Optimizing the Leaching Parameters and Studying the Kinetics of Copper Recovery from Waste Printed Circuit Boards

Juanjuan Hao, Xiaolu Wang, Yishu Wang, Yufeng Wu, and Fu Guo*

ABSTRACT: The study of copper (Cu) recovery is crucial for the entire recovery process of waste printed circuit boards (WPCBs), and Cu can be leached efficiently via a sulfuric acid–hydrogen peroxide (H_2SO_4–H_2O_2) system. To achieve high Cu recovery, it is important to evaluate the parameters of the leaching process and understand the Cu leaching kinetics. Applying statistical and mathematical techniques to the leaching process will further benefit the optimization of the Cu leaching parameters. Moreover, the leaching kinetics of Cu in the H_2SO_4–H_2O_2 solution is yet to be fully understood. Hence, in the present work, process parameters, such as temperature, H_2SO_4 and H_2O_2 concentrations, solid–liquid ratio, particle size, and stirring speed, were optimized statistically by the response surface methodology (RSM). The results showed that the leaching kinetics conformed to the Avrami model. The maximum Cu leaching efficiency was 99.47%, and it was obtained based on the following optimal conditions: 30.98 °C, 2.6 mol/L H_2SO_4, 1.87 mol/L H_2O_2, a solid–liquid ratio of 0.05 g/mL, 135 mesh, and 378 rpm. RSM was used for the optimization of the process parameters, and the leaching kinetics in this system was clarified. This study provides an important pathway for the investigation of other metal recoveries from WPCBs.

INTRODUCTION

With the advancement of technology and the development of society, the lifespan of electronic and electrical equipment (EEE) has been foreshortened. This has resulted in an alarming increase in the number of waste EEE (WEEE). Waste printed circuit boards (WPCBs), the core component of WEEE, which were originally manufactured to provide reliable electrical connections for electronic components, are also largely produced. These WPCBs contain abundant high-value metals (e.g., gold, silver, copper, etc.), and copper, which predominantly makes up the content of the conductive circuits of printed circuit boards, is the most abundant metal. This makes WPCBs important secondary copper sources, and the recovery of copper from WPCBs is of great economic and environmental benefits.

Several studies have been carried out to recover copper from WPCBs based on physical processes, pyrometallurgy, hydrometallurgy, and biometallurgy. Compared with other recovery processes, hydrometallurgy has attracted extensive attention due to its cost effectiveness, ease of operation, and being relatively environmentally friendly. Common copper leaching solutions include inorganic acids, ionic liquids, ammonia-based solutions, ethylenediaminetetraacetic acid (EDTA), and citrate. Among them, ammonia-based solutions and H_2SO_4 are widely used due to their simple operation and low cost. However, the toxicity and volatility of ammonia is a cause of environmental and operational safety concerns. Meanwhile, the low solubility of copper in the H_2SO_4 solution due to the poor oxidation of H_2SO_4 is the major limitation of its application. Therefore, the search for appropriate oxidants toward the improvement of the leaching efficiency of copper in the H_2SO_4 solution is of high necessity.

Hydrogen peroxide (H_2O_2), as an efficient oxidant, has been used in combination with H_2SO_4 for copper recovery. The literature studies showed that the temperature, H_2SO_4 concentration, H_2O_2 concentration, a solid–liquid ratio, particle size, and stirring speed have significant effects on the copper leaching process. To the best of our knowledge, for the H_2SO_4–H_2O_2 leaching system, only the effect of a single parameter on the leaching efficiency was investigated in the complex solid–liquid mixed system, thus ignoring the influence of the interactions of experimental parameters playing different roles in the process. This therefore creates an information gap that needs to be espied. Therefore, the influence of the interactions of key experimental
parameters on the leaching efficiency still needs to be studied comprehensively.

Response surface methodology (RSM), which is a powerful statistical analysis technique that analyzes the influence of the interactions of several variables, has been widely applied in deciding optimum conditions for chemical or physical processes. For instance, by modeling the relationships between different experimental parameters, the RSM can optimize the desirable ones. RSM has also been used in metal leaching processes, such as gold leaching in thioulate solution, and the leaching of Cu, Fe, Ni, and Ag in the H\textsubscript{2}SO\textsubscript{4}−CuSO\textsubscript{4}−NaCl solution. A survey of literature proves that there is no available information on the application of the RSM for copper leaching in the H\textsubscript{2}SO\textsubscript{4}−H\textsubscript{2}O\textsubscript{2} system. Therefore, as a powerful tool, RSM has the potential of being applied to copper leaching in the H\textsubscript{2}SO\textsubscript{4}−H\textsubscript{2}O\textsubscript{2} system, which has not yet been researched.

Leaching kinetic studies are very meaningful for understanding leaching mechanisms and the improvement of recovery rates. Han et al. used glycine with H\textsubscript{2}O\textsubscript{2} to leach 94.08% of copper from WPCBs, and the leaching kinetics were also studied with a shrinkage core model. The result showed that the leaching kinetics conformed to diffusion and chemically controlled reactions. Jadhao et al. used chelation technology with EDTA to recover 83.8% of copper, and the leaching rate reached 99.47% at 2.5 mol/L. As the temperature increased, a high hydrogen ion concentration promoted copper leaching, and the leaching rate reached 99.47% at 2.5 mol/L. As shown in Figure 1c, the leaching efficiency increased with temperature increment below 30 °C. As the temperature increased, the reactivities of the metals also increased, which promoted the leaching of other active metals competing with copper. In addition, a high temperature promotes the rapid decomposition of hydrogen peroxide producing oxygen. However, the solubility of oxygen in aqueous phases decreases with increasing temperature, which further inhibits copper leaching. Therefore, the leaching efficiency decreased with increasing temperature, which may be attributed to the decomposition of H\textsubscript{2}O\textsubscript{2} at high temperatures. The highest leaching efficiency of copper was obtained when the optimum leaching temperature was 30 °C.

The effect of the H\textsubscript{2}SO\textsubscript{4} concentration on the copper leaching efficiency is shown in Figure 1b. The leaching efficiency of copper, which is sensitive to the H\textsubscript{2}SO\textsubscript{4} concentration, first increased and then decreased with increasing H\textsubscript{2}SO\textsubscript{4} concentration. As the H\textsubscript{2}SO\textsubscript{4} concentration increased, a high hydrogen ion concentration promoted copper leaching, and the leaching rate reached 99.47% at 2.5 mol/L. When the H\textsubscript{2}SO\textsubscript{4} concentration was higher than 2.5 mol/L, more active metals were leached consuming more acid. The metal leaching process generates hydrogen, which would adsorb on the surface of copper, thereby reducing its leaching efficiency. In addition, high metal leaching efficiencies lead to increases in the viscosities of leaching solutions, which consequently hinder leaching processes. Therefore, the optimum concentration of H\textsubscript{2}SO\textsubscript{4} was 2.5 mol/L.

The effect of the H\textsubscript{2}O\textsubscript{2} concentration was studied in the concentration range of 1–2.5 mol/L. As shown in Figure 1e, copper leaching was first enhanced and then decreased with increasing H\textsubscript{2}O\textsubscript{2} concentration, and the leaching efficiency reached a maximum of 99.47% at 2.0 mol/L H\textsubscript{2}O\textsubscript{2}. As a strong oxidant, the increase of the H\textsubscript{2}O\textsubscript{2} concentration improved the

Figure 1. Effect of variables on the copper leaching efficiency: (a) temperature, (b) H\textsubscript{2}SO\textsubscript{4} concentration, (c) H\textsubscript{2}O\textsubscript{2} concentration, (d) solid−liquid ratio, (e) particle size, and (f) stirring speed.

## RESULTS AND DISCUSSION

### Leaching Studies

Figure 1 illustrates the effect of various experimental parameters on the copper leaching efficiency. The initial leaching efficiency of copper was high and reached equilibrium above 60 min as shown in Figure 1a. The leaching efficiency increased with temperature increment below 30 °C. As the temperature increased, the reactivities of the metals also increased, which promoted the leaching of other active metals competing with copper. In addition, a high temperature promotes the rapid decomposition of hydrogen peroxide producing oxygen. However, the solubility of oxygen in aqueous phases decreases with increasing temperature, which further inhibits copper leaching. Therefore, the leaching efficiency decreased with increasing temperature, which may be attributed to the decomposition of H\textsubscript{2}O\textsubscript{2} at high temperatures. The highest leaching efficiency of copper was obtained when the optimum leaching temperature was 30 °C.

The effect of the H\textsubscript{2}SO\textsubscript{4} concentration on the copper leaching efficiency is shown in Figure 1b. The leaching efficiency of copper, which is sensitive to the H\textsubscript{2}SO\textsubscript{4} concentration, first increased and then decreased with increasing H\textsubscript{2}SO\textsubscript{4} concentration. As the H\textsubscript{2}SO\textsubscript{4} concentration increased, a high hydrogen ion concentration promoted copper leaching, and the leaching rate reached 99.47% at 2.5 mol/L. When the H\textsubscript{2}SO\textsubscript{4} concentration was higher than 2.5 mol/L, more active metals were leached consuming more acid. The metal leaching process generates hydrogen, which would adsorb on the surface of copper, thereby reducing its leaching efficiency. In addition, high metal leaching efficiencies lead to increases in the viscosities of leaching solutions, which consequently hinder leaching processes. Therefore, the optimum concentration of H\textsubscript{2}SO\textsubscript{4} was 2.5 mol/L.

The effect of the H\textsubscript{2}O\textsubscript{2} concentration was studied in the concentration range of 1–2.5 mol/L. As shown in Figure 1e, copper leaching was first enhanced and then decreased with increasing H\textsubscript{2}O\textsubscript{2} concentration, and the leaching efficiency reached a maximum of 99.47% at 2.0 mol/L H\textsubscript{2}O\textsubscript{2}. As a strong oxidant, the increase of the H\textsubscript{2}O\textsubscript{2} concentration improved the
leaching efficiency of copper, and a high H2O2 concentration can limit the reduction or precipitation of copper species. The growth rate of the leaching efficiency decreased over time, which may be due to the self-decomposition of H2O2. At a high H2O2 concentration, the active metals (Sn, Fe, and Ni) were leached preferentially, which catalyzed the decomposition of H2O2, generating a large number of oxygen bubbles. The oxygen bubbles would adsorb on the copper surface and hinder the contact between the WPCB powder and the leaching solution, thus reducing the leaching efficiency. Therefore, the optimum H2O2 concentration was 2 mol/L.

Under the condition of 30 °C, 2.5 mol/L H2SO4, 2 mol/L H2O2, and a leaching time of 180 min, the effect of a solid–liquid ratio was studied, and the results showed that the pulp density had an adverse effect on the copper leaching process (Figure 1d). At a solid–liquid ratio of 0.05 g/mL, the highest leaching rate of 99.47% was attained. However, only 55.30% of copper was leached at 0.1 g/mL. As a solid-to-liquid ratio increases, the increase in the quantity of nonmetallic materials would promote the agglomeration of raw materials, causing collisions and frictions between the WPCB powders during the leaching process, which would impede the full contact of metals with the leaching solutions, thereby reducing the leaching efficiency. In addition, the contents of active metals increase in the raw materials with the increase in the solid–liquid ratio, which reduces copper ions in the leaching solution through replacement reactions, hence reducing the leaching efficiency of copper. Therefore, the optimum solid–liquid ratio was 0.05 g/mL.

The effect of particle size on the leaching efficiency is shown in Figure 1e. With a decrease in particle size between 18 and 150 mesh, the leaching efficiency of copper increased and then decreased. The morphologies of the different particle sizes are shown in Figure 2. Copper was present in the middle layer of the WPCBs. When the particle size was large (such as 18 mesh), copper was still covered with the organic matter layer due to the complex composition of WPCBs. At low speeds, the WPCB powder does not suspend completely, and the heavier metal particles are deposited at the bottom of the beaker and are covered by the lighter nonmetal particles, thereby hindering the full contact of the metal with the leaching reagent and decreasing the leaching efficiency. Increasing the stirring speed will promote the diffusion rate of the metal particles in the leaching solution, hence increasing the leaching efficiency. When the stirring speed reached 400 and 500 rpm, the leaching efficiencies increased to 99.47 and 99.62%, respectively. Therefore, a further increase in the stirring speed cannot increase the leaching efficiency significantly.

**Modeling and Statistical Analysis of Data.** Based on the abovementioned results, the key experimental parameters, such as temperature, concentrations of H2SO4 and H2O2, solid–liquid ratio, particle size, and stirring speed, were optimized by the BBD. Table 1 shows the results produced by the BBD including the synergistic effects of combining different parameters and their corresponding leaching efficiencies. The results show that the leaching efficiencies of copper were in the range of 27.27–99.57%, and the maximum yield (99.57%) was obtained at the medium value of each experimental parameter.

According to the experimental results from Table 1, the model was fitted by multiple linear regressions. A second-order regression model with a coefficient of $R^2 = 0.9521$ is derived from eq 1. From the equation, the response (leaching efficiency, $\gamma$) at any coded level for various experimental parameters can be predicted.

$$\gamma = 62.93 - 11.69A - 7.92C - 18.96D + 1.57E + 2.40F + 1.87AB + 3.21AC + 1.82AD + 1.02AE - 0.0587AF + 1.16BC - 2.03BD + 0.37BE + 2.38BF + 0.7863CD + 0.4962CE - 1.49CF + 1.42DE - 1.72DF - 1.15EF - 3.07A^2 - 2.54B^2 - 12.77C^2 + 5.32D^2 - 1.58E^2 + 1.86F^2$$ (1)

The reliability of the regression model was investigated by analysis of variance (ANOVA), as shown in Table 2. The significance test was performed at a 95% confidence level using $p$-values. The model is said to be statistically significant if the $p$-values are less than 0.05.
value is less than 0.05. Accordingly, the p-value (<0.0001) of the regression model is indicative of the adequacy of the model at a 95% confidence level (Table 2). The terms with p-values greater than 0.05 have insignificant effects on predicted responses. The statistical significance of the linear and quadratic terms of the various parameters as well as their interactions is shown in Table 2. The terms with underscore are statistically insignificant at a confidence level of 95%.

Table 1. BBD Design Arrangement and Results

| run | temperature (°C) | [H_2SO_4] (mol/L) | [H_2O_2] (mL/L) | solid–liquid ratio (g/mL) | particle size (mesh) | stirring speed (rpm) | actual | predicted |
|-----|----------------|-----------------|-----------------|------------------------|---------------------|---------------------|-------|------------|
| 1   | 40             | 2               | 1.5             | 0.075                  | 200                 | 400                 | 62.35 | 55.39      |
| 2   | 40             | 3               | 2               | 0.075                  | 200                 | 300                 | 53.27 | 59.43      |
| 3   | 50             | 2.5             | 1.5             | 0.075                  | 150                 | 500                 | 40.37 | 45.80      |
| 4   | 40             | 2               | 2               | 0.075                  | 150                 | 400                 | 60.58 | 62.93      |
| 5   | 30             | 3               | 2               | 0.1                    | 150                 | 400                 | 53.32 | 50.08      |
| 6   | 50             | 2.5             | 2.5             | 0.075                  | 150                 | 500                 | 42.57 | 33.40      |
| 7   | 40             | 2.5             | 2.5             | 0.5                    | 150                 | 300                 | 67.52 | 64.96      |
| 8   | 40             | 2.5             | 2.5             | 0.1                    | 150                 | 400                 | 37.32 | 32.05      |
| 9   | 50             | 2               | 2               | 0.05                   | 150                 | 400                 | 61.45 | 63.74      |
| 10  | 30             | 2.5             | 2               | 0.1                    | 100                 | 400                 | 52.40 | 52.55      |
| 11  | 30             | 3               | 2               | 0.05                   | 100                 | 400                 | 95.44 | 95.72      |

value is less than 0.05. Accordingly, the p-value (<0.0001) of the regression model is indicative of the adequacy of the model at a 95% confidence level (Table 2). The terms with p-values greater than 0.05 have insignificant effects on predicted responses. The statistical significance of the linear and quadratic terms of the various parameters as well as their interactions is shown in Table 2. The terms with underscore are statistically insignificant at a confidence level of 95%.
The predicted vs practical plot for copper leaching efficiencies is shown in Figure 3. There is a good linear relationship between the predicted values and the actual values. This result shows that the regression model obtained through the BBD is consistent with the experimental results and can be used to optimize the experimental parameters.

To study the effect of the relationships between variables on the response, three-dimensional (3D) response surface plots of the regression model were constructed. Figure 4 shows the 3D response surface plots of the experimental parameters with high reciprocity, and others are shown in Figure S1. As shown in Figure 4, the interaction of AD, BD, CD, DE, and DF has a significant effect on response, and the effect of D (solid—liquid ratio) exhibited a greater influence on the copper leaching efficiency than A (temperature), B (H₂SO₄ concentration), C (H₂O₂ concentration), E (particle size), and F (stirring speed), which is the same with the F-value results in Table 2.

From the results, the predicted model shows a good reflection of the relationships between the experimental and predicted results. Therefore, RSM was also used to optimize the leaching conditions. The obtained optimal experimental parameters were 30.98 °C, 2.6 mol/L H₂SO₄, 1.87 mol/L H₂O₂, a solid—liquid ratio of 0.05 g/mL, 135 mesh, and 378 rpm. The predicted leaching efficiency was 99.62% while the experimental result at the optimum experimental parameters was 99.47%. Due to the closeness between both results, the experimental parameters can be optimized by the RSM.

### KINETIC ANALYSIS OF COPPER LEACHING

**Kinetic Model.** Leaching kinetics is expressed by homogeneous or heterogeneous models. In heterogeneous models, the leaching process usually includes the following steps: (i) diffusion through boundary layers (external diffusion), (ii) diffusion through solid product layers (internal diffusion), (iii) surface chemical control reactions, and (iv)

| source | sum of square | df | mean square | F value | p-value |
|--------|--------------|----|-------------|---------|---------|
| model  | 16371.99     | 27 | 606.37      | 19.13   | <0.0001 |
| A-temperature | 3280.68   | 1  | 3280.68      | 103.48  | <0.0001 |
| B-H₂SO₄ concentration | 4.66      | 1  | 4.66        | 0.1471  | 0.7044  |
| C-H₂O₂ concentration | 1505.91  | 1  | 1505.91     | 47.5    | <0.0001 |
| >D-solid—liquid ratio | 8627.56  | 1  | 8627.56     | 272.13  | <0.0001 |
| E-particle size | 59.38      | 1  | 59.38       | 1.87    | 0.1829  |
| F-stirring speed | 138.67    | 1  | 138.67      | 4.37    | 0.0464  |
| AB | 0.048        | 1  | 0.048       | 0.00278 | 0.9587  |
| AC | 157.5        | 1  | 157.5       | 9.18    | 0.009   |
| AD | 0.018        | 1  | 0.018       | 0.00102 | 0.907   |
| AE | 8.38         | 1  | 8.38        | 0.2645  | 0.6114  |
| AF | 0.0276       | 1  | 0.0276      | 0.0009  | 0.9767  |
| BC | 0.21         | 1  | 0.21        | 0.012   | 0.9131  |
| BD | 0.012        | 1  | 0.012       | 0.000705| 0.92    |
| BE | 2.19         | 1  | 2.19        | 0.0691  | 0.7947  |
| BF | 45.17        | 1  | 45.17       | 1.42    | 0.2434  |
| CD | 3.67         | 1  | 3.67        | 0.21    | 0.023   |
| CE | 1.97         | 1  | 1.97        | 0.0621  | 0.8051  |
| CF | 35.52        | 1  | 35.52       | 1.12    | 0.2996  |
| DE | 16.16        | 1  | 16.16       | 0.5097  | 0.4816  |
| DF | 23.63        | 1  | 23.63       | 0.7454  | 0.3958  |
| EF | 10.65        | 1  | 10.65       | 0.3399  | 0.5672  |
| A²  | 121.8        | 1  | 121.8       | 7.1     | 0.0185  |
| B²  | 0.041        | 1  | 0.041       | 0.0024  | 0.9616  |
| C²  | 944.28       | 1  | 944.28      | 55.04   | <0.0001 |
| D²  | 45.58        | 1  | 45.58       | 2.66    | 0.1244  |
| E²  | 25.56        | 1  | 25.56       | 0.8064  | 0.3774  |
| F²  | 35.48        | 1  | 35.48       | 1.12    | 0.2999  |
| residual | 824.30    | 26 | 31.70       |         |         |
| lack of fit | 693.24    | 21 | 33.01       | 1.26    | 0.4340  |
| pure error | 131.06    | 5  | 26.21       |         |         |
| cor total | 17196.29  | 53 |             |         |         |

aR² = 0.9521, R_adj² = 0.9023.
mixed reactions. The shrinking core model (SCM) is the most commonly used kinetic equation. The rate equation of SCM controlled by a chemical reaction, diffusion reaction, and mixed reactions is shown in eqs 2–4.

\[
1 - (1 - X)^{1/3} = k_r t 
\]

\[
1 - \frac{2}{3}X - (1 - X)^{2/3} = k_d t 
\]

\[
1 - (1 - X)^{1/3} - \frac{1}{3} \ln(1 - X) = k_M t 
\]

where \(X\) is the leaching efficiency, \(k_r, k_d,\) and \(k_M\) are the chemical reaction rate constant, diffusion reaction rate constant, and mixed control reaction rate constant, respectively; and \(t\) is the leaching time. In addition, homogeneous models could also be used to determine leaching kinetics as in the following eqs 5–7.

\[
\ln(1 - X) = kt \quad (“first order pseudo”) 
\]

\[
X / (1 - X) = kt \quad (“second order pseudo”) 
\]

\[
\ln(1 - X) = k t^n \quad (“avrami model”) 
\]

where \(X\) is the leaching efficiency, \(k\) is the apparent kinetic constant, \(t\) is the leaching time, and \(n\) is the feature parameter.

**Kinetic Studies.** The leaching of copper from WPCBs in the \(H_2SO_4-H_2O_2\) system is a complicated solid–liquid reaction process. The leaching kinetics of copper was examined by varying the \(H_2SO_4\) and \(H_2O_2\) concentrations, temperature, solid–liquid ratio, particle size, and stirring speed. First of all, the leaching data obtained at different temperatures was fitted with different standard kinetic equations, and the fitting results are shown in Figure S2, while the corresponding fitting correlation coefficients are shown in Table S1. As shown in Figure S2 and Table S1, the fitting results of the different kinetic equations had large errors. Due to the high initial
leaching efficiency, the leaching process was found to fit the Avrami model most satisfactorily as shown in Figure 5a. The slope and intercept are denoted as \( n \) and \( \ln k \), respectively. The different \( n \) and \( \ln k \) corresponding to the different temperatures are summarized in Table 3. The value of \( n \) is almost constant with an average value of 0.1695. Therefore, the Avrami model is given in eq 8.

\[
\ln(1 - X) = kt^{0.1695}
\]  

(8)

According to the fitting results of Figure 5a, the plots of \( \ln k \) versus \( 1/T \) are shown in Figure 5b. Therefore, the kinetic equation on the effect of temperature on the copper leaching efficiency is obtained from eq 9.

\[
\ln k = -1.3402 \ln T + 5.9049
\]  

(9)

In addition, the relationship between the leaching rate constant and various factors were also studied. According to the experimental results shown in Figure 1, \(-\ln (1 - X) \) vs \( t^{0.1695} \) is plotted to obtain the fitting equations at different \( H_2SO_4 \) concentrations, \( H_2O_2 \) concentrations, solid–liquid ratios, particle size and stirring speeds. The leaching efficiency showed good linear relationships at different leaching times as shown in Figure 6. The slope \( k \) of each fitted straight line is the rate constant of the different experimental conditions.

The plots of \( \ln k \) vs \( \ln B, \ln C, \ln E, \) and \( \ln F \) for the different experimental parameters are shown in Figure 7. The kinetic equations on the influence of \( H_2SO_4 \) concentration, \( H_2O_2 \) concentration, solid–liquid ratio, particles size, and stirring speed on the copper leaching efficiency are shown in eqs 10–14. By combining these equations with eq 8, the leaching efficiency \( X \) can be predicted. The copper leaching kinetics in the \( H_2SO_4-H_2O_2 \) system is clarified as well.

\[
\ln k = 0.817 \ln B - 0.50
\]  

(10)

\[
\ln k = 1.391 \ln C - 0.517
\]  

(11)

\[
\ln k = -2.79 \ln D - 7.62
\]  

(12)

\[
\ln k = 0.522 \ln E - 1.95
\]  

(13)

\[
\ln k = 0.4996 \ln W - 2.42
\]  

(14)

Table 3. Values of \( n \) and \( \ln k \) at Different Temperatures

| \( T (K) \) | \( n \)  | \( \ln k \)  | \( R^2 \) |
|-----------|------|------|------|
| 293.15    | 0.1798 | -0.6597 | 0.97706 |
| 303.15    | 0.1749 | 0.05778 | 0.94413 |
| 313.15    | 0.1641 | -0.17542 | 0.97419 |
| 323.15    | 0.1593 | -0.6597 | 0.98726 |

Figure 5. Relationship (a) between \(-\ln(1 - X)\) and \( \ln t \) and (b) between \( \ln k \) and \( 1/T \) at different temperatures.

Figure 6. Plots of \(-\ln(1 - X) \) vs \( t^{0.1695} \) at different experimental conditions: (a) \( H_2SO_4 \) concentration, (b) \( H_2O_2 \) concentration, (c) solid–liquid ratio, (d) particle size, and (e) stirring speed.
CONCLUSIONS

In this paper, the leaching of Cu from WPCBs using the H$_2$SO$_4$−H$_2$O$_2$ system has been comprehensively studied, and the influence of various parameters on the leaching efficiency of copper was experimentally investigated. The results showed that the temperature, solid−liquid ratio, and H$_2$O$_2$ concentration had significant effects on the leaching efficiency. BBD based on the RSM was used to study the effects and reciprocity of various parameters on the leaching efficiency and also to optimize the experimental parameters. From the response surface plots, the interactive relationships between each of the following pairs of A (temperature)−C (H$_2$O$_2$ concentration), A (temperature)−D (solid−liquid ratio), B (H$_2$SO$_4$ concentration)−D (solid−liquid ratio), C (H$_2$O$_2$ concentration)−D (solid−liquid ratio), E (particles sizes)−D (solid−liquid ratio), and F (stirring speed)−D (solid−liquid ratio) showed significant effects on the copper leaching efficiency. Based on the results of the leaching experiments, the leaching mechanism of copper in the H$_2$SO$_4$−H$_2$O$_2$ system has been established. The copper leaching process and data were well fitted to the Avrami model. Moreover, the kinetic equations of various parameters were established.

EXPERIMENTAL SECTION

Materials. WPCBs derived from end-of-life mobile phones of different brands (Figure 8a,b) were disassembled, cut, and crushed to small sizes. The size distribution range of the particles is shown in Figure 8c, and particles with sizes between 150 and 200 mesh were used for the leaching experiments. The WPCB particles used in this study were obtained after leaching tin and lead with hydrochloric acid (HCl). Typically, 1.0 g of WPCB powder was digested in aqua regia at 100 °C, and the
contents of the main metals were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES). The metal contents of the WPCBs and HCl leached residue are shown in Tables 4 and 5, respectively.

Table 4. Metal Content of WPCB Powders (wt %)

| metal | Au | Ag | Cu | Fe | Ni | Sn | Pb | Zn |
|-------|----|----|----|----|----|----|----|----|
| content | 0.017 | 0.13 | 88.49 | 1.06 | 0.59 | 5.21 | 1.63 | 1.71 |

All of the solutions were prepared with deionized water. The leaching experiments were designed to understand the effects of several independent parameters on a response, and the Box–Behnken design (BBD), which is a typical method of the RSM, is used to optimize the experimental parameters. Based on the leaching experimental results, a reasonable range for each experimental parameter was chosen for the experimental design. The total number of experiments (N) are determined from eq 16.

\[ N = 2^k + 2k + n_0 \]  

where \( k \) is the number of experimental parameters and \( n_0 \) is the number of repetitions at the center points. The response (\( \gamma \)) was estimated using a second-order mathematical model based on the experimental data (eq 17).

\[ \gamma = a_0 + a_1x_1 + a_2x_2 + a_3x_3 + a_4x_4 + a_5x_5 + a_6x_6 + a_1^2x_1^2 + a_2^2x_2^2 + a_3^2x_3^2 + a_4^2x_4^2 + a_5^2x_5^2 + a_6^2x_6^2 + a_{12}x_1x_2 + a_{13}x_1x_3 + a_{14}x_1x_4 + a_{15}x_1x_5 + a_{16}x_1x_6 + a_{23}x_2x_3 + a_{24}x_2x_4 + a_{25}x_2x_5 + a_{26}x_2x_6 + a_{34}x_3x_4 + a_{35}x_3x_5 + a_{36}x_3x_6 + a_{45}x_4x_5 + a_{46}x_4x_6 + a_{56}x_5x_6 + a_{40}x_4x_0 + a_{50}x_5x_0 + a_{60}x_6x_0 \]  

Leaching Experiments. The leaching experiments were conducted in a 250 mL beaker. The temperature of the experiment was maintained using a water bath. Briefly, 100 mL of fresh leaching solution for each experiment was prepared by adding certain concentrations of H_2SO_4 and 30 vol % H_2O_2. All of the solutions were prepared with deionized water. The leaching experiments were designed to understand the effects of the H_2SO_4 concentration (1.5−3.0 mol/L), H_2O_2 concentration (1.0−2.5 mol/L), solid−liquid ratio (0.05−0.1 g/mL), and temperature (20−60 °C) on copper leaching efficiency. Liquid samples, about 5−6 mL each, were taken at regular intervals, and their compositions were analyzed by ICP-AES. Each experiment was carried out three times and the average values were reported. This was done to prevent experimental errors. The leaching efficiency of copper is calculated by the following eq 15.

\[ X_i = \frac{[V_0 - \sum_{i=1}^{n-1} V_i]C_i + \sum_{i=1}^{n-1} V_iC_i}{M} \]  

where \( X_i \) is the leaching rate of the \( i \)-th sampling, wt %; \( V_0 \) is the total volume of the leaching solution, \( V_i \) is the volume of the solution taken out of every time, mL; \( C_i \) is the concentration of copper of solution taken out of every time, g/L; and \( M \) is the total mass of copper in raw materials, g.

**Optimization of Experimental Parameters.** RSM is a powerful tool for the investigation of the effects of several independent parameters on a response, and the Box–Behnken design (BBD), which is a typical method of the RSM, is used to optimize the experimental parameters. Based on the leaching experimental results, a reasonable range for each experimental parameter was chosen for the experimental design. The total number of experiments (N) are determined from eq 16.

\[ N = 2^k + 2k + n_0 \]  

where \( k \) is the number of experimental parameters and \( n_0 \) is the number of repetitions at the center points. The response (\( \gamma \)) was estimated using a second-order mathematical model based on the experimental data (eq 17).
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Notes
The authors declare no competing financial interest.

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