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COPPER RECOVERY FROM WASTE PRINTED CIRCUIT BOARDS AND THE CORRELATION OF Cu, Pb, Zn BY IONIC LIQUID

Waste printed circuit boards (WPCBs) contain not only harmful materials but also many valuable resources, especially metals, which attracts more and more attention from the public. In this study, a sulfonic acid functionalized ionic liquid ([BSO₃HPy]OTf) was used to recycle copper from WPCBs. Zinc and lead, represented as typical heavy metals, were chosen to study the leaching behavior and their relation to copper. Five factors such as particle size, ionic liquid (IL) concentration, H₂O₂ dose, solid to IL ratio and temperature were investigated in detail. The results showed that copper leaching rate was high, up to 99.77%, and zinc leaching rate reached the highest value of 74.88% under the optimum conditions. Lead cannot be leached effectively and the leaching rate was mostly low than 10%, which indirectly indicated that [BSO₃HPy]OTf has a good selectivity to lead. Besides, the interaction of copper, lead and zinc was characterized macroscopically by means of statistical methods. The Spearman correlation analysis showed that copper and zinc had a highly positive correlation. Lead had little relation to copper, which to some extent indicated that the effect of zinc on copper leaching behavior was bigger than that of lead.

1. INTRODUCTION

In the last decades, the revolution of global information communication technology (ICT) industry is accelerating and electrical and electronic products have become an indispensable part in people's daily life [1]. The fast renewal of electronic products and the change of people's consumption concept continuously shorten the actual service life of electronic products, thereby leading to huge amounts of waste electronic and electric equipment (WEEE). It is reported that WEEE generation is 2 or 3 times faster than other municipal solid wastes [2]. According to the report released by the United Nations University in April 19th, 2015, global electronic waste in 2014 has an increase of 5.0%

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compared to 39.8 million metric tons in 2013, reaching to 41.8 million metric tons. However, the recycle of global e-waste is less than one in six in 2014 [3].

Waste printed circuit boards (WPCBs) are the basic components of almost all WEEE, e.g., household appliances, personal computers and mobile phones. Thus, the recovery of WEEE is more inclined to the recycling of WPCBs [4]. WPCBs consist of environmentally poisonous materials such as persistence organic pollutants (POPs) and heavy metals (Pb, Cd, Cr). If not treated appropriately, it could badly threaten environment and human health [5]. In other sides, electronic wastes as the effective secondary resources contain many valuable substances. For example, a typical WPCBs constitute by more than 70 wt. % non-metal (i.e., plastic, resins, glass fibers) and metals (copper 16 wt. %, iron 3 wt. %, nickel 2 wt. %, silver 0.05 wt. %, gold 0.03 wt. % and palladium 0.01 wt. %) [6]. Generally copper content in WPCBs is much higher than that of other metals, and the market demand for copper increases year and year [7], which makes copper an important economic driver. Therefore, the recycling of WPCBs is an urgent environmental problem to be solved not only from the perspective of environmental protection but also the resource reuse.

Many researchers have studied the recycling of WPCBs, including the mechanical-physical process [8, 9], pyrometallurgy [10], hydrometallurgy [11, 12] and biometallurgy [13, 14]. The mechanical-physical process is the most widely used for the industrial treatment but it is usually as the preparation due to the limitation of metal alloy separation. The development of pyrometallurgy, a traditional technology for recycling precious metals from WPCBs, is restricted by the emission of harmful gases and high-energy consumption. Nowadays, biometallurgy is regarded one of the promising technologies due to the less capital investment, energy consumption and labor need. However, only few species are found for the treatment of WPCBs and microorganisms are also hard to cultivate. Thus, hydrometallurgy obtains more and more attention due to its moderate working conditions and high metal recovery. Leaching is the most common disposal procedure in hydrometallurgy, and the common leaching systems for metal recovery include sulfuric acid [15], nitric acid [16], hydrochloric acid [17], ammonia [18]. However, common inorganic solvents will result in amounts of waste acid or alkali solutions, which is hard to treat.

Recently the study about ionic liquid (IL) provides a new possibility for the pollution-free hydrometallurgical process [19, 20]. Ionic liquids, also called room temperature ionic liquids (RTILs), are known as a perspective green solvent because of special properties, such as negligible volatility, low toxicity, thermal stability, high conductivity and wide electrochemical window. In this work, we choose [BSO₃HPy]OTf, a sulfonic functionalized acid ionic liquid, to leach copper from WPCBs and simultaneously study the relationship of copper, lead and zinc leaching behavior during the leaching process, aiming to determine the optimum experimental conditions for copper recovery.

2. MATERIALS AND METHODS

Sample preparation. WPCBs in the experiment originated from waste computers. First, the motherboards were cut into 50 mm×50 mm pieces using a high speed cutting machine (XQPI-66, China). Next, these coarse fractions were further shredded in a Retsch SE-2000 Cutting Mill (Retsch, Germany). Finally, a standard sieve was used to separate the crushed materials into five fractions: F₁ (<0.075 mm), F₂ (0.075 mm–0.1 mm), F₃ (0.1 mm–0.25 mm), F₄ (0.25 mm–0.5 mm), and F₅ (>0.5 mm).

Experiments. All the experiments were carried using a constant temperature water bath oscillator for 2 h, which kept at a fixed oscillating frequency of 250 rpm. The ionic liquid, [BSO₃HPy]OTf (N-sulfobutylpyridinium trifluoromethanesulfonate, ≥98.5%), was provided by Lanzhou Institute of Chemical Physics, Chinese Academy of Science. 30 wt. % hydrogen peroxide was used as the oxidant. After each leaching experiment, the lixivium was filtered by means of a vacuum suction device and filtrate was preserved for analyses. WPCBs powders were digested using a HNO₃–H₂O₂–HF system to obtain metals [21]. Metal concentration was tested using an inductively coupled plasma optical emission spectrometer (ICP-OES, Perkin Elmer, Optima 8300).

The chemical reagents used in the experiment were all analytical grade and the detailed experiment arrangements are showed in Table 1.

Table 1

Detailed experimental arrangements

Factor	Level
Particle size, mm	F ₁ (<0.075 mm), F ₂ (0.075–0.1 mm), F ₃ (0.1–0.25 mm), F ₄ (0.25–0.5 mm), F ₅ (>0.5 mm)
Temperature, °C	40, 50, 60, 70
H ₂ O ₂ dose, cm ³ /20 cm ³	0, 2, 5, 7, 10, 15
IL concentration, vol. %	10, 20, 40, 60, 80
Solid/IL ratio, g/cm ³	1:2.5, 1:5, 1:7.5, 1:10, 1:15

To verify the validity of the data, all the experiments were conducted twice and mean values were given. The metal leaching rate was calculated as follows:

$$X_i = \frac{M_i}{M} \times 100\% \quad (1)$$

where X_i is the metal leaching rate, %, M_i is the metal weight extracted into the lixivium, g, M is the metal weight in WPCBs, g.

The Spearman correlation analysis was applied for the data analysis, aiming to figure out the relationship of copper, lead and zinc leaching behavior. Spearman correlation coefficient is an important index to measure the correlation degree of two samples, and the formula is as follows:

$$r_s = \frac{\sum_{i=1}^N (x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum_{i=1}^N (x_i - \bar{x})^2 \sum_{i=1}^N (y_i - \bar{y})^2}} \quad (2)$$

where r_s is the Spearman correlation coefficient, the value of $|r_s|$ closer to 1 means a higher correlation, N is the sample number, x_i and y_i are the metal leaching rates.

3. RESULTS AND DISCUSSION

3.1. EFFECT OF PARTICLE SIZE

The metal contents are given in Table 2. The copper content increases upon increasing particle size, and the highest copper content is 20.4 wt. % when particle size is over 0.5 mm. Zinc content shows a slight increase from 1.28 wt. % to 2.24 wt. % with the increase of particle size. Lead content fluctuates in the range of 0.6–1.6 wt. %, but it is still 10 times higher than the threshold of lead 0.1 wt. % according to the *Directive 2011/65/EU on the restriction of the use of certain hazardous substances (ROHS) in the electrical and electronic equipment* [22].

Table 2

Contents of Cu, Pb and Zn in WPCBs powders [wt. %]

Particle size [mm]	[Cu]	[Pb]	[Zn]
<0.075	6.75	1.67	1.28
0.075–0.1	6.87	0.97	1.23
0.1–0.25	10.3	1.29	1.30
0.25–0.5	19.6	1.42	2.21
>0.5	20.4	0.62	2.24

The results show that particle size has a vital effect on the distribution of metal content. According to the study of Guo et al. [23], metals in WPCBs are easy to deform and hard to break under loads, so they are mainly concentrated in the larger size. This is well consistent with the trend of copper and zinc content distribution. However, lead

content greatly differs from those of copper and zinc. One probable reason is the different metal breaking style, which is affected by metal ductility. Lead is classified as brittle metal, so it mainly enriches in relatively fine particle size.

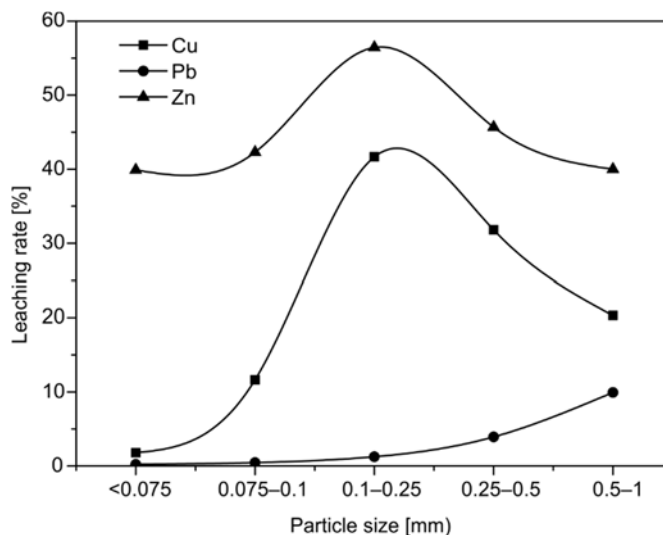


Fig. 1. Effect of particle size on the metal leaching rate (solid/IL ratio 1 g WPCBs/20cm³, IL concentration 10 vol. %, H₂O₂ dose 5 cm³/20 cm³, leaching temperature 50 °C, leaching time 2 h)

Particle size plays a vital role in the metal leaching, and most of recovery processes have a certain effective size range. As can be seen from Fig. 1, when particle size increases from <0.075 mm to 0.10–0.25 mm, copper and zinc leaching rates increase from 1.79% to 41.67% and from 39.9% to 56.45%, respectively. With the further increase of particle size, copper and zinc leaching rates decrease. It is reasonable that smaller the particle size is, higher the metal leaching rate, because the surface area of particle increases by the decrease of particle size, which is beneficial for the metal leaching. However, particle size below a critical value will result in particle–particle agglomerations, hindering the leaching liquid permeate through fine powders [24]. Obviously, the leaching behavior of copper and zinc is in agreement with the theoretical data. Lead leaching rate slightly increases from 0.22% to 9.93% when the particle size is more than 0.5 mm. As discussed before, lead mainly exists in finer powders, which is easy to unit. Therefore, the leaching rate is generally low.

3.2. EFFECT OF IL CONCENTRATION

IL as the lixiviant has an important influence on the metal leaching. All three metal (copper, zinc and lead) leaching rates increase upon the increasing IL concentration as

shown in Fig. 2. When IL concentration increases from 10 to 80 vol. %, copper and zinc leaching rates increase by 4–5 times, from 25.44% to 99.77% and from 16.68% to 74.88%, respectively. The leaching rate of lead only increases by 3.63% when the IL concentration increases up to 80 vol. %. Increasing IL concentration means strengthening the acidity of leaching solution, thereby improving the leaching efficiency.

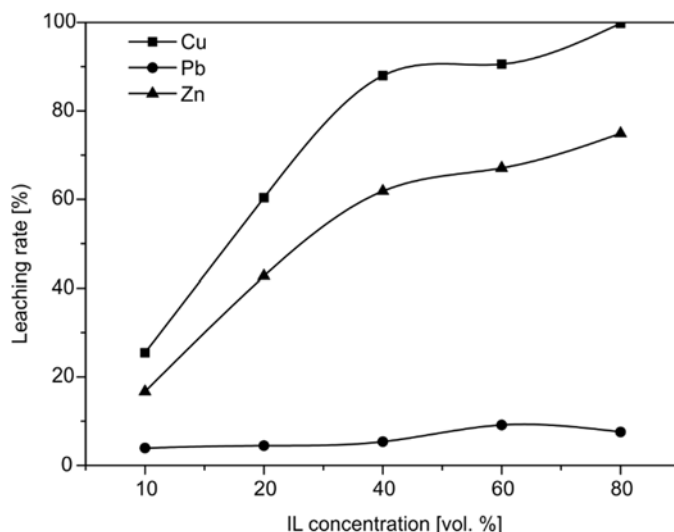
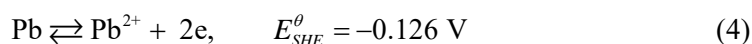
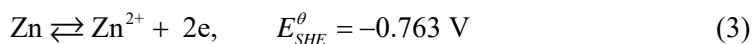


Fig. 2. Effect of IL concentration on the metal leaching rate (solid/IL ratio 1 g WPCBs/20 cm³, H₂O₂ dose 5 cm³/20 cm³, particle size 0.1 to 0.25 mm, leaching temperature 50 °C, leaching time 2 h)

Some researchers studied the leaching reaction of copper by inorganic acids. For example, Long Le et al. [16], who studied the recovery of metal using nitric acid, report that copper leaching rate increases upon increasing nitric acid concentration, and reaches nearly 99% when nitric acid concentration is 3.5 mol/dm³. In addition, lead leaching rate is still low and far lower than that of zinc despite the fact that the contents of both metals is similar under the experimental conditions. One possible explanation are differences in the standard electrode potentials of zinc and lead in the leaching solutions. Zinc is easier to be oxidized than lead:



The copper and zinc leaching rates increase quickly when IL concentration changes from 10 to 40 vol. %, then their increase rates tend to reach steady levels upon increasing IL concentration. This is determined by the characteristics of IL, at high concentration it becomes more viscous, which is not efficient in the metal leaching.

3.3. EFFECT OF H₂O₂ DOSE

Figure 3 shows that H₂O₂ dose has a significant effect on the metal leaching rate. For example, copper leaching rate increases upon increasing H₂O₂ dose, reaching the maximum value of 31.8% for H₂O₂ contents of 5 cm³/20 cm³. Then the copper leaching rate tends to be stable, around 26.70%.

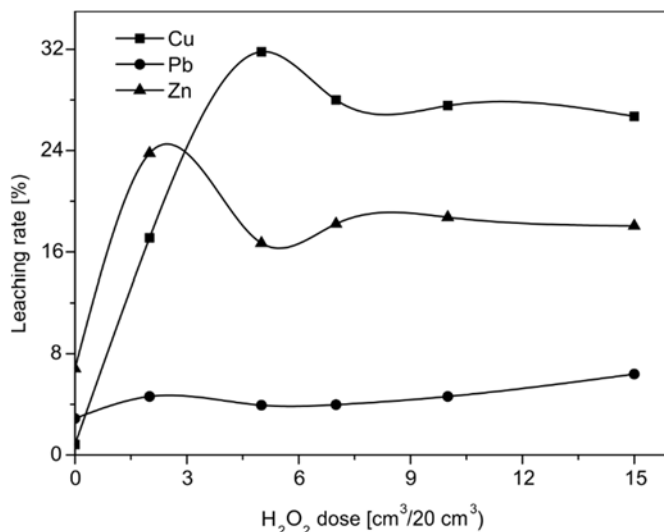


Fig. 3. Effect of H₂O₂ dose on the metal leaching rate (solid/IL ratio 1 g WPCBs/20 cm³, IL concentration 10 vol. %, particle size 0.10 to 0.25 mm, leaching temperature 50 °C, leaching time 2 h)

The leaching rate of zinc also increases upon increasing H₂O₂ dose, but it reaches the maximum already at 2 cm³/20 cm³ of H₂O₂ probably due to higher zinc activity than that of copper. It is easy to understand that the leaching rate increases upon increasing H₂O₂ dose, because H₂O₂ as the oxidant will decompose to produce oxygen and oxygen reacts with metal to form metallic oxide, which can further react with IL acid to be leached. However, excess of H₂O₂ may cause partial oxidation of IL, thereby affecting the leaching reaction. Lead leaching rate remains relatively constant at a low level, reaching the maximum of 6.39% when the H₂O₂ dose is 15 cm³/20 cm³.

3.4. EFFECT OF SOLID/IL RATIO

Solid to IL ratio has an apparent impact on the metal leaching rate as illustrated in Fig. 4. Cu and Zn leaching rates show similar tendencies, and both increase significantly upon decreasing solid/IL ratio. For example, when solid/IL is diminished from 1/2.5 to 1/15 g/cm³, the copper leaching rate increases from 11.98 to 87.21% and zinc leaching

rate from 9.61 to 73.41%. The decrease of solid/IL, to some extent means increasing the IL volume, which makes the contact between WPCBs powder and leaching solution easier. This improves the efficiency of mass transfer to accelerate the metal leaching. The result is in accordance with the results of other authors who used inorganic acids. For example, Calgaro et al., who used sulfuric acid to recycle copper from WPCBs, reported that the copper leaching rate sharply increases when solid/liquid ratio decreases from 1/10 to 1/30 [15].

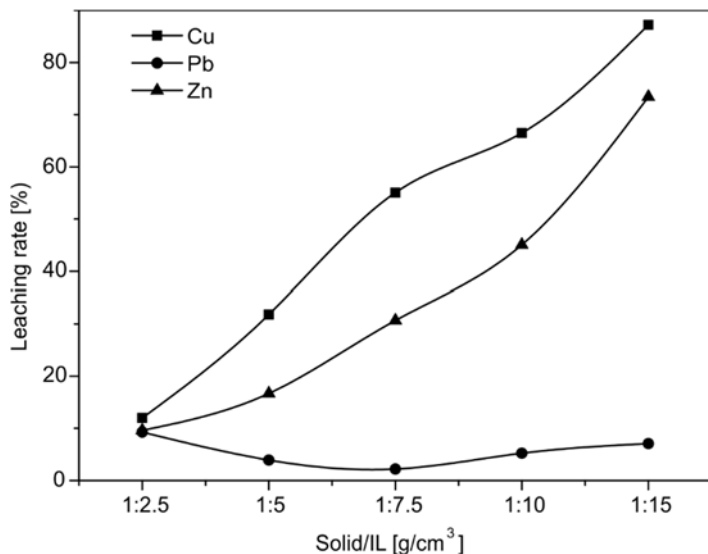


Fig. 4. Effect of solid/IL on metal leaching rate (IL concentration 10 vol. %, H₂O₂ dose 5 cm³/20 cm³, particle size 0.10 to 0.25 mm, leaching temperature 50 °C, leaching time 2 h)

However, the leaching rate of lead still is low, generally at around 7.0%. A possible explanation is that the standard electrode potential (Pb/Pb⁴⁺, $E^\theta = 0.784$ V at 25 °C) is very high, and lead is classified as moderately stable metal from the thermodynamic point of view. The reaction between lead and IL is very slow, thus the lead leaching rate is always very low. In other words, this data also shows the selectivity of IL to lead.

3.5. EFFECT OF TEMPERATURE

Figure 5 shows the effect of temperature on the metal leaching rate. It can be seen that the leaching behavior of copper, lead and zinc vary greatly. When temperature increases from 40 °C to 60 °C, the copper leaching rate changes negligibly and the zinc leaching rate moderately increases from 6.11 to 11.14%. Further heating to 70 °C causes both copper and zinc leaching rates to decrease. However, the leaching rate of lead shows a sharp decrease from 27.57 to 7.24% as the temperature increases from 40 to 50 °C, and it appears to be

steady, about 7.28%, when temperature increases to 70 °C. This could indicate that lower temperature is more beneficial to lead leaching reaction.

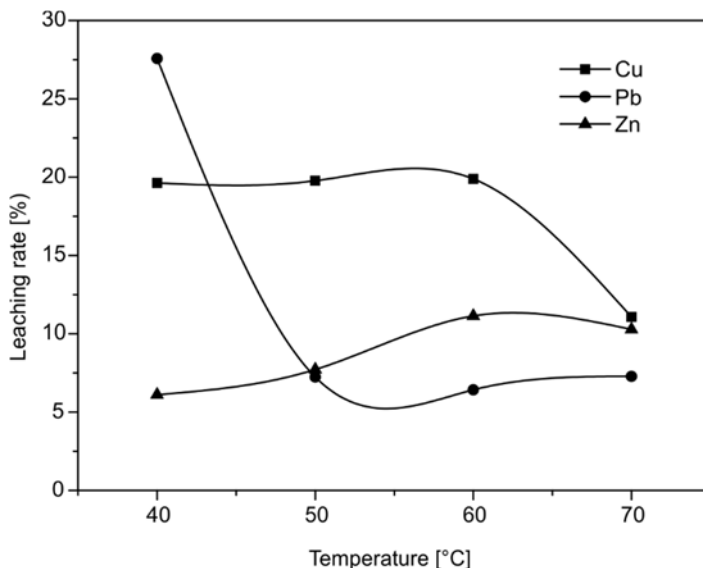


Fig. 5. Effect of temperature on the metal leaching rate (solid/IL ratio 1 g WPCBs/20 cm³, IL concentration 10 vol. %, H₂O₂ dose 5 cm³/20 cm³, particle size 0.10–0.25 mm, leaching time 2 h)

In general, elevated temperatures favor leaching reactions, but it obviously is not the case. Probably increasing temperature will boost decomposition of H₂O₂ and at the same time the solubility of oxygen produced by H₂O₂ in solution also reduces. On the other hand, according to the study on the properties of IL [25], increasing temperature will decrease the viscosity of IL and to some extent this does favor the leaching reaction. IL is a complex organic synthetic substance, and its interaction with metal under various conditions still needs further study.

3.6. EFFECT OF PB AND ZN ON CU LEACHING

In this study, IL ([BSO₃HPy]OTf) was used to recycle copper, however other metals were also leached, e.g., zinc and lead, showing that ILs just like many other inorganic acid have not good selectivity to single metals. Therefore, some relationship of the leaching behaviors between copper and other metals from a macro point of view have been investigated. The overall data under similar conditions on different metals were analyzed by the statistical analysis. The Spearman correlation analysis method was chosen and carried out with the IBM SPSS Statistic 21 software considering the type of data.

Table 3

Spearman correlation analysis between leaching rates of Cu, Pb, and Zn

r_s	Cu	Pb	Zn
Cu	1		
Pb	0.04	1	
Zn	0.735 ^a	-0.15	1

^aAt 0.01 levels (bilateral) were significantly correlated (sig = 0).

The correlation coefficients between the leaching rates of Cu, Pb, and Zn are listed in Table 3. There is a highly positive correlation, around 0.735, between copper and zinc leaching rate at the confidence level of 0.01. The result shows that copper and zinc have similar leaching behavior, which can also be seen from the discussion before. In other words, the leaching of copper and zinc affect each other interactively. There is an extremely low correlation between copper and lead leaching rate. The lead leaching rate is always low during the whole leaching process, which shows this kind of IL has a good selectivity to lead. The correlation results indicate however that lead has little effect on copper leaching rate and it has an adverse effect on zinc leaching. All in all, applying statistical methods to research the leaching behavior of different metals may provide a new way of thinking to further improve the recovery rate and purity of the target metal.

4. CONCLUSIONS

Acid ionic liquid (IL) – [BSO₃HPy]OTf was used to leach metals from waste printed circuit boards. The results show that copper can be successfully leached, and the maximum leaching rate reaches up to 99.77% when solid/IL ratio is 1 g WPCBs/20 cm³, IL concentration 80 vol. %, H₂O₂ dose 5 cm³/20 cm³, particle size 0.1 to 0.25 mm, leaching temperature 50 °C and leaching time 2 h. During the whole leaching process, Cu and Zn show a similar leaching behavior. The leaching rate of copper and lead firstly increases and then begins to decrease upon increasing particle size and H₂O₂ dose. The decrease of solid/IL ratio and increase of IL concentration cause continuous increase of Cu and Zn leaching rates. However, the lead leaching rate is low during the whole process, which shows that [BSO₃HPy]OTf cannot leach lead from WPCBs. The reaction mechanism between IL and metals is still not clear, which is worth further studies considering the good characteristics of ILs as green leaching agents.

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