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Behaviour of Zinc during the Process of Leaching Copper from WPCBs by Typical Acidic Ionic Liquids

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Waste printed circuit boards (WPCBs) have attracted more and more attention, mainly focused on the recovery of valuable metals, especially copper. Few studies were reported on the behaviour of heavy metals during the process of recycling copper from WPCBs. Hence, we selected zinc to represent the heavy metals and examined its behaviour in typical acidic ionic liquids (ILs) leaching system. The factors that affect zinc leaching rate, such as particle size, temperature, ionic liquid concentration, H_2O_2 adding amount and solid to liquid ratio, were examined in details. The result showed that zinc could be leached successfully in the five typical acidic ILs and the zinc leaching rate was significantly impacted by H_2O_2 adding amount, solid to liquid ratio and temperature. In addition, the tendency of zinc leaching rate by $[BSO_3HMIm]OTf$ was almost the same as $[BSO_3HPy]OTf$. Moreover, acidic IL with $CF_3SO_3^-$ was less efficient than the acidic IL with HSO_4^-. Although zinc could restrain the leaching of copper because of the substitution reaction between metallic zinc and Cu^{2+}, the two almost show the same tendency. The results of zinc leaching kinetics analysis indicated that diffusion played a more important role than surface reaction, which was the same as copper, but different from the inorganic acids which was usually controlled by surface reaction.

Introduction

Recently, with the development of technology, more and more electronic devices are proliferated wildly. Printed circuit boards (PCBs) is an essential part of almost all electric and electronic products, from personal computer (PC), TV set, to electronic toy. PCBs manufacture has been developed dramatically with the rapid development of information industry. It is reported that the average increasing rate of PCBs manufacture is 14.4% in China, which is much higher than the world (8.7%)[1], leading to a huge quantity of waste printed circuit boards (WPCBs). WPCBs not only contain abundant valuable substances, i.e., copper, gold, silver and so on, but also environmentally harmful matters, i.e., halogenated flame retardants and heavy metals. For example, copper and gold content in a typical WPCB from PC contains is about 20 wt.% and 250 g/t, respectively, which is 20–40 fold or 25–250 fold higher than that of a copper or gold ore[2]. However, zinc (1.5%), cadmium (0.015%) and chromium (0.05%) would greatly threaten the environment and human health if they are not disposed properly[3]. Hence, an understanding that we should build for WPCBs recycling is not only respect to the recovery of valuable materials but also consider from the angle of environment[4].

In the past few years, plenty of studies on recycling copper from WPCBs were carried out. Among them, the mechanical, pyrometallurgical, bioleaching and hydrometallurgical approaches were widely investigated[5-10], especially, hydrometallurgical methods because of the higher mental recovery rate. During the hydrometallurgical process, it would be harmful to the environment due to the large amounts of acid and alkali used which contribute to the formation of waste water. Therefore, green extractants need to be developed to avoid these adverse effects. In recent years, it has been found that ionic liquids (ILs) are regard as the most promising extractants for leaching and a new green hydrometallurgical method using ionic liquids will replace the conventional method consuming acid or alkali[11]. Ionic liquids (ILs) including an organic cation with an inorganic or organic anion, also called room temperature ionic liquids (RTILs), are basically liquid at low temperature. The unique properties, such as negligible volatility, vapour pressure, thermal stability, low toxicity, high conductivity and wide electrochemical window, make them widely used[12]. In addition, the price of ionic liquid is low. So, the leachability using ionic liquid could avoid efficiently environmental, healthy, economic, safe issues which the conventional method often brought. Previous studies reported the use of ILs to leach chalcopyrite, and the results indicated that pure IL and its aqueous solutions were more effective than the conventional acid solutions[13]. For example, A. Kilicarslan et al.[11] founded that 82% of copper were leached from brass wastes by $[bmim]HSO_4$. For ILs used as extractants to leaching copper from WPCBs, Huang et al.[14] first reported that copper could be successfully leached out by acidic IL, 1-butyl-3-methyl-imidazolium hydrogen sulfate ([bmim]HSO_4), from WPCBs with a leaching rate up to 99%. However, almost all the previous researches are focused on the recovery of valuable resources, mainly copper, without considering the heavy metals, for example zinc.

As reported by Huang et al.[14], [bmim]HSO_4 could successfully leach copper out from WPCBs, we examined other five typical acidic ILs, [BSO_4HPy]HSO_4, [BSO_3HMIm]HSO_4, [BSO_3HMIm]OTf, [BSO_3HMIm]OTf and [BSO_3HPy]OTf, and found that these five acidic ILs could also successfully leach copper out from WPCBs. In this study, we try to investigate the behaviour of zinc during the process of leaching copper from WPCBs by these five ILs, with the purpose to examine if zinc could be leached out simultaneously as copper and to find out the regularity between copper, the target metal for valuable resource recycle, and zinc, the selected metal presenting for heavy metals. According to the regularity, the potential methods may be developed to make the biggest amount recovery of valuable metals and the smallest amount leachability of heavy metals in the further study. Factors, such as WPCBs particle size, IL concentration, liquid to solid ratio and temperature, were studied in details. Furthermore, the leaching kinetics was also analysed.

Experimental Section

Sample preparation

WPCBs, without disassembling electronic components, used in this study were obtained from waste computers. The first step is to cut these WPCBs to small pieces, around 50 mm × 50 mm, by cutting machine. Then it were sent to further comminute by the Retsch SM-2000 Cutting Mill (Retsch, Germany), and sieved into different fractions using standard sieves: 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, which was described elsewhere[14]. After that, they were dried at 105℃ for 24h.

Characterization

microwave aided HNO_3-H_2O_2-HF system[15] were applied to digest the obtained powders and zinc concentration of the leaching solutions were tested by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, Thermo Scientific, iCAP 6500), shown in Table 1.

Table 1. Zinc contents in WPCBs specimens

Particle size, mm	F1 (<0.075)	F2 (0.075-0.1)	F3 (0.1-0.25)	F4 (0.25-0.5)	F5 (>0.5)
Zn wt. %	1.28	1.23	1.3	2.21	2.24

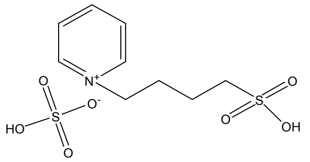
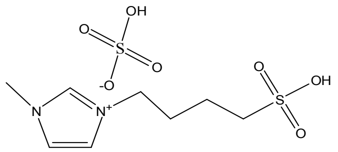
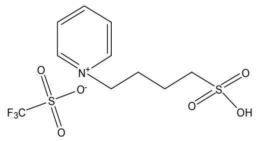
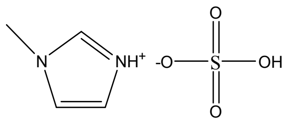
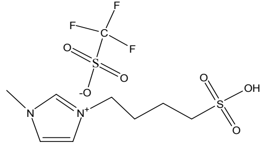
As is shown in Table 1, Zn content varied as WPCBs particle size. For example, Zn content decreased from 1.28% to 1.23%, when WPCBs particle size increases from <0.075mm to 0.075-0.1mm. However, as WPCBs particle size increased from 0.075-0.1mm to >0.5, Zn content increased from 1.23% to 2.24%. It is reasonable that the bigger particle size contains the more zinc. And this result consists with Wang et al., which reported that the content of zinc reached 2.044% in WPCBs when the particle size of zinc was less than 200 meshes (about ＞ 0.075mm) during the ammonia/ammonium leaching process[16].

Reagents

[BSO_4HPy]HSO_4 (N-sulfobutylpyridinium hydrosulfate, 99%), [BSO_3HMIm]HSO_4 (1-sulfobuty-3-methylimidazolium hydrosulfate, 99%), [BSO_3HMIm]OTf (N-sulfobutylpyridinium trifluoromethanesulfonate, 99%), [MIm]HSO_4 (Methylimidazolium hydrosulfate, 98%) and [BSO_3HPy]OTf (1-sulfobutyl-3-methylimidazolium trifluoromethanesulfate, 98.5%) used in this experiment were provided by Lanzhou Institute of Chemical Physics and the structures are shown in Table 2. Chemicals applied in the experiments were all analytical reagents except those specially mentioned and all aqueous IL leaching solutions were prepared using deionized water.

Leaching experiments

Table 2. Acidic ionic liquids used in this study

[BSO_4HPy]HSO_4, $C_9H_{15}NS_2O_7$, N-butylsulfonate Pyridinium hydrosulfate: 
[BSO_3HMIm]HSO_4, $C_8H_{16}N_2S_2O_7$, 1-sulfobuty-3-methylimidazolium hydrosulfate: 
[BSO_3HMIm]OTf, $C_{10}H_{14}NS_2O_6F_3$, N-sulfobutylpyridinium trifluoromethanesulfonate: 
[MIm]HSO_4, $C_4H_8N_2SO_4$, N-methylimidazolium hydrogen sulfate: 
[BSO_3HPy]OTf, $C_9H_{15}N_2S_2O_6F_3$, 1-sulfobutyl-3-methylimidazolium trifluoromethanesulfate: 

A constant temperature water bath oscillator, using a constant oscillating frequency of 250 rpm in the temperature range of 40 to 70 ℃, were applied to place a batch of 250 mL glass conical flasks, in which all the leaching experiment were carried out. Subsequently, the effect of WPCBs particle size, IL concentration (V/V, in liquid solution), acidic ILs adding amount, H_2O_2 (30 wt.%) adding amount and temperature on zinc leaching rate by the five acidic ILs were investigated separately and the detailed experiment arrangements are given in Table 3. The data for copper leaching by these five ILs were provided in the Supplementary Information (SI) for comparison. As a previous study on copper leaching[15], the leaching efficiency for zinc was also determined according to the following formula:

$$\text{Zinc leaching rate}(\pm 0.05) = \frac{\text{Zinc extracted}}{\text{Total zinc in WPCBs}} \times 100\% \qquad (1)$$

The relative standard deviations were within the limited range and mean values were given in the Tables and Figures without error bar.

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)
Temperature, ^{o}C	40, 50, 60, 70
acidic IL concentration, v/v	10%, 20%, 40%, 60%, 80%
H_2O_2 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

Results and discussion

Particle size

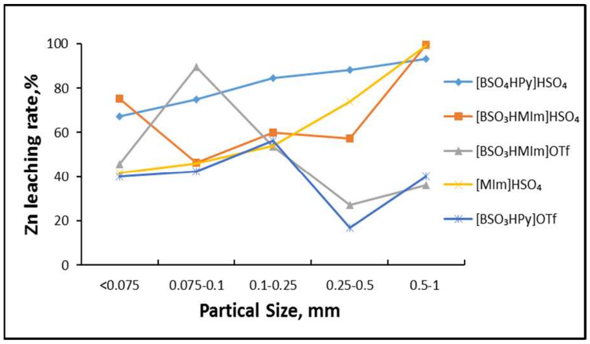


Figure 1. Effect of particle size on zinc leaching rate by acidic ionic liquids (1g WPCBs powders, 15ml, 10% (v/v) ionic liquid, 5ml hydrogen peroxide, leaching temperature 50℃, leaching time 2h)

It can be seen from Fig. 1, generally, as the increase of particles size in the whole investigated range, Zn leaching rate for $[BSO_4HPy]HSO_4$ and $[MIm]HSO_4$ increased from 67.2% and 41.7% to 93.0% and 99.0%, respectively. However, Zn leaching rate for $[BSO_3HMIm]OTf$ and $[BSO_3HPy]OTf$ displayed a different tendency, which increased first and then decreased as the increase of particles size, i.e., for $[BSO_3HPy]OTf$, Zn leaching rate first increased from 39.9% to 56.5% when particle size increased from <0.075mm to 0.1-0.25mm, then decreased from 56.5% to 16.7% when the particle size increased from 0.1-0.25 mm to 0.25-0.5 mm. None is the same as $[BSO_3HMIm]HSO_4$, which decreased from 75.2% to 57.2% first and then increased from 57.2% to 99.3% when the particles size increased from <0.075 mm and 0.25-0.5 mm to 0.25-0.5 mm and 0.5-1 mm, respectively.

Compared with copper (SI, Fig. S1), zinc leaching rate was higher than copper when WPCBs particle was <0.075mm. This is may be caused by the significant increase of particle-particle collision when the particle size was reduced to a critical level[18], <0.075 mm in this study. In this condition, leaching liquid is hard to permeate through the fine WPCBs powders. Since the metallicity of zinc is stronger than that of copper, zinc leaching rate would be a lighter higher than copper.

Temperature

Fig. 2 showed that Zn leaching rate decreased with the increase of temperature for $[BSO_4HPy]HSO_4$, $[BSO_3HMIm]HSO_4$ and $[MIm]HSO_4$ in the whole investigated range. For example, Zn leaching rate for $[BSO_3HMIm]HSO_4$ decreased from 51.4% to 15.9% when the temperature increased from 40 ℃ to 70 ℃. However, for $[BSO_3HMIm]OTf$ and $[BSO_3HPy]OTf$, Zn leaching rate slightly increased as the increase of temperature, i.e., for $[BSO_3HPy]OTf$, Zn leaching rate increased from 6.1% to 11.1% when the temperature increased from 40 ℃ to 60 ℃ and then, as the temperature increased from 60 ℃ to 70 ℃, Zn leaching rate almost kept the same, changed from 11.1% to 10.3%.

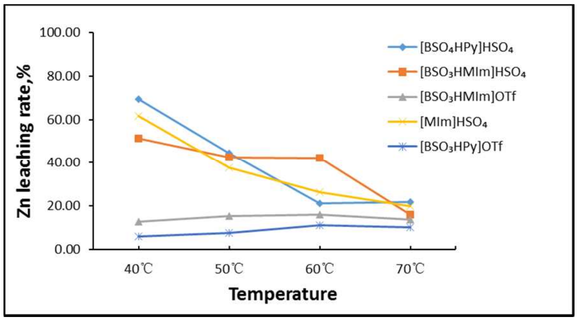


Figure 2. Effect of leaching temperature on zinc leaching rate by acidic ionic liquids (5g WPCBs powders, 75ml, 10% (v/v) ionic liquid, 25ml hydrogen peroxide, leaching time 2h)

Considering the effect of temperature on both copper (SI, Fig. S2) and zinc, the two almost presented the same trend. It is logical that both of copper and zinc leaching rate decreased finally as the increase of temperature because the hydrogen peroxide would be decomposed and the copper leaching rate as well as zinc leaching rate would decrease relatively as the temperature increasing. Furthermore, it can be seen that zinc and copper leaching rate for $[BSO_3HMIm]OTf$ and $[BSO_3HPy]OTf$ changed greater than the other three ionic liquids. It also can be found that temperature showed a much stronger effect on copper leaching rate than zinc.

Ionic liquid concentration

As shown in Fig. 3, Zn leaching rate increased with the acidic ILs concentration for $[BSO_3HMIm]HSO_4$, $[BSO_3HPy]OTf$ and $[BSO_3HMIm]OTf$. Take $[BSO_3HPy]OTf$ as an example, zinc leaching rate increased from 16.7% to 74.9% as acidic ionic liquid concentration increased from 10% to 80%. However, for $[BSO_4HPy]HSO_4$, Zn leaching rate was almost constant, with a relatively higher leaching rate of about 90% in the whole investigated range. In addition, zinc leaching rate, for $[MIm]HSO_4$, decreased from 73.7% to 17.3% as ionic liquid concentration increase from 10% to 80%. It is uncommon that zinc leaching rate decreases with the increase of ionic liquid concentration because it should display an increasing trend as the increase of ionic liquid concentration, which should be studied further.

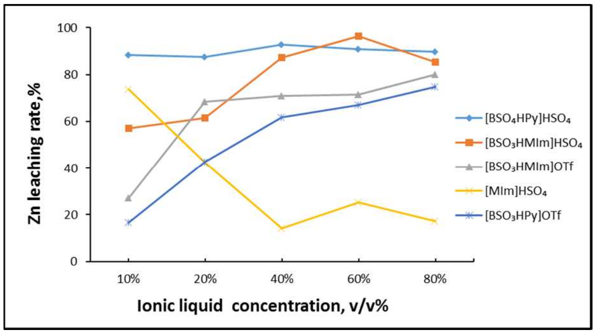


Figure 3. Effect of acidic ionic liquid concentration on zinc leaching rate by acidic ionic liquids (1g WPCBs powders, 15ml, 10% (v/v) ionic liquid, 5ml hydrogen peroxide, leaching temperature 50℃, leaching time 2h)

For the effect of ILs concentration, it is the same as temperature: it showed almost the same effect on both copper (SI, Fig. S3) and zinc leaching rate. Furthermore, it can also be found that zinc leaching rate is higher than copper leaching rate when the acidic ionic liquid is at a lower level. For these five acidic ILs, they can instantly release H^+ into aqueous solution owing to the strong acidity. Obviously, at a lower level, acidic ILs are not sufficient for leaching both zinc and copper out. The metallicity of zinc is stronger than that of copper so that zinc is leached by these five ionic liquids firstly. In addition, substitution between metallic zinc and copper ion, leading copper ion in the liquid reduced to metallic copper, which also restrains the leaching of copper.

Effect of H_2O_2 dosage

Fig. 4 indicated that the zinc leaching rate increased as the increase of H_2O_2 adding amount until it reached 5 mL, and then decreased when H_2O_2 adding amount was higher than 5 ml. Take $[BSO_3HMIm]HSO_4$ as an example, zinc leaching rate increased from 11.9% to 57.2% when H_2O_2 adding amount increased from 0 mL to 5 mL, and then decreased from 57.2% to 11.6% when H_2O_2 adding amount increased from 5 mL to 15 mL.

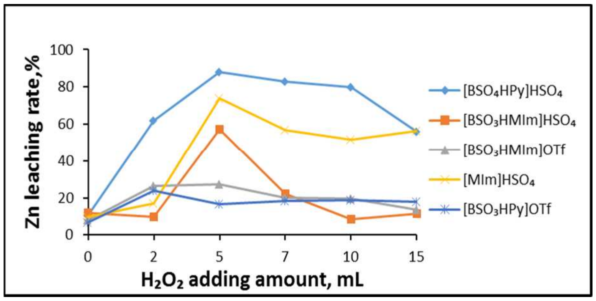


Figure 4. Effect of H_2O_2 adding amount on zinc leaching rate by acidic ionic liquids (1g WPCBs powders, 15ml, 10% (v/v) ionic liquid, leaching temperature 50℃, leaching time 2h)

Compared with copper (SI, Fig. S4), H_2O_2 adding amount shows the same tendency as zinc leaching rate. Hydrogen peroxide could decompose and release oxygen which combine with H^+ and copper or zinc as reactants to form Cu^{2+} or Zn^{2+}, resulting in the increase of copper and zinc leaching rate when H_2O_2 adding amount was less than 5 mL. However, the overdosed hydrogen peroxide could decompose greatly and release a great deal of oxygen into the ionic liquid, which may cause oxidation of acidic ionic liquids. Therefore, all of them showed a decreasing trend when the H_2O_2 adding amount was higher than 5 mL. It also can be seen that the peak value of zinc leaching rate appeared in a lower H_2O_2 adding amount for $[BSO_3HMIm]OTf$ and $[BSO_3HPy]OTf$ than copper leaching rate. As is known to us, the acidity of $[BSO_3HMIm]OTf$ and $[BSO_3HPy]OTf$ is lower than the other three ionic liquids and the metal activity of zinc is stronger than copper. Hence, it is reasonable that the peak value of zinc leaching rate appeared in a lower H_2O_2 adding amount for $[BSO_3HMIm]OTf$ and $[BSO_3HPy]OTf$ than copper leaching rate.

Effect of solid to liquid ratio

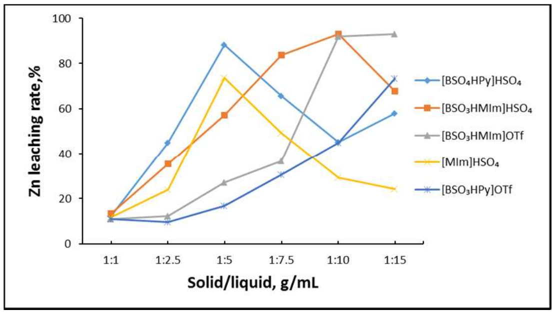


Figure 5. Effect of solid/liquid on zinc leaching rate by acidic ionic liquids (1g WPCBs powders, 15ml, 10% (v/v) ionic liquid, 5ml hydrogen peroxide, leaching temperature 50℃, leaching time 2h)

It can be seen from Fig. 5 that Zn leaching rate increased first and then decreased as the decrease of solid/liquid for $[BSO_3HMIm]HSO_4$, $[BSO_4HPy]HSO_4$ and $[MIm]HSO_4$. For example, for $[MIm]HSO_4$, when solid/liquid decreased from

1:1 to 1:5, Zn leaching rate increased from 11.6% to 73.7% and then the Zn leaching rate decreased from 73.7% to 24.3% as the solid/liquid decreased from 1:5 to 1:15. However, for $[BSO_3HPy]OTf$ and $[BSO_3HMIm]OTf$, zinc leaching rate increased all the time as the decrease of solid/liquid in the whole investigated range.

The effects of solid to liquid ratio on both copper (SI, Fig. S5) and zinc leaching rate were almost the same: copper and zinc leaching rate increased first when the value of solid to liquid ratio was larger and then decreased when the value of solid to liquid ratio was less than a critical value. It is reasonable that the reaction of WPCBs powder with ionic liquid was more severe with the decrease of solid to liquid ratio and the overdosed WPCBs powder make it difficult to adequately react with acidic ionic liquids. Perhaps, zinc was also an important factor that affected copper leaching rate because of the substitution reaction as mentioned previously. It also can be seen that zinc leaching rate was higher than copper when the solid to liquid value is larger. This could also explained by the metallicity, as mentioned previously. Besides, the acidity of $[BSO_3HMIm]OTf$ and $[BSO_3HPy]OTf$ is weaker than the $[BSO_4HPy]HSO_4$, $[BSO_3HMIm]HSO_4$ and $[MIm]HSO_4$. Hence, it is logical that the peak values of copper leaching rate and zinc leaching rate by $[BSO_3HMIm]OTf$ and $[BSO_3HPy]OTf$ was lower than the other three ionic liquids when the value of solid to liquid ratio was at a lower level.

Kinetics analysis

Fig. 6 presented the zinc leaching rate by the investigated five acidic ILs as the time extension. For further study, kinetics analysis was conducted based on the results of zinc leaching rate by leaching versus time.

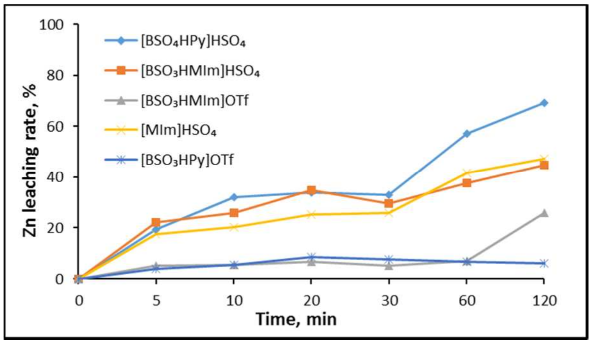


Figure 6. Effect of time on zinc leaching rate by acidic ionic liquids (5g WPCBs powders, 75ml, 10% (v/v) ionic liquid, 25ml hydrogen peroxide, leaching temperature 50℃)

The system of a reaction between a solid and a fluid can be described as heterogeneous models. In a heterogeneous solid-liquid reaction system, it is extremely difficult to express the overall leaching rate because of the complicated interaction between physical and chemical processes. To better explain the process of zinc dissolution, the metal particles are considered as spherical particles and the leaching process is described as the shrinking core model. According to this model, the following steps are considered to occur in succession during the dissolution[17]:

I. Lixiviant diffuses from the solution to the fluid film surrounding the solid.

II. Lixiviant diffuses from fluid film to solid surface

III. Chemical reaction occur on the surface of unreacted particles core between the lixiviant and the solid.

IV. Formation of products at the surface of unreacted particles core and the products diffuse from the interface into fluid film.

V. Products diffuse from fluid film to solution.

The reaction rate primarily lies on the step with the highest resistance, and if the reaction is controlled by surface chemical reaction, the kinetics equation is as follows[18]:

$$1 – (1 – x)^{1/3} = kt \tag{1}$$

If the reaction is controlled by diffusion, the kinetics equation is as follows[18]:

$$1 – 2/3x – (1-x)^{2/3} = kt \tag{2}$$

where “x” is zinc leaching rate, “t” is the reaction time (min or h) and “k” is the apparent rate constant (min−1 or h−1).

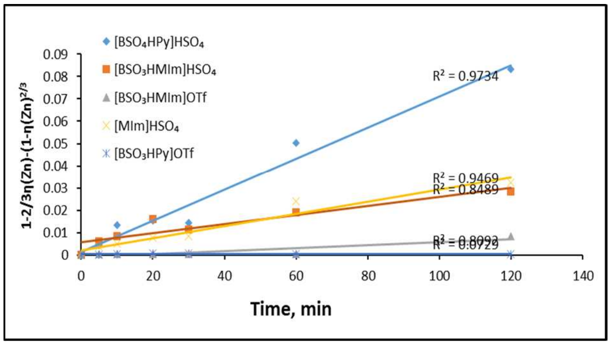


Figure 7. Plots of shrinking core model for diffusion control

Eq. (1) and Eq. (2) shows that if the leaching reaction is controlled by diffusion through the product layers or the surface reaction, there must be a linear relationship between the left side of equation and time. For Eq. (1), the fit data shows a weak linear relationship with time, which is not given. Hence, this leaching zinc reaction from WPCBs could not controlled by a surface reaction. For Eq. (2), which the reaction is controlled by diffusion, a better linear relationship is obtained for the fit data, which is shown in Fig. 7. It can be seen from Fig. 7 that two acidic ILs, $[BSO_4HPy]HSO_4$ and $[MIm]HSO_4$ present a better linear relationship, and the values of R^2 are 0.9734 and 0.9469, respectively. For $[BSO_3HMIm]OTf$ and $[BSO_3HMIm]HSO_4$, the values of R^2 are 0.8092 and 0.8489, respectively. For $[BSO_3HPy]OTf$, it does not fit well. Thus, one conclusion can be drawn from these results is that diffusion plays a more important role than surface reaction.

Clearly, for [BSO$_3$HMIm]HSO$_4$, [BSO$_4$HPy]HSO$_4$ and [MIm]HSO$_4$, the linear relationships of zinc for the reaction controlled by diffusion are better than copper (SI, Fig. S6) R2 of which were 0.5986, 0.8759 and 0.3108, respectively. In addition, both zinc and copper showed a weak linear relationship for [BSO$_3$HPy]OTf. This could be attributed to the weak acidity of [BSO$_3$HPy]OTf, which the surface chemical reaction step is the highest resistance. However, for [BSO$_3$HMIm]OTf, it is strange that a better linear relationship is obtained for copper than zinc, the reason needed to further study.

Conclusions

Zinc in the WPCBs was leached successfully in the [BSO$_4$HPy]HSO$_4$, [BSO$_3$HMIm]HSO$_4$, [BSO$_3$HMIm]OTf, [MIm]HSO$_4$ and [BSO$_3$HPy]OTf, and zinc leaching rate was affected greatly by hydrogen peroxide adding amount, solid to liquid ratio and temperature. In addition, the tendency of zinc leaching rate in the [BSO$_3$HMIm]OTf was almost the same as [BSO$_3$HPy]OTf. Moreover, acidic IL with CF$_3$SO$_3^-$ was less efficient than acidic IL with HSO$_4^-$.

The behaviour of zinc almost presents a same tendency as copper during leaching process in the five acidic ionic liquids. The leaching of zinc restrains the leaching of copper to an extent. But, the detail interaction between copper and zinc during leaching process need to be studied further for us. In addition, for acidic ILs, diffusion plays a more important role than surface reaction during the zinc leaching process, which is the same as copper, but different from inorganic acids controlled by surface reaction usually.

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Notes and references

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