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## Comparative study on copper leaching from waste printed circuit boards by typical ionic liquid acids

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## ABSTRACT

Waste printed circuit boards (WPCBs) are attracting increasing concerns because the recovery of its content of valuable metallic resources is hampered by the presence of hazardous substances. In this study, we used ionic liquids (IL) to leach copper from WPCBs. [BSO<sub>3</sub>HPy]OTf, [BSO<sub>3</sub>HMIm]OTf, [BSO<sub>4</sub>HPy]HSO<sub>4</sub>, [BSO<sub>4</sub>HMIm]HSO<sub>4</sub> and [MIm]HSO<sub>4</sub> were selected. Factors that affect copper leaching rate were investigated in detail and their leaching kinetics were also examined with the comparison of [Bmim]HSO<sub>4</sub>. The results showed that all six IL acids could successfully leach copper out, with near 100% recovery. WPCB particle size and leaching time had similar influences on copper leaching performance, while IL acid concentration, hydrogen peroxide addition, solid to liquid ratio, temperature, showed different influences. Moreover, IL acid with HSO<sub>4</sub><sup>-</sup> was more efficient than IL acid with CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>. These six IL acids indicate a similar behavior with common inorganic acids, except temperature since copper leaching rate of some IL acids decreases with its increase. The results of leaching kinetics studies showed that diffusion plays a more important role than surface reaction, whereas copper leaching by inorganic acids is usually controlled by surface reaction. This innovation provides a new option for recovering valuable materials such as copper from WPCBs.

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### 1. Introduction

Waste electric and electronic equipment (WEEE), also called as electronic waste or e-waste, has been attracting more and more concerns from scientists, entrepreneurs, journalists to governors all over the world. First WEEE is increasing sharply due to the technology innovation and shorter life spine, e.g., the lifespan of a personal computer (PC) and a central processing unit (CPU) decreased from 4.5 to 2–3 years (1992–2005) and from 4–6 to 2 years (1997–2005), respectively (Yazici and Deveci, 2013). E-waste generation, 3–5% of the total solid waste, is 2–3 times faster than solid wastes (U.S.-EPA, 2008; Erust et al., 2013). According to the United States Environmental Protection Agency (US-EPA), it is estimated that approximately 500 million computers were discarded annually between the years 2000 and 2007. Second, e-waste is known to all because of its notorious pollution caused by artisanal recycling. Guiyu, a small town in Guangdong Province, in the south of China,

is severely contaminated because people there recycle resources from e-waste by artisanal mining (Duan et al., 2011a). The concentrations of polybrominated diphenyl ethers (PBDEs) and polybrominated dibenzo-p-dioxins, dibenzofurans (PBDD/Fs) there were about 58–691 ng/g, 30 times higher than other urban sites (Duan et al., 2011b; Nguyen Minh et al., 2013). Heavy/toxic metals (Kolias et al., 2014; Maragkos et al., 2013; Oguchi et al., 2012), such as lead, cadmium, chromium, and persistence organic pollutants, e.g., polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polybrominated biphenyls (PBBs), polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), were found in surface water, underground water, soil, atmosphere, sludge under the river. More seriously, these highly toxicants were all found in human's blood, hair, urine, including fetus, gravely threatening the environment and human health (Huo et al., 2007; Leung et al., 2008; Zhao et al., 2008). The last reason and also the motivation is that WEEE contain valuable metals, mainly copper and precious metals (gold, silver and platinum) in particular. For example, copper (20%) and gold content (250 g/t) of a typical personal computer printed circuit board (PCB) are much higher

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than that of a copper or gold ore, i.e., 20–40 fold and 25–250 fold, respectively (Christian, 2006).

The key to WEEE recycle is waste printed circuit boards (WPCBs), which is an essential part of almost all electric and electronic equipment, such as laptops, air conditioners, TVs, etc. Therefore, both traditional and advanced methods, such as mechanical–physical approaches, especially corona electrostatic separation which has obtained great success in China (Li and Xu, 2010), hydrometallurgy (Kim et al., 2011), pyrometallurgy (Zhan and Xu, 2008), bioleaching (Yang et al., 2014) and sub/supercritical fluid (Xiu and Zhang, 2010), are widely discussed for the recovery of metals from WPCBs. Among these processes, hydrometallurgical processes offer high metal selectivity and recovery with a flexible mode of operation and suitability for small scale applications, making it an attractive alternative for the treatment of WPCBs. In previous studies, different lixiviant systems, including sulfuric acid, hydrochloric acid, nitric acid, iodide, ammonia, cyanide, thiourea, thiosulphate and microbes, were examined (Huang et al., 2014; Li et al., 2012; Oishi et al., 2007; Hu et al., 2006; Yang et al., 2011). In most cases, an oxidant, usually hydrogen peroxide ( $H_2O_2$ ) and ferric ( $Fe^{3+}$ ) due to their high reduction potentials of 1.78 V and 0.77 V, was involved given that metals in WPCBs are found in native and/or alloy form (Birloaga et al., 2013). However, there has been no process solely based on hydrometallurgical methods at the industrial scale (Yazici and Deveci, 2013).

Recently, Zhu et al. found a novel method to recycle resources from WPCBs, using organic solvent dimethyl sulfoxide (DMSO) or ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate ( $[EMIM^+][BF_4^-]$ ) to dissolve bromine epoxy resin (Zhu et al., 2012a,b, 2013). Meanwhile, Zeng et al. also reported the use of water soluble ionic liquid 1-Butyl-3-methylimidazolium tetrafluoroborate ( $[BMIM]BF_4$ ) to melt solders, disassembling electric and electronic components from WPCBs (Zeng et al., 2013). Ionic liquids (ILs), also called as room temperature ionic liquids (RTILs), are basically liquid at low temperature. Typically, it consists of an organic cation with an inorganic or organic anion. ILs have a wide liquid temperature range and also possess numerous unique properties, such as negligible volatility, vapor pressure, thermal stability, high conductivity and wide electrochemical window. (Berenblyum et al., 2006). Currently, ILs were successfully applied in leaching metals from ores (Whitehead et al., 2007). However, the literature on leaching metals from WPCBs by ILs is limited.

In a previous study, Huang et al. found that 1-butyl-3-methylimidazolium hydrogen sulfate ( $[bmim]HSO_4$ ) could successfully leach copper out from WPCBs (Huang et al., 2014). At optimized conditions, copper leaching rate was up to 99%. This leaching process can be modeled by the shrinking core model, showing that it is controlled by diffusion. In order to obtain a detailed and fundamental understanding about leaching copper from WPCBs by ILs, five typical ionic acids were selected and the results were compared with published data using  $[Bmim]HSO_4$ . Factors that affect copper leaching efficiency, such as WPCBs particle size, IL acid concentration, liquid to solid ratio, leaching time and temperature were studied in detail. In addition, their leaching kinetics were also investigated.

## 2. Materials and methods

### 2.1. Sample preparation

First, WPCBs, without disassembling electronic components, were cut into small pieces, around 50 mm × 50 mm. Then it were further shredded using Retsch SM-2000 Cutting Mill (Retsch, Germany), and sieved into five fractions: F1 < 0.075 mm, 0.075 mm < F2 < 0.1 mm, 0.1 mm < F3 < 0.25 mm, 0.25 mm < F4 < 0.5 mm and F5 > 0.5 mm, as described elsewhere (Huang et al.,

2014). After that, the obtained powders were digested by microwave aided  $HNO_3$ – $H_2O_2$ –HF system (Yamasaki, 1997). Cu concentration of the digested solutions was analyzed by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, Thermo Scientific, iCAP 6500) and the results are shown in Table 1.

### 2.2. Leaching

All the leaching experiments were carried out in a batch of 250 mL glass conical flasks placed in a constant temperature water bath oscillator, using a constant oscillating frequency of 250 rpm at 40–70 °C. After each experiment, the leachate was filtered through a glass fiber filter of 0.45 μm pore size and preserved using 2 mL nitric acid before being analyzed by ICP-OES. Five ionic liquid acids,  $[BSO_4HPy]HSO_4$  (N-sulfobutylpyridinium hydrosulfate),  $[BSO_3HMIm]HSO_4$  (1-sulfobutyl-3-methylimidazolium hydrosulfate),  $[BSO_3HMIm]OTf$  (N-sulfobutylpyridinium trifluoromethanesulfonate),  $[MIm]HSO_4$  (Methylimidazolium hydrosulfate),  $[BSO_3HPy]OTf$  (1-sulfobutyl-3-methylimidazolium trifluoromethanesulfate), were provided by Lanzhou Institute of Chemical Physics, Chinese Academy of Science, and their structures as well as the structure of  $[bmim]HSO_4$  are given in Table 2. Hydrogen peroxide ( $H_2O_2$ , 30 wt.%) was used as oxidant. Chemicals used in the experiments were all analytical reagents unless otherwise mentioned. Factors that affect the leaching efficiency for the five IL acids were investigated separately, which were WPCBs particle size, IL acid concentration (V/V, in liquid solution), IL acid adding amount,  $H_2O_2$  adding amount, temperature and time, and the detailed parameters associated with each experiment are given in Table 3. When concerning about the reaction time, 2 mL suspension was sampled at certain fixed intervals and filtered by a 0.45 μm glass fiber filter prior to determination. Data of  $[bmim]HSO_4$  leaching system were cited from a previous study (Huang et al., 2014).

The copper leaching rate was expressed as the percentage of copper extracted into leaching solution from original specimen. For quality control, the relative standard deviations of the triplicates were in the limited ranges of a certified commercial laboratory and mean values are given in the Tables and Figures without error bar.

## 3. Results and discussion

### 3.1. Particle size

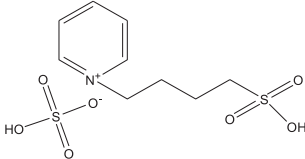
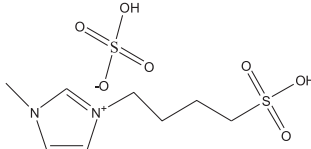
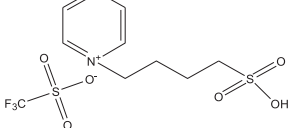
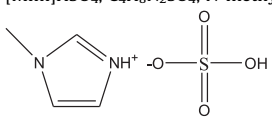
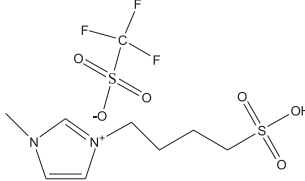
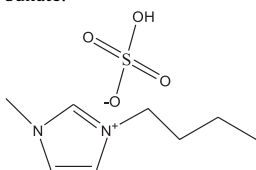
As it can be seen in Table 1, Cu content varies as WPCBs particle sizes, e.g., Cu concentration increases from 6.75% to 20.36% when WPCBs particle size increases from <0.075 mm to >0.5 mm. It is reasonable that the smaller the particle size, the lower the Cu content because, compared to polymers and ceramics, it is more difficult to smash metals to fine powders. This result consists with the study of Veit et al. (2006), which reported that copper enriched in the fraction of 0.5–1 mms. Since copper contained in the fraction of particle size >0.5 mm is the highest, this fraction was selected for the study of other sections.

Particle size plays a crucial role in metal recovery, and most of the recycling processes have a certain effective size range. Zhu et al. (2011) showed that the maximum leaching efficiency of

**Table 1**  
Copper contents in WPCBs specimens.

Particle size, mm	F1 (<0.075 mm)	F2 (0.075–0.1 mm)	F3 (0.1–0.25 mm)	F4 (0.25–0.5 mm)	F5 (>0.5 mm)
Cu wt.%	6.75	6.87	10.25	19.62	20.36

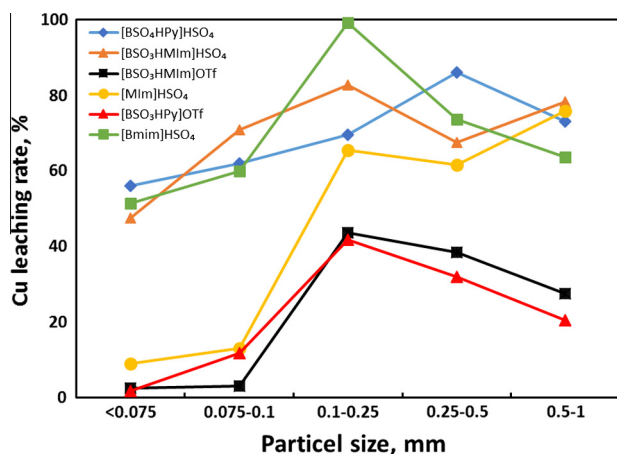
**Table 2**  
Ionic liquid acid used in this study.

[BSO <sub>4</sub> HPy]HSO <sub>4</sub> , C <sub>9</sub> H <sub>15</sub> NS <sub>2</sub> O <sub>7</sub> , N-butylsulfonate Pyridinium hydrosulfate:	[BSO <sub>3</sub> HMIIm]HSO <sub>4</sub> , C <sub>8</sub> H <sub>16</sub> N <sub>2</sub> S <sub>2</sub> O <sub>7</sub> , 1-sulfobuty-3-methylimidazolium hydrosulfate:
	
[BSO <sub>3</sub> HMIIm]OTf, C <sub>10</sub> H <sub>14</sub> NS <sub>2</sub> O <sub>6</sub> F <sub>3</sub> , N-sulfobutylpyridinium trifluoromethanesulfonate:	[MIm]HSO <sub>4</sub> , C <sub>4</sub> H <sub>8</sub> N <sub>2</sub> SO <sub>4</sub> , N-methylimidazolium hydrogen sulfate:
	
[BSO <sub>3</sub> HPy]OTf, C <sub>9</sub> H <sub>15</sub> N <sub>2</sub> S <sub>2</sub> O <sub>6</sub> F <sub>3</sub> , 1-sulfobutyl-3-methylimidazolium trifluoromethanesulfonate:	[Bmim]HSO <sub>4</sub> , C <sub>8</sub> H <sub>16</sub> N <sub>2</sub> SO <sub>4</sub> , 1-Butyl-3-methylimidazolium Hydrogen Sulfate:
	

**Table 3**  
Experimental arrangement.

Factors	Levels investigated
WPCBs particle size, mm	F1 (<0.075 mm), F2 (0.075–0.1 mm), F3 (0.1–0.25 mm), F4 (0.25–0.5 mm), F5 (>0.5 mm)
IL acid concentration, v/v	10%, 20%, 40%, 60%, 80%
IL acid adding amount, mL	2, 5, 10, 15, 20, 30
H <sub>2</sub> O <sub>2</sub> adding amount, mL	0, 2, 5, 7, 10, 15
Solid/liquid, g/mL	1:1, 1:2.5, 1:5, 1:7.5, 1:10, 1:15
Time, min	5, 10, 20, 30, 60, 120, 240, 480
Temperature, °C	40, 50, 60, 70

copper was obtained when the particle size was 60–80 mesh (about 18–25 mm). In this study, the effect of particle size on copper leaching rate is shown in Fig. 1. Generally, Cu leaching rate increases first and then decreases as the particles size increases for the six IL acids except [MIm]HSO<sub>4</sub>, which increases with the particles size in the whole investigated range. Take [Bmim]HSO<sub>4</sub> as an example, Cu



**Fig. 1.** Effect of particle size on copper leaching rate by ionic liquid acids.

leaching rate first increases from 51.25% to 99.17% when the particle size increases from <0.075 mm to 0.1–0.25 mm, then it decreases from 73.47% to 63.52% as particle size consecutively increases from 0.25–0.5 mm to >0.5 mm. Generally, copper leaching rate increases with the decrease of particle size because the surface area per unit mass is increased. However, the reduction of particle size below a critical level would increase the particle–particle collision and impose severe attrition (Zhu et al., 2011), hindering the leaching liquid permeates through the fine WPCBs powders. Therefore, copper leaching rate of particle size of <0.075 mm and 0.075–0.1 mm is lower than that of 0.1–0.25 mm.

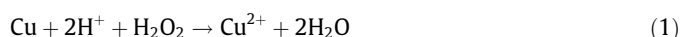
What should also be pointed out is that, for the six IL acids, Cu leaching rate of [BSO<sub>4</sub>HPy]OTf and [BSO<sub>3</sub>HMIIm]OTf is lower than that of [BSO<sub>4</sub>HPy]HSO<sub>4</sub>, [BSO<sub>4</sub>HMIIm]HSO<sub>4</sub> and [Bmim]HSO<sub>4</sub>, while [MIm]HSO<sub>4</sub> is in the middle. One conclusion can be drawn from this phenomena is that, among these six IL acids, compared to the IL acid with CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>, it is much easier for the IL acid with HSO<sub>4</sub><sup>-</sup> to leach copper out from WPCBs powders. Usually, according to the inductive effect, the electron-withdrawing power and electron-donating power, IL acid, whose cation part possesses a structure of butanesulfonate, shows a stronger acidity than those cation part with an ordinary carbon chain; and second, IL acid, the negative part of which possess a structure of trifluoromethanesulfonate, shows a stronger acidity than those anion with a hydrosulfate structure. What should be emphasized is that these two rules are referred to organic acids but not inorganic acid, usually, the acidity of which is stronger than that of organic acid. Therefore, as shown in Table 2, a possible line based on acidity from the strongest to the weakest for the six investigated IL acids could be: [BSO<sub>4</sub>HPy]HSO<sub>4</sub> > [BSO<sub>3</sub>HMIIm]OTf, [BSO<sub>3</sub>HMIIm]HSO<sub>4</sub> > [Bmim]HSO<sub>4</sub> > [MIm]HSO<sub>4</sub> > [BSO<sub>4</sub>HPy]OTf. Since IL acid with HSO<sub>4</sub><sup>-</sup> could release H<sup>+</sup> to SO<sub>4</sub><sup>2-</sup> and IL acid with CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> is organic acid, copper leaching rate of the former should be higher than the latter, which consists with our experimental results. The details of copper leaching rate will be further discussed in the kinetics section.

### 3.2. Ionic liquid acid concentration

The effect of IL acid concentration (IL acid/water, V/V%) on copper leaching rate is shown in Fig. 2. As shown in Fig. 2, almost all the copper leaching rates increase with the increase of IL acid

concentration for all the six IL acids, except [MIm]HSO<sub>4</sub>. For example, for [BSO<sub>3</sub>HPy]OTf, when its concentration increases from 10% to 40%, copper leaching rate increases rapidly from 25.44% to 87.96% and then it increases with a much lower rate to almost 100% as [BSO<sub>3</sub>HPy]OTf concentration continuously increasing to 80%. This is the same as other lixiviant systems. Hoang et al. reported that when nitric acid concentration was increased from 1.2 to 3.5 mol/L, copper leaching increased from 72.3% to 99% in 60 min time (Hoang et al., 2011). Yang et al. (2011) also found the same phenomena when sulfuric acid was used. It's confused that copper leaching rate decreases with the increase of [MIm]HSO<sub>4</sub> since usually it should increase as the increase of lixiviant, as described in this work for other 5 IL acids and reported on other studies (Hoang et al., 2011; Yang et al., 2011; Zhu et al., 2011). Reasons for this should be further studied.

As it is demonstrated in Fig. 2 that copper leaching is not significantly affected by IL acid concentration for these three since in the whole investigated range of IL acid concentration, from 10% to 80%, copper leaching rate for this three IL acids does not increase significantly. For example, copper leaching rate slightly increases from 73% to 83% as [Bmim]HSO<sub>4</sub> concentration increased from 10% to 80% (v/v). On the other hand, for [BSO<sub>3</sub>HPy]OTf and [BSO<sub>3</sub>HMIIm]OTf, copper leaching rate for these two IL acids first increases rapidly from 38.29% and 25.44% to 89.62% and 87.96%, respectively, when their concentration increases from 10% to 40%, and then increases steadily to around 100% when [BSO<sub>3</sub>HPy]OTf and [BSO<sub>3</sub>HMIIm]OTf concentration increases to 80%. According to Dong and his coworkers (Dong et al., 2009), who carried out the experiment of leaching copper directly from the chalcopyrite with ionic liquid [bmim]HSO<sub>4</sub> with dissolved oxygen as oxidant, IL acids here act like nitric acid, and hydrogen peroxide played as oxidant (Whitehead et al., 2007). Then, the overall reaction for copper dissolution can be expressed as:



According to Eq. (1), hydrogen ion concentration was already overdose when IL acid concentration of [BSO<sub>4</sub>HPy]HSO<sub>4</sub>, [BSO<sub>3</sub>HMIIm]SO<sub>4</sub> and [Bmim]HSO<sub>4</sub> in aqueous solution was 10%. Thus, copper leaching rate of this three IL acids would not be affected significantly under the experimental conditions in this study. For [BSO<sub>3</sub>HMIIm]OTf and [BSO<sub>3</sub>HPy]OTf, they are organic acid, whose acidity is much lower than these three IL acids with HSO<sub>4</sub><sup>-</sup> that can instantly release H<sup>+</sup> in aqueous solution. Hence, they show a similar phenomenon as reported by Dong et al. (2009).

### 3.3. Effect of H<sub>2</sub>O<sub>2</sub> dosage

Fig. 3 presents the copper leaching rate with the variation of hydrogen peroxide. It can be seen from Fig. 3 that copper leaching

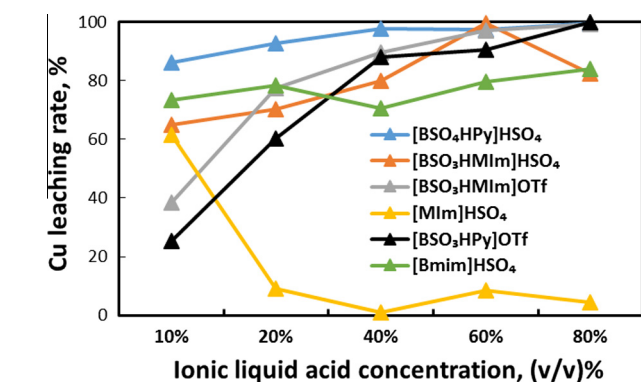


Fig. 2. Effect of Ionic liquid acid concentration on copper leaching rate.

rate increases with the increase of hydrogen peroxide adding amount until it reaches to or over 5 mL. According to previous studies, oxygen, from the decomposition of hydrogen peroxide, reacts with metal copper to form cupric oxide, which further reacts with IL acid to form cupric sulfate (Yang et al., 2011; Zhu et al., 2011). Then, IL acid and hydrogen peroxide together act as the reactants. Therefore, copper leaching rate increases with the increase of their concentrations. However, from Fig. 3, further increasing hydrogen peroxide, copper leaching rate decreases, especially for [BSO<sub>3</sub>HMIIm]HSO<sub>4</sub>, which decrease from 65.01% to around 1% when hydrogen peroxide adding amount increases from 5 mL to 10 or 15 mL. This is quite different from other inorganic acid leaching system (Yang et al., 2011, 2014). Overdosed hydrogen peroxide may cause the oxidation of IL acid since it decomposes to release fresh oxygen.

### 3.4. Effect of Solid to liquid ratio

Fig. 4 gives the effect of solid to liquid ratio on copper leaching rate for the six IL acids. For the other four IL acids with HSO<sub>4</sub><sup>-</sup>, copper leaching rate increases first and then decreases as the decrease of solid/liquid in the investigated range. [MIm]HSO<sub>4</sub> is a typical example, copper leaching rate of which first increased from 3.71% to 61.58% when solid/liquid was decreased from 1:1 to 1:5, and then decreased to 3.11% as solid/liquid consecutively decreased to 1:10. A lower solid/liquid ratio is favorable for the extraction of copper since increasing the volume of leaching solution could increase the efficiency of mass transfer, thus accelerating the copper recovery. However, an over low solid/liquid ratio is not conducive to the extraction of copper, as shown in Fig. 4, for the four IL acids. On the other hand, copper leaching rate of [BSO<sub>3</sub>HMIIm]OTf and [BSO<sub>3</sub>HPy]OTf increases steadily from 2.31% and 3.42% to 99.86% and 87.21%, respectively, as solid/liquid increases from 1:1 to 1:15. Thus the optimum solid/liquid ratio for [BSO<sub>4</sub>HPy]HSO<sub>4</sub>, [BSO<sub>3</sub>HMIIm]SO<sub>4</sub>, [Bmim]HSO<sub>4</sub>, [MIm]HSO<sub>4</sub>, [BSO<sub>3</sub>HMIIm]OTf and [BSO<sub>3</sub>HPy]OTf is 1:5, 1:10, 1:7.5, 1:5, 1:15 and 1:15.

### 3.5. Effect of temperature

Fig. 5 demonstrates the relationship between copper leaching rate and reaction temperature. The results indicate that temperature plays an important role in copper leaching rate: (1) Temperature has no significant impact on the copper leaching rate for [BSO<sub>3</sub>HPy]OTf when it is in a range from 40 °C to 70 °C; (2) Copper leaching rate decreases with the increase of temperature for [MIm]HSO<sub>4</sub> and [BSO<sub>4</sub>HPy]HSO<sub>4</sub>, especially for [BSO<sub>4</sub>HPy]HSO<sub>4</sub>, which decreases from around 100% at 40 °C to

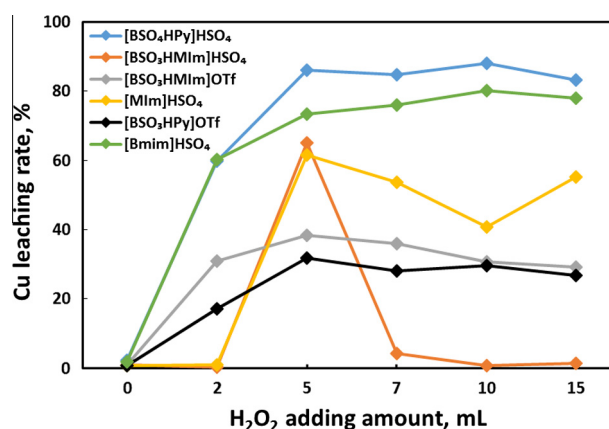


Fig. 3. Effect of hydrogen peroxide adding amount on copper leaching rate.

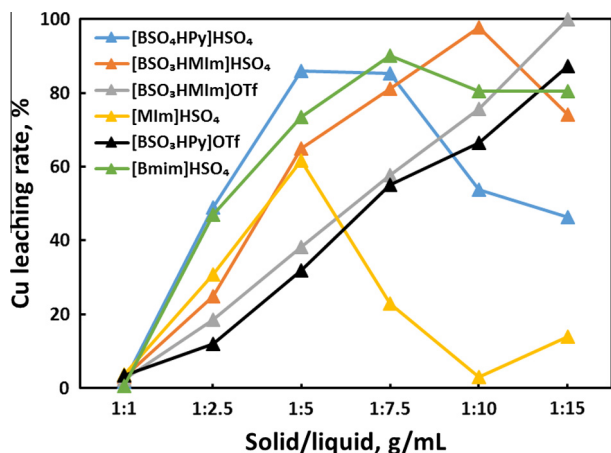


Fig. 4. Effect of solid to liquid ratio on copper leaching rate.

10.75% at 70 °C; (3) On the contrary, copper leaching rate of [Bmim]HSO<sub>4</sub> increases as increasing the temperature; (4) For [BSO<sub>3</sub>HMIm]OTf, copper leaching rate increases first and then decreases with the increase of reaction temperature. Generally, with the increase of reaction temperature, the reaction and the decomposition of hydrogen peroxide will be speeded. However, the content of dissolved oxygen in aqueous phase decreases (Gubbins and Walker, 1965). Therefore, temperature shows a different effect on the copper leaching rate for these six IL acids.

### 3.6. Effect of reaction time

The results of copper leaching rate by leaching versus time are presented in Fig. 6. Copper leaching rate of the six investigated IL acids increases as the time extension. For further investigation, kinetics analysis is conducted based on the relationship between copper leaching rate and time.

The rate of a reaction between a solid and a fluid such as the system considered here can be expressed by heterogeneous models. In a heterogeneous system, the overall rate expression becomes complicated because of the interaction between physical and chemical processes. To interpret the results of copper dissolution in this study, the kinetic has been assessed on the basis of the shrinking core model. According to this model, the following steps are considered to occur in succession during the dissolution:

- I. Lixiviant transports from the bulk of the solution to the fluid film which surrounds the solid.
- II. Lixiviant transports from fluid film to solid surface.
- III. Reaction on the surface between the lixiviant and the solid.

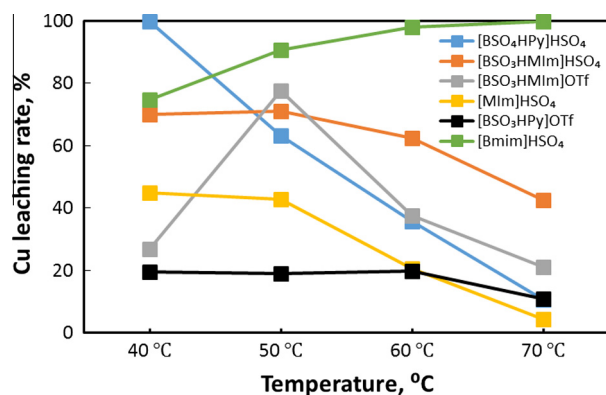


Fig. 5. Effect of leaching temperature on copper leaching rate.

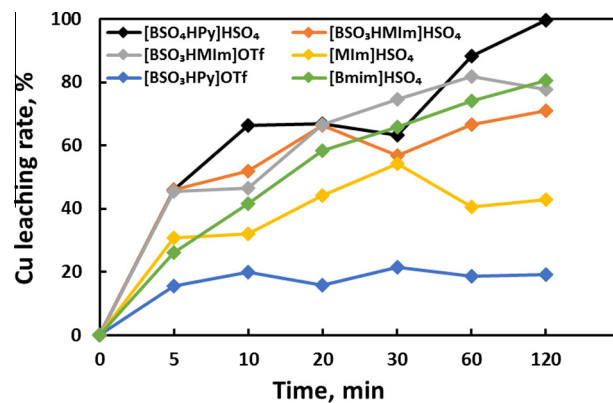


Fig. 6. Effect of leaching time on copper leaching rate.

IV. Formation of the products on the surface layer of the reaction zone and their transport from the interface into the fluid film.

V. Products transports into the bulk of the solution.

As the reaction proceeds, a product layer forms around the unreacted core. With the increase conversion of the unreacted core, the particle shrinks and the layer of the product thickens. The overall leaching process may be controlled by the mass transfer or the chemical reaction. In this model, (1) the solid reactant is considered to be non-porous with a spherical shape and its chemical properties at each direction is equal; (2) the aqueous solution is uniform and lixiviant concentration is assumed to be constant. Based on these assumptions, two models are used to describe the dissolution process:

$$1 - 2/3x - (1 - x)^{2/3} = kt \quad \text{for diffusion control} \quad (2)$$

$$1 - (1 - x)^{1/3} = kt \quad \text{for chemical reaction control} \quad (3)$$

where “ $x$ ” is copper leaching rate, “ $t$ ” is the reaction time (min or h) and “ $k$ ” is the apparent rate constant ( $\text{min}^{-1}$  or  $\text{h}^{-1}$ ).

Eqs. (2) and (3) shows that if the leaching reaction is controlled by mass transfer or the surface reaction, there must be a linear relationship between the left side of equation and time. The fit data for Eq. (3) is extremely week, which are not given. Thus, leaching copper from WPCBs by these six IL acids could not be controlled by surface chemical reaction. In fact, such process by inorganic acids usually control by surface chemical reaction (Habbache et al., 2009).

If the rate limiting step is diffusion, Eq. (2) was applied and a much better fit result was obtained, as presented in Fig. 7. However, Fig. 7 demonstrates that only two IL acids, [BSO<sub>3</sub>HMIm]OTf and [Bmim]HSO<sub>4</sub>, indicate a good linear fit. The third is [BSO<sub>4</sub>HPy]HSO<sub>4</sub>. The rest does not fit well. Hence, apparent rate constants and values of activation energies are also not provided here. One conclusion can be drawn from these results is that diffusion plays a more important role than surface reaction.

Research on leaching kinetics has difficulties, especially for most multiphase systems because too much physical and chemical factors to be considered. Moreover, modeling usually means simplification, as mentioned previously. In this study, some IL acids need hydrolysis to release H<sup>+</sup>, and these solutions usually have a higher viscosity than water or common inorganic acid solution (Harris and Woolf, 2005). Both cation and anion part of IL acids should also be discussed since they have a much bigger structure than common inorganic acid. Hydrogen peroxide may cause IL acids oxidation. In addition, copper usually embedded in WPCBs (Zeng et al., 2013), which means lixiviant is more difficult to contact metal copper and chemical properties at each direction would

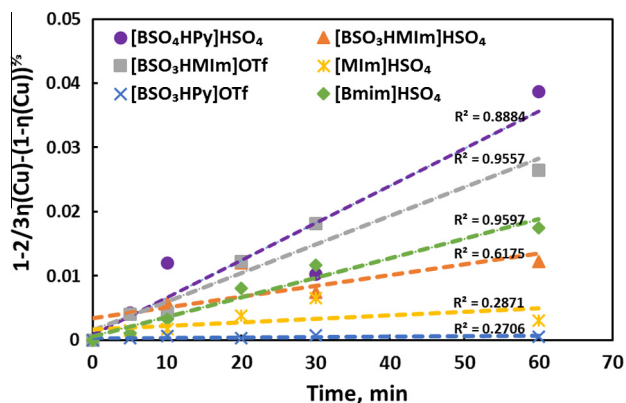


Fig. 7. Plots of shrinking core model for diffusion control.

not be equal. Since WPCBs contain many kinds of metals, such as Fe, Ni, Sn, Pb, Ag, et al., these metals may play a significant role in copper leaching process. For example, if Fe content is high, once it is leached to the solution as  $\text{Fe}^{3+}$ , copper leaching rate would be accelerated by  $\text{Fe}^{3+}$ , which is one of the main reasons that microbes can leaching copper out (Yang et al., 2014). Therefore, copper leaching kinetics of IL acids should be further studied.

#### 4. Conclusions

In this study, we demonstrated that copper can be successfully leached out by all the six IL acids. Particle size and time present a similar impact on copper leaching rate, while IL acid concentration, hydrogen peroxide adding amount, solid to liquid ratio, temperature, show a different effect on copper leaching from WPCBs. For example, among these six IL acids, compared to the IL acid with  $\text{CF}_3\text{SO}_3^-$ , it is much easier for the IL acid with  $\text{HSO}_4^-$  to leach copper out from WPCBs powders. In addition, these six IL acids indicate a similar behavior as common inorganic acids, except temperature and kinetics. For IL acids, diffusion plays a more important role than surface reaction, while copper leaching by inorganic acids usually control by surface reaction.

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