Ag recovery from AS could be obtained as lower than 10% by using [Bmim]HSO_4 as a leaching agent. This may be attributed to silver compounds available in AS which have low solubility in [Bmim]HSO_4 IL. In this study, the structure of silver in AS could not be clearly determined. But, it is known that CuAgSe as a common type of compound in AS (Chen and Dutrizac 2005; Kılıç et al. 2013) can be dissolved in acidic media by formation of Ag_2Se structure according to following chemical reaction (Rx. 9) (Chen et al. 2015):

$$2CuAgSe + O_2 + 2H_2SO_4 \rightarrow 2CuSO_4 + Ag_2Se + 2H_2O. \quad (9)$$

Since [Bmim]HSO_4 has acidic properties with HSO_4 anion, Rx. 9 may describe the low dissolution rate of silver in IL media. For this reason, the optimum condition for silver recovery was not determined. The experimental conditions and results of leaching efficiency with the performance statistic for Cu, Au and Ag recoveries are given in Table 1 and Fig. 4.

As it is well known, in Taguchi method the performance statistic graphs are used to determine the optimum working conditions by selecting maximum point for each parameter. Therefore, the top of the peak in each column of Fig. 4 was marked to define the optimum condition for Cu and Au recovery separately. According to Fig. 4, the optimum condition for copper recovery by using [Bmim]HSO_4 was detected as; IL concentration: 60% (v/v), temperature: 50 °C, reaction time: 2 h and pulp density: 40 g/L, which corresponds to A_3, B_2, C_3, and D_4. Also, the optimum condition for gold recovery was determined as; ionic liquid concentration: %80 (v/v), temperature 95 °C, reaction time: 4 h and pulp density: 40 g/L, namely A_4, B_4, C_4, and D_4.

If the orthogonal array experimental design for Cu and Au recovery is analyzed carefully, it can be noticed that the detected optimum experimental conditions have not been performed during the experimental trials as a leaching experiment for both of them. Therefore, the predicted recovery rate for Cu and Au under the optimum conditions

Table 1 Experimental conditions and results of leaching efficiency with the performance statistics for Cu and Au recovery

Exp. no.	Experimental parameters and their levels				Recovery (%)			SN_L		
	IL conc. (v/v)	Rx. temp. (°C)	Rx. time (h)	Pulp density (g/ml)	Copper	Gold	Silver	Copper	Gold	Silver
1	20	25	0.5	1/10	36.73	3.83	0.07	31.30	11.67	– 2300
2	20	45	1	1/15	60.58	9.63	1.59	35.65	19.67	402
3	20	75	2	1/20	83.61	18.29	2.59	38.45	25.24	826
4	20	95	4	1/25	71.34	27.44	2.86	37.07	28.77	913
5	40	25	1	1/20	44.58	46.11	4.50	32.98	33.28	1306
6	40	45	0.5	1/25	82.01	60.23	0.29	38.28	35.60	– 1071
7	40	75	4	1/15	53.93	23.51	0.58	34.64	27.42	– 469
8	40	95	2	1/10	69.46	36.23	1.11	36.83	31.18	089
9	60	25	2	1/25	55.73	72.99	2.82	34.92	37.26	901
10	60	45	4	1/20	73.53	85.75	1.22	37.33	38.66	173
11	60	75	0.5	1/15	60.15	66.28	3.80	35.58	36.43	1160
12	60	95	1	1/10	73.18	42.19	0.99	37.29	32.50	– 012
13	80	25	4	1/15	56.37	82.94	9.92	35.02	38.37	1993
14	80	45	2	1/10	54.25	48.73	2.66	34.69	33.76	851
15	80	75	1	1/25	62.41	94.29	0.08	35.90	39.49	– 2156
16	80	95	0.5	1/20	38.10	67.86	4.65	31.62	36.63	1334

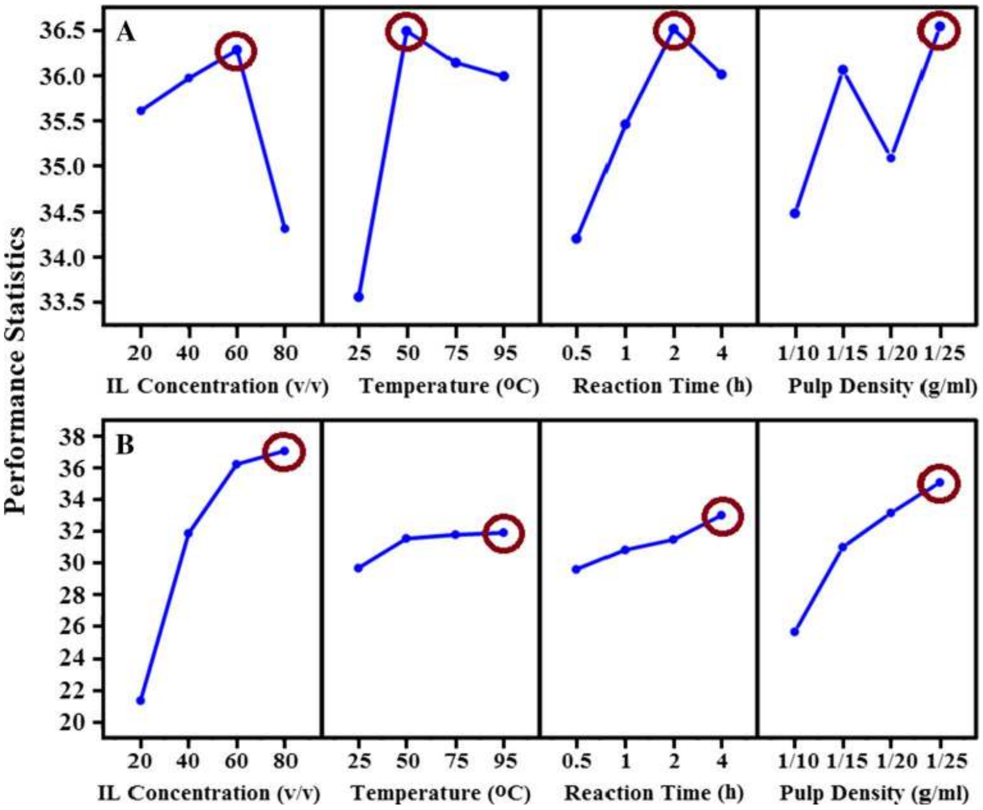


Fig. 4 Effects of each parameter on the statistics for **a** copper recovery, **b** gold recovery

must be calculated theoretically and confirmed experimentally (Kim et al. 2009). Under the optimum conditions (A_3, B_2, C_3, and D_4), the predicted theoretical recovery rate and the leaching efficiency obtained after the verification tests for Cu are 90.31 and 87.52%, respectively. On the other hand, for Au at the optimum conditions (A_4, B_4, C_4, and D_4) calculated theoretical recovery value and experimental leaching efficiency of verification test are obtained as 99.97 and 97.32%, respectively.

According to the results, almost whole of the gold (97.32%) and most of the copper (87.52%) could be extracted experimentally from AS by [Bmim]HSO_4 IL leaching under the optimum conditions. Moreover, there is a remarkable agreement between theoretical and experimental quantities for Cu and Au recoveries. Both metal leaching efficiencies are within the 5% margin of error.

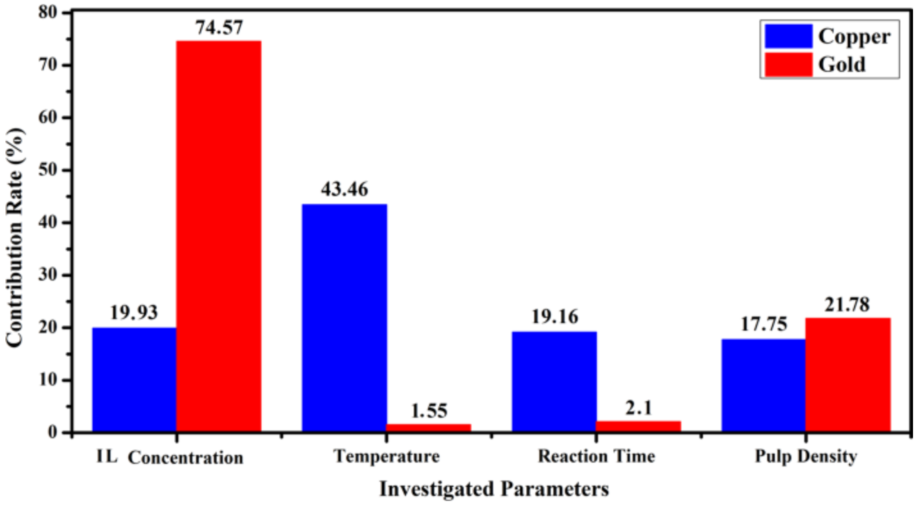
In Taguchi method, only the performance statistic graphs given in Fig. 4 are not sufficient to directly describe the effect of the studied parameters on the recovery process. Therefore, many scientists were used Analysis of Variance (ANOVA) approach to define which investigated parameters are predominant on the performance characteristics (Mbuya et al. 2017; Behnajady and Moghaddam 2017). For this reason, the *F* test was used to specify which process parameters had a significant effect on the leach efficiency. Results of the ANOVA analyses and contribution percentages of the investigated parameters for Cu and Au are presented in Table 2 and Fig. 5, respectively.

These results should be examined separately for these two metals (Cu and Au) in terms of four different parameters (IL Concentration, Temperature, Reaction Time, and Pulp Density). As seen from Fig. 5, temperature is the most effective parameter on copper recovery from AS with 43.46 percentage of the contribution (Cr %) in [Bmim]HSO_4 media. When looking at the Fig. 4a, it can be seen that Cu extraction increased with increasing temperature until 50 °C. However, after this critical point Cu recovery decreased slightly. In aqueous solutions of ILs, there are several factors such as dissolved oxygen, acidity and ionic strength which affect the copper dissolution. Dong et al. (2009) was emphasized that dissolved oxygen decreased with increasing temperature. Thus, the low copper recovery from AS in [Bmim]HSO_4 solution at high temperature could be attributed to a decrease in dissolved oxygen ratio. This may be overcome by adding H_2O_2 to the leach system as an oxidant.

Table 2 ANOVA results for copper and gold recovery

	Source	*df*	SS	MSS	*F* ratio	Cr (%)
Cu	IL concentration	3	429.7	143.2	0.42	19.63
	Temperature	3	952.2	317.4	0.93	43.46
	Reaction time	3	418.2	139.4	0.41	19.16
	Pulp density	3	393.4	131.1	0.38	17.75
	Error	3	1029.0	343.0		
	Total	15	3222.6			
Au	IL concentration	3	1403.32	467.77	23.77	74.57
	Temperature	3	207.57	69.19	3.52	1.55
	Reaction time	3	84.11	28.04	1.42	2.10
	Pulp density	3	2930.80	976.93	49.65	21.78
	Error	3	59.03	19.68		
	Total	15	4672.30			

Fig. 5 Contribution percentage of the investigated parameters on Cu and Au leaching metal recovery



According to the ANOVA analysis, the other parameters which are IL concentration, Reaction time and Pulp density with 19.63%, 19.16, 17.75% contribution ratio, respectively, have similar effects on copper recovery from AS. The solubility as well as miscibility of ILs in water makes them a good hydrogen ion donor, which results in the acidic aqueous solution. Acidity of the ILs depends on the concentration and also highly dissolved hydrogen sulphate ions (Zhou et al. 2008). The decomposing of $[\text{Bmim}]\text{HSO}_4$ in water was demonstrated by Crowhurst et al. (2003) by the following chemical reaction (Rx. 10):

$$[\text{Bmim}]\text{HSO}_4 \leftrightarrow \text{Bmim}^+ + \text{H}^+ + \text{SO}_4^{2-}. \quad (10)$$

Therefore, it is reasonable to propose Rx. 11 as the main dissolution reaction of copper in $[\text{Bmim}]\text{HSO}_4$ IL, because Cu_2O was detected as the main phase containing copper in AS by XRD analysis.

$$\text{Cu}_2\text{O} + 4\text{H}^+ + {}^1\!/\!{}_2\text{O}_2 \longleftrightarrow 2\text{Cu}^{2+} + 2\text{H}_2\text{O}. \quad (11)$$

According to chemical reaction 8, the acidity level of the IL and the dissolved oxygen ratio are two main parameters which affect the dissolution of copper.

As illustrated in Fig. 4a, the copper recovery increased by increasing IL concentration up to 60% (v/v) and then decreased sharply at a high IL concentration. This could be attributed to the high viscosity of IL as compared to conventional solvents. In order to overcome this manner, higher agitation speed should be performed during the leaching process at high IL concentration.

As for gold recovery, experimental results showed that almost all of the gold contained in the AS could be recovered by IL leaching under the optimum condition. It is known from the previous studies that the aqueous solution of $[\text{Bmim}]\text{HSO}_4$ IL has a suitable environment for oxidative leaching of gold extraction with acidic properties (Whitehead et al. 2004). The high $[\text{Bmim}]\text{HSO}_4$ concentration used in this study with high acidity (measured as pH = 0.7) affects positively the gold recovery from AS. This is also supported by the ANOVA analysis as seen in Table 2 and Fig. 5 the most effective parameter on gold recovery from AS was IL concentration with 74.57% ratio. As given in Fig. 3b, the gold recovery increased with increasing IL concentration, and reached quite high level with 97.32% recovery ratio at 80% (v/v) IL concentration after verification test. Considering the results of initial studies on gold recovery (Whitehead et al. 2004, Rüşen and Topçu 2017a), the leaching yield obtained in this study seems to be quite compatible with the literature.

Second effective parameter for gold recovery is pulp density with 21.78% Cr-ratio. The last column in Fig. 4b shows that the gold recovery increases rapidly by decreasing the pulp density. Due to the volume enlargement of the solution, the decrease in pulp density is favourable for gold extraction by acceleration of the reaction and mass transfer between gold in AS and $[\text{Bmim}]\text{HSO}_4$ IL. According to ANOVA analysis of Au, there is no significant effect of reaction temperature and time on Au recovery from AS in the presence of IL media.

After the leach experiments under the optimum conditions for Au and Cu recovery, the residual secondary wastes were analyzed by X-ray diffractometer to reveal their mineralogical contents, and they were compared to the original anode slime pattern. The XRD patterns are presented in Fig. 6.

As seen in XRD patterns, after the both optimum leaching, the Cu_2O peaks (PDF# 01-071-3645) are diminished or disappeared due to the dissolution of the copper-containing phases in IL solution, which leads to become more apparent

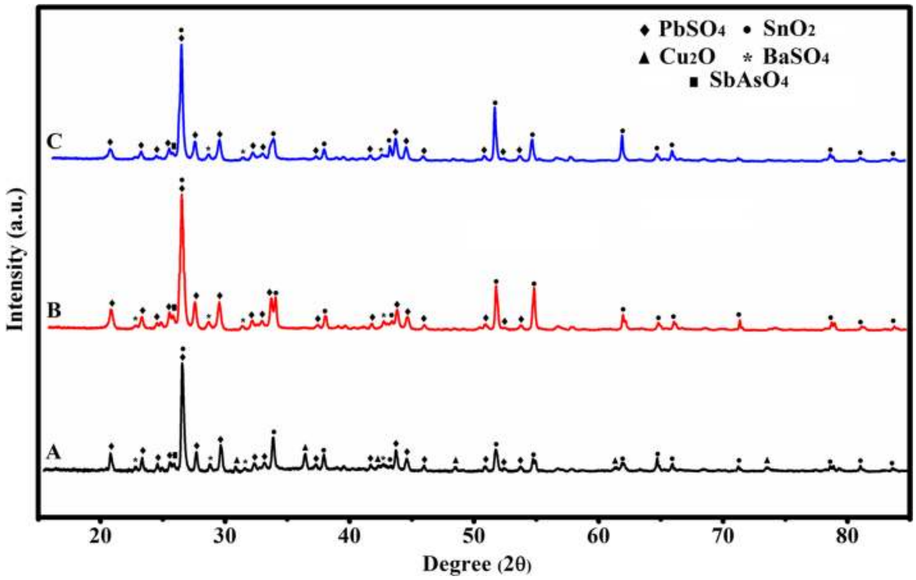
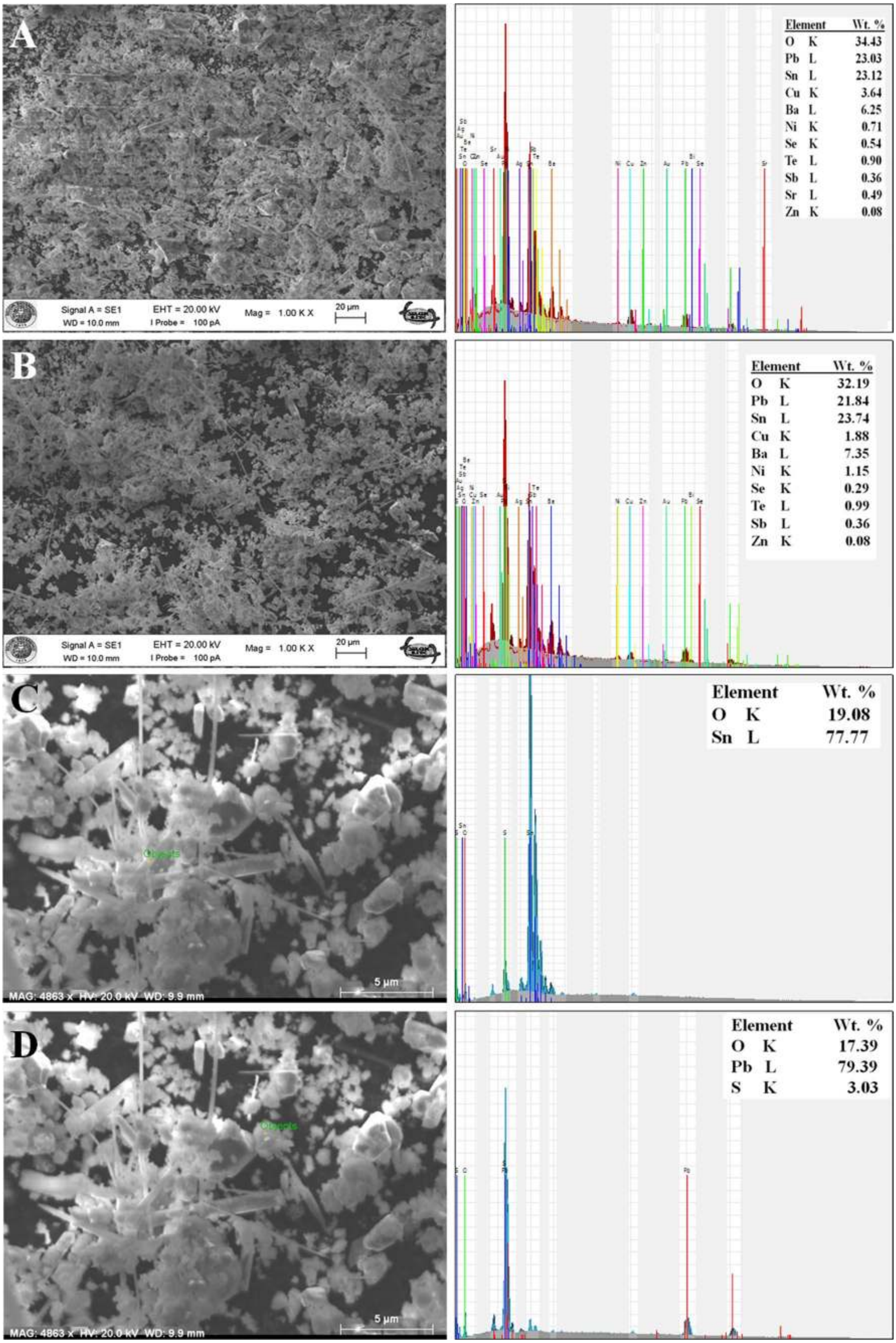


Fig. 6 Comparison of XRD patterns belonging to **a** original anode slime, **b** the secondary residue after gold optimum leaching **c** the secondary residue after copper optimum leaching



Element		Wt. %
O	K	34.43
Pb	L	23.03
Sn	L	23.12
Cu	K	3.64
Ba	L	6.25
Ni	K	0.71
Se	K	0.54
Te	L	0.90
Sb	L	0.36
Sr	L	0.49
Zn	K	0.08

Element		Wt. %
O	K	32.19
Pb	L	21.84
Sn	L	23.74
Cu	K	1.88
Ba	L	7.35
Ni	K	1.15
Se	K	0.29
Te	L	0.99
Sb	L	0.36
Zn	K	0.08

Element		Wt. %
O	K	19.08
Sn	L	77.77

Element		Wt. %
O	K	17.39
Pb	L	79.39
S	K	3.03

◂**Fig. 7** SEM images and EDX results of secondary leach residue; **a** leaching experiments under Au optimum conditions, **b** leaching experiments under Cu optimum conditions, **c** for $PbSO_4$ structure, **d** for SnO_2 (rod bar) structure

in the peak intensities of the insoluble phases of SnO_2 (PDF# 01-070-4175) in secondary leach residues of anode slime. This was also observed by SEM–EDX analysis of secondary leach residues which obtained after the leach experiments carried out under the optimum conditions for both metals (Fig. 7). Figure 7c, d show that SnO_2 and $PbSO_4$ structures remained in the leach residue without any change after leach experiments. Since the phase of the gold could not be determined in the XRD pattern, comparison of XRD patterns only indicates that the copper-containing phases are dissolved and the copper recovery is realized by [Bmim]HSO_4 leaching.

As seen from the EDX analyses (Fig. 7a, b.), considerable amount of copper was dissolved in both experiments. The difference between copper content in the original AS (23.1%) and that of secondary leach residue determined by EDX result (~2% from Fig. 7b) is very prominent. These results almost coincide with leaching efficiency of copper (~90%) obtained under optimum conditions.

In the literature, recovery of valuable metals from AS has been tested by using several leaching agents such as H_2SO_4 (Dönmez et al. 1998; Hait et al. 2002; Khaleghi et al. 2014), thiourea (Amer 2003; Ranjbar et al. 2014), thiosulfate (Xu et al. 2016,) ammonia (Meng and Han 1996; Tan and Bedard 2013), EmimHSO_4 (Rüşen and Topçu 2017a, b). Depending on the extraction processes and conditions, various leaching efficiency results have been obtained with these leach agents for Cu between 80 and 90%, for Au between 70 and 95%, and for Ag up to 85%. When the leaching efficiency results by [Bmim]HSO_4 obtained under the optimum conditions compare to those by other methods, [Bmim]HSO_4 represent very promising result for gold and copper.

Considering that the production cost of 1-methyl-imidazolium hydrogen sulfate at bulk scale is ranging between 2.96 and 5.88 USD/kg which are relatively close to costs of organic solvents (Chen et al. 2014) the results showed that aqueous solution of [Bmim]HSO_4 could be offer a suitable leaching media for copper and gold recovery from AS. By this way, low consumption of acid or cyanide based leach agent, less energy usage as well as low environmental pollution could be resulted. Beside this, due to the very high presence of the Pb and Sn in AS, removing of them from the original sample will cause to increase in the concentration of the precious metals, which results in less consumption of the [Bmim]HSO_4 IL for chemical treatment of the AS. Moreover, as described in the previous studies (Nakashima et al. 2005; Abbott and McKenzie 2006; Zhang et al. 2009; Hoorgerstraete et al. 2013), most of the metals have been extracted by liquid–liquid extraction and electrodeposition from ILs aqueous media due to their excellent physico-chemical properties such as high solubility of metal compound, high conductivity compared to non-aqueous solvents, adjustable hydrophobicity, wide temperature range and potential window for liquid phase.

Conclusions

In this study, copper, gold and silver recoveries were investigated by using [Bmim]HSO_4 ionic liquid which can be consider as an environmentally sensitive solvent. In the experimental trials, the copper anode slime was used as a valuable metal source in which $PbSO_4$, SnO_2 and Cu_2O were detected as the main components. Under the optimum conditions, remarkable recovery ratios were obtained for copper and gold recovery as 87.52 and 97.32%, respectively. The Ag solubility in IL leaching could be remained very low due to the form of silver compound available in AS. After leaching experiments, it is seen clearly that [Bmim]HSO_4 aqueous solution was an alternative leaching solution for copper and gold recovery from AS because of its acidic nature and oxidative media in water. Although a reasonable amount Cu and Au were recovered from the AS after the IL leaching step, it is necessary to evaluate the economics of the suggested process before industrial application due to the relatively high cost of ILs. However, as the costs of the ILs are lowered to feasible level, these solvents will play a very important role on the recovery of precious metals from primary or secondary sources in the future.

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