



## Effect of 1-butyl-3-methylimidazolium based ionic liquids with different anions on copper recovery from copper anode slime

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### Abstract

In this study, the usage of 1-butyl-3-methylimidazolium based ionic liquids (ILs) with different anions ( $\text{HSO}_4^-$ ,  $\text{Cl}^-$  and  $\text{BF}_4^-$ ) was investigated for copper recovery from anode slime. Initially, chemical composition and mineralogical structure of anode slime (AS) were determined by ICP-MS, fire assaying and XRD methods. The anode slime used in the leaching experiments includes %23.1 Cu, 15.42 Pb and 20.5% Sn as major elements. The anion effects of 1-butyl-3-methylimidazolium based ionic liquids were studied under conditions of %50 ionic liquid concentrations at 50 °C reaction temperature and 1/20 g/mL solid/liquid ratio with reaction time in range of 1-8 hours. According to the experimental results, the copper recovery increased by increasing leaching time for all ionic liquids. The most effective ionic liquid on copper recovery was determined as 1-butyl-3-methylimidazolium hydrogen sulphate ( $\text{BmimHSO}_4$ ) and 27.7% of copper recovery was obtained after 8 hours of leaching time at 50 °C.

**Keywords:** ionic liquids, anode slime, leaching, characterization.

### 1. Introduction

Ionic liquids are generally described as compounds completely formed of ions with melting point below 100 °C. Although the first ionic liquid, ethylammonium nitrate ( $[\text{EtNH}_3][\text{NO}_3]$ ), was synthesized about a hundred years ago by Paul Walden in 1914, ionic liquids have gained attention in the last 20 years as an innovative liquid for many fields. [1-2] Ionic liquids are basically a family of molten salts containing an organic cation and organic/inorganic anions. While ionic salts such as sodium chloride and potassium chloride are solids at room temperature, ionic liquids have low melting point below 100 °C due to their different ionic dimension and low lattice energies. [3] Since ionic liquids are synthesized by the combination of a small inorganic anion and a large organic cation, many researchers have stated that considering the variety of cations and anions, thousands of ionic liquids can be synthesized. [4] Among many ionic liquids, the most commonly used are those formed by addition of a small inorganic anion such as  $\text{BF}_4^-$ ,  $\text{PF}_6^-$ ,  $\text{HSO}_4^-$ ,  $\text{Cl}^-$  and  $\text{CH}_3\text{CO}_2^-$  to organic cations such as imidazolium, pyrrolidinium and pyridinium. The physical properties of ionic liquids such as melting point, density, viscosity hydrophilicity/hydrophobicity can be controlled with the appropriate combination of cation and anions [1,3] Up to now, ionic liquids was used many fields such as

organic synthesis, polymer, fuel cell, solar cell and extraction/separation studies due to their chemical and physical properties like good thermal and electrochemical stability, negligible vapour pressure, non-flammability, easy recycling and solvent property.

A few number of studies have indicated that ILs play a significant role as a reaction media for recovery of precious metals from various metal sources [5-7] It stated by Whitehead et al., (2007) [5] the physical properties of ionic liquids based on short alkyl chain methyl imidazolium (1-butyl-3-methylimidazolium;  $\text{bmim}^+ \text{X}^-$ ), such as water miscibility (hydrophobicity) or viscosity, are more advantageous in terms of metal recovery considering the studies on the copper recovery from ore or secondary sources with ionic liquids. Therefore, in this study, the ionic liquids having short alkyl chain methyl imidazolium cation with  $\text{HSO}_4^-$ ,  $\text{BF}_4^-$  and  $\text{Cl}^-$  anions were preferred as the solvent for copper recovery from anode slime (AS). In this study, the effect of time on the recovery of copper metal from AS with high copper content in the presence of ionic liquids with different anions was investigated in the range of 1 - 8 hours. Also, the chemical and mineralogical characterization of AS were detailed by several methods.

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## 2. Materials and Methods

AS used in study was obtained from copper plant where copper wire produced from secondary sources. Before leaching experiments and characterization of AS, the supplied sample was ground to obtain a homogenous particle size. Particle size of the AS was detected laser diffraction method by Malvern Mastersizer. The chemical analysis of the AS was detected by ICP-MS and fire assaying method. Mineralogical structure of the AS and secondary leach residues were investigated by XRD (Bruker D8 Advance Da Vinci) and SEM/EDS (Hitachi SU5000) analyses.

The ionic liquids used in the leaching experiments as reagent was obtained commercially from Sigma Aldrich for 1-butyl-3-methylimidazolium hydrogen sulphate (BmimHSO<sub>4</sub>, ≥ 98%) and 1-butyl-3-methylimidazolium chloride ((BmimCl ≥ 98.5%) and 1-butyl-3-methylimidazolium tetrafluoroborate (BmimBF<sub>4</sub> ≥ 98.5%) from ABCR GmbH.

In this study, the effect of leaching time was investigated in range of 1 – 8 hour by changing the anion of imidazolium based ionic liquids. All leaching experiments performed for copper recovery from AS were carried out in three-necked glass placed in jacketed

heater. The heater was controlled by a thermocouple with a sensitivity ±0.5 °C. During the leaching experiments, leaching temperature, the speed of the magnetic stirrer and volume of the ionic liquids solution were kept constant as 50 °C, 600 rpm and 50 mL, respectively. After leaching experiments, solid/liquid separation was carried out by a vacuum pump and after filtration the leach residue was washed with deionized water.

The pregnant solution was diluted gradually with deionized water for AAS analysis. Then, the diluted pregnant solution was analyzed by using Perkin Elmer PinAccl 900T model atomic absorption spectrometer. Copper recovery from AS was calculated by using Equation 1:

$$\text{Recovery (\%)} = \frac{C * V}{m * w} * 100 \quad (1)$$

where C is average of three replicates of diluted leach solution (in mg.L<sup>-1</sup>), V is the volume of the leach solution (in L), m is initial amount of anode slime (in mg) and w is metal content of anode slime (in mg/g).

## 3. Results and discussion

### 3.1. Characterization of anode slime

Characterization of AS was performed by detecting the particle size, chemical composition and mineralogical structure of pulverized sample. Particle size distribution of AS with digital image is illustrated in Fig. 1. Expression such as Dv(90), Dv(50) and Dv(10) obtained from the particle size analysis of AS indicate the point in the size distribution up 90%, 50% and %10 of the total material volume in the sample. As seen from the Fig.1, 71µm corresponds to the Dv(90) value, that is

%90 of the particles has a size 71µm or less. According to the ISO standard, Dv(50) is called as the median which indicates half of the particle size above this point in micron size. This value is the most practical and significant value used to describe the particle size distribution. Fig. 1 shows that half of the particle size are lower than 23.3 µm. Chemical analysis of AS was determined by ICP-MS and fire assaying methods. Chemical analysis of AS is shown in Fig. 2.

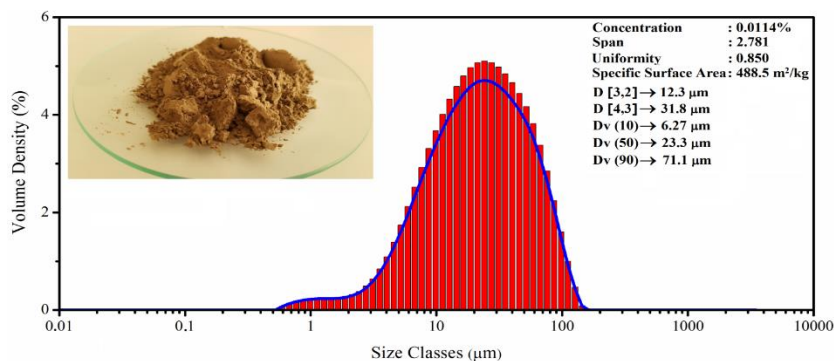


Figure 1: Particle size distribution of anode slime.

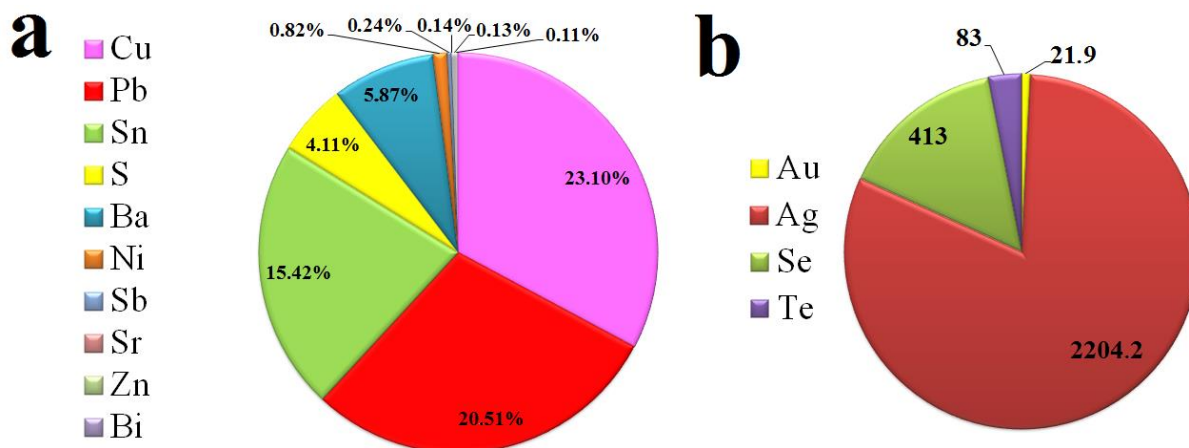


Figure 2: Chemical composition of anode slime a) major elements as percentage, b) minor elements as ppm.

As seen in Fig. 2.a, AS includes remarkable amount copper, tin and lead as 23.1%, 20.51% and 15.42%, respectively. Besides these metals, AS also contains various elements such as barium, sulphur, zinc, nickel, antimony, bismuth and strontium. According to the chemical analysis for precious metals (Fig.2.b), it was found that AS comprise significant amount of gold, silver, tellurium and selenium. Mineralogical characterization of AS and secondary leach residues obtained after experiments were detected by XRD analysis with Cu  $K\alpha$  radiation at 40 kV at scanning rate of  $0.4^\circ \text{ min}^{-1}$ . As stated by our previous studies [8,9]  $\text{Cu}_2\text{O}$ ,  $\text{SnO}_2$  and  $\text{PbSO}_4$  constitute the main structures of

AS. Also, AS includes  $\text{BaSO}_4$  and  $\text{SbAsO}_4$  phases. As stated by previous studies [10,11] AS which form electrorefining stage of copper production have different chemical compositions and mineralogical structures depending on raw material and operation condition. SEM images and elemental colour mapping was taken by SEM devices equipped with energy dispersive X-ray spectrometer. In elemental colour mapping of AS represent a separate element, O=green, S=yellow, Sn=orange, Cu=blue, Pb=red, Ba=white and Ni=dark green. Fig. 3 shows SEM/EDS results for selected area of AS.

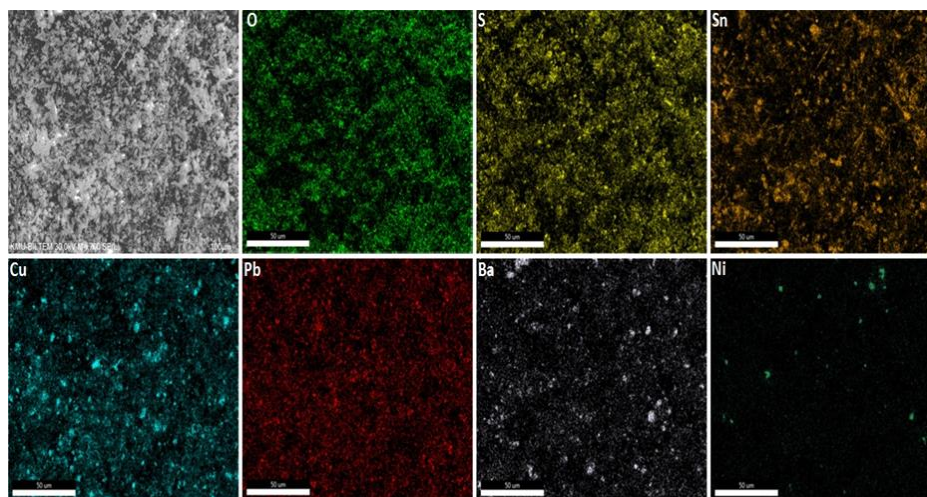


Figure 3: SEM elemental color mapping of anode slime.

As seen from Fig. 3., AS have various particles in different size and shape. This result is compatible with particle size distribution of AS. According to the elemental color mapping, the AS was mainly composed of Cu, Sn, Pb, S, O and Ba elements. The color mapping

of AS showed that all main elements homogeneously distributed in AS. In addition,  $\text{NiO}$ , which couldn't be determined with XRD analysis, found as mineralogical structure by SEM/EDS analysis.

### 3.2. Experimental results

Effect of leaching time on copper recovery were investigated at 50 °C leaching temperature, 1/20 solid/liquid ratio and 600 rpm stirring speed as experimental conditions. Leaching times were selected as 1, 2, 4 and 8 hours. Experimental results are given in Table 1 and illustrated in Fig. 4.

Table 1. Experimental results obtained after leaching experiment.

Experimental Condition	Leaching Time (hour)	%Recovery of Cu (for each Anion of Ionic Liq.)		
		HSO <sub>4</sub> <sup>-</sup>	Cl <sup>-</sup>	BF <sub>4</sub> <sup>-</sup>
Ionic Liquid Concentration: %50 v/v	1	19,7	8,37	0,05
Temperature: 50 °C	2	22,5	10,2	0,12
Solid/Liquid Ratio: 1/20 g/mL	4	26	15,71	0,56
Stirring Speed: 600 rpm	8	27,7	22,3	1,56

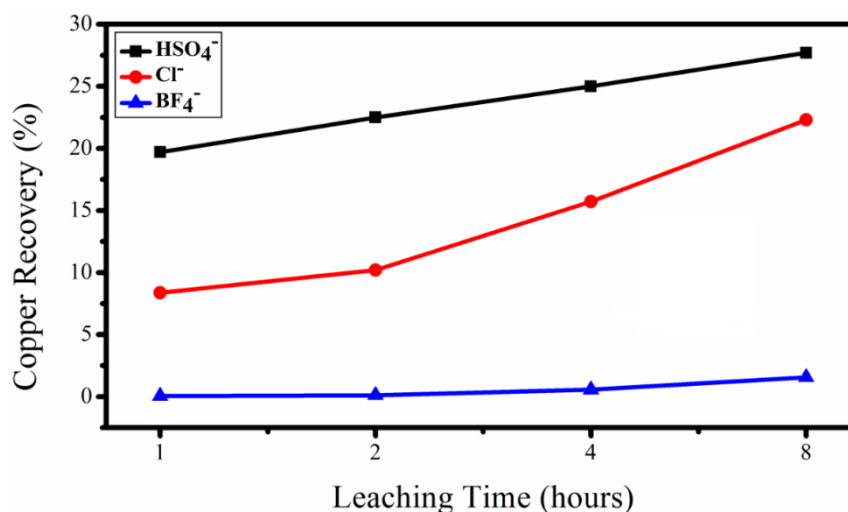


Figure 4: The effect of leaching time on copper recovery of from copper anode slime in the presence of 1-butyl-3-methylimidazolium ionic liquid with different anions.

As seen in Fig., 4, the copper recovery increased with increasing leaching time for all ionic liquids. It has been observed that ionic liquid with HSO<sub>4</sub><sup>-</sup> anion gives best results at all leaching temperatures. Even if the copper recovery increased by increasing leaching time with BmimBF<sub>4</sub>, the copper recovery rate did not exceed 2% even after 8 hours of leaching time. In the experiments performed with BmimCl, the copper recovery raised gradually with increasing leaching time and reached 22.3% at the end of 8 hours leaching period. Also, Fig. 4 indicates that copper recovery increased linearly with increasing leaching time and the highest copper recovery was obtained by using BmimHSO<sub>4</sub> as

27.7% after 8 hour leaching time. According to the experimental results, the most effective ionic liquid on copper recovery from copper anode slime was determined as BmimHSO<sub>4</sub> and the least effective ionic liquid on copper recovery was found to be BmimBF<sub>4</sub>. In this study the copper recovery was investigated in the range of 1 – 8 hours at 50 °C and copper recovery rates remained very low. In order to increase the copper recovery from copper anode slime, higher leaching temperatures or longer leaching times can be employed for all ionic liquids. Moreover, oxidizing agent such as H<sub>2</sub>O<sub>2</sub>, Fe(III), K<sub>2</sub>SO<sub>4</sub> and HBF<sub>4</sub> could be used with BmimBF<sub>4</sub> [12].

### 3.3. Mineralogical structure of leach residual

In this study mineralogical structures of the secondary leach residues obtained after 8 hours of leaching experiments were analyzed by XRD in order to determine possible phase changes between the initial and the last state of the samples. XRD patterns of the anode slime as a starting material and the secondary leach residues were given comparatively in Fig 5. As stated before, the AS includes Cu<sub>2</sub>O, PbSO<sub>4</sub>, SnO<sub>2</sub>,

BaSO<sub>4</sub> and SbAsO<sub>4</sub> phases (seen also in Fig.5). As compared to starting AS phases with the phases of the secondary residues obtained after different ionic liquid leaching experiments, it is concluded that some Cu<sub>2</sub>O phases are disappeared or diminished due to the dissolution of copper-containing phases in BmimHSO<sub>4</sub> and BmimCl ionic liquid solution. It is observed from Fig. 5 that other phases in AS were not dissolved in

BmimHSO<sub>4</sub> and were more visible after the dissolution of Cu<sub>2</sub>O phase. After leaching experiments with BmimCl ionic liquid, it was observed that PbSO<sub>4</sub> structure were slightly soluble.

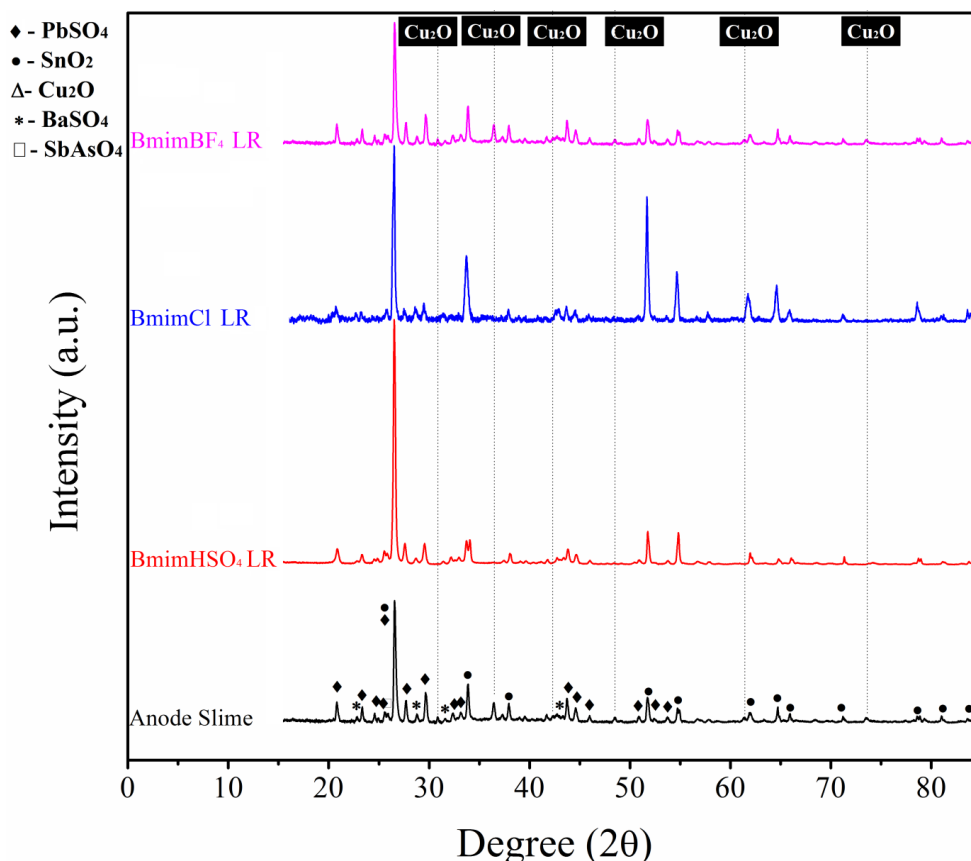


Figure 5: XRD pattern of anode slime and the leach residues obtained after leaching experiments with BmimHSO<sub>4</sub>, BmimCl and BmimBF<sub>4</sub>.

SnO<sub>2</sub> phases in leach residue obtained after BmimCl leaching became more apparent because of dissolution of Cu<sub>2</sub>O and PbSO<sub>4</sub> phases. After the leaching experiments with BmimBF<sub>4</sub> ionic liquid, it

was determined that there were no significant changes in the mineralogical structure of the anode slime due to the very low dissolution in the phases.

#### 4. Conclusion

In this paper, imidazolium based ionic liquids with various anions were used as leaching agent for copper recovery from anode slime. According to the chemical analysis of anode slime used as a copper source in the leaching experiments, high amount of copper, as 23.1%, was detected in anode slime. PbSO<sub>4</sub>, SnO<sub>2</sub> and Cu<sub>2</sub>O phases are found as major components by XRD analysis. As a result of leaching experiments, BmimHSO<sub>4</sub> was the most effective ionic liquids for copper recovery from anode slime and the highest copper recovery rate was obtained approximately 28% after 8 hours of leaching time at

50 °C. In addition, although close results were obtained after the experiments with BmimCl, it was determined that BmimBF<sub>4</sub> ionic liquid has little effect on copper recovery from anode slime. According to the XRD analysis of leach residues obtained after leaching experiment, copper bearing phases (Cu<sub>2</sub>O) are very soluble BmimHSO<sub>4</sub> and BmimCl ionic liquid solution. According to the results, it can be clearly stated that in the presence of BmimHSO<sub>4</sub> and BmimCl ionic liquids, copper recovery from anode slime can be successfully applied at high leaching temperatures and long leaching times.

#### References

- [1] Lei, Z., Chen, B., Koo, Y. M., & MacFarlane, D. R., (2017). Introduction: ionic liquids. *Chemical Reviews*, 117(10), 6633 – 6635.
- [2] Welton, T. (2018). Ionic liquids: a brief history.

- Biophysical Reviews, 10(3), 691-706.
- [3] Park, J., Jung, Y., Kusumah, P., Lee, J., Kwon, K., & Lee, C. K., (2014). Application of ionic liquids in hydrometallurgy. *International Journal of Molecular Sciences*, 15(9), 15320-15343.
- [4] Tian, G. C., Jian, L. I., & Hua, Y. X., (2010). Application of ionic liquids in hydrometallurgy of nonferrous metals. *Transactions of Nonferrous Metals Society of China*, 20(3), 513-520.
- [5] Whitehead, J. A., Zhang, J., Pereira, N., McCluskey, A., & Lawrance, G. A., (2007). Application of 1-alkyl-3-methyl-imidazolium ionic liquids in the oxidative leaching of sulphidic copper, gold and silver ores. *Hydrometallurgy*, 88(1-4), 109-120.
- [6] Dong, T., Hua, Y., Zhang, Q., Zhou, D., (2009). Leaching of chalcopryrite with Bronsted acidic ionic liquid, *Hydrometallurgy*, 99, 33-38.
- [7] Huang, J., Chen, M., Chen, H., Chen, S., Sun, Q., (2014) Leaching behavior of copper from waste printed circuit boards with Brønsted acidic ionic liquid'', *Waste Management*, 34, 483-488.
- [8] Rüßen, A., & Topcu, M. A. (2017). Optimization of gold recovery from copper anode slime by acidic ionic liquid. *Korean Journal of Chemical Engineering*, 34(11), 2958-2965.
- [9] Rüßen, A., & Topçu, M. A. (2017). EmimHSO<sub>4</sub> (1-Etil-3-Metil-İmidazolyum Hidrojen Sülfat) iyonik sıvısının anot çamurundan bakır geri kazanımı üzerine etkisi. *Afyon Kocatepe Üniversitesi Fen Ve Mühendislik Bilimleri Dergisi*, 17(2), 696-703.
- [10] Lee, J. C., Kurniawan, K., Chung, K. W., & Kim, S. (2020). Metallurgical Process for Total Recovery of All Constituent Metals from Copper Anode Slimes: A Review of Established Technologies and Current Progress. *Metals and Materials International*.
- [11] Liu, G., Wu, Y., Tang, A., & Li, B. (2020). Recovery of scattered and precious metals from copper anode slime by hydrometallurgy: A review. *Hydrometallurgy*, 197, 105460.
- [12] Topçu, M. A., Rüßen, A., & Küçük, Ö. (2019). The Effect of Reaction Time on Copper Recovery from Anode Slime by Using BmimBF<sub>4</sub> 1-Butyl-3-Methylimidazolium Tetrafluoroborate Ionic Liquid. Presented at the 4th International Energy and Engineering Congress, Gaziantep.