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Column bioleaching copper and its kinetics of waste printed circuit boards (WPCBs) by *Acidithiobacillus ferrooxidans*

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HIGHLIGHTS

- Column bioleaching of waste printed circuit boards by *Acidithiobacillus ferrooxidans* was examined.
- The kinetic process was fitted using conventional kinetic models and modified kinetic models.
- The column bioleaching of rate was controlled by the diffusion of ions through the liquid boundary layer.

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ABSTRACT

Application of bioleaching process for metal recovery from electronic waste has received an increasing attention in recent years. In this work, a column bioleaching of copper from waste printed circuit boards (WPCBs) by *Acidithiobacillus ferrooxidans* has been investigated. After column bioleaching for 28 d, the copper recovery reached at 94.8% from the starting materials contained 24.8% copper. Additionally, the concentration of Fe^{3+} concentration varied significantly during bioleaching, which inevitably will influence the Cu oxidation, thus bioleaching process. Thus the variation in Fe^{3+} concentration should be taken into consideration in the conventional kinetic models of bioleaching process. Experimental results show that the rate of copper dissolution is controlled by external diffusion rather than internal one because of the iron hydrolysis and formation of jarosite precipitates at the surface of the material. The kinetics of column bioleaching WPCBs remains unchanged because the size and morphology of precipitates are unaffected by maintaining the pH of solution at 2.25 level. In bioleaching process, the formation of jarosite precipitate can be prevented by adding dilute sulfuric acid and maintaining an acidic condition of the leaching medium. In such way, the Fe^{2+}–Fe^{3+} cycle process can kept going and create a favorable condition for Cu bioleaching. Our experimental results show that column Cu bioleaching from WPCBs by *A. ferrooxidans* is promising.

1. Introduction

Waste printed circuit boards (WPCBs) is an important resource of metal pollutions in the environment (Cui and Forssberg, 2003; Veit et al., 2005; Wu et al., 2008). In WPCBs, the main metallic elements include copper 20.19%, aluminum 5.7%, nickel 0.43%, iron 7.33%, tin 8.83%, lead 5.53% and precious metals such as silver and gold about 0.3% (Yamane et al., 2011). WPCBs also contains a large number of hazardous substances such as brominated flame retardants and other heavy metals. Therefore recycling and decontamination of the WPCBs are necessary for the protection of the environment.

The technologies used for treatment of WPCBs include pyrometallurgical and hydrometallurgical (Pant et al., 2012; Tuncuk et al., 2012). However, the process of recycling WPCBs using pyrometallurgical and hydrometallurgical is difficult to meet the requirements of the low-cost, green process and simple production technology and management. In recent years, bio-hydrometallurgical approach has increasingly gained attentions for recovery of metals from WPCBs, since it is simple, environmental friendly, and economical (Brandl et al., 2001; Erüst et al., 2013; Wang et al., 2009). Bioleaching process, also known as microbial leaching, is based on the ability of microorganisms to recover metals via the production of metabolites. Both

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autotrophic and heterotrophic microorganisms have been reported to be used in the bioleaching process (Li et al., 2014; Qu and Lian, 2013).

A number of researches (Ilyas et al., 2007; Xiang et al., 2010) have demonstrated the ability of microorganisms in leaching metals contained in WPCBs. For example, several studies have reported the ability of *Acidithiobacillus ferrooxidans* (*A. ferrooxidans*) in bioleaching copper from WPCBs (Liang et al., 2013; Zhu et al., 2011). sulfuric acid and ferrous ion are involved in the bioleaching process, where ferrous ions are oxidized to ferric ions (Eq. (1)). Cu^0 in WPCBs is in turn oxidized by Fe^{3+}, while Fe^{3+} itself is reduced to Fe^{2+} (Eq. (2)). In such a way, a Fe cycle is established in the leaching process. As a result, the rate of the overall reaction is which significantly increased.

$$4Fe^{2+} + 4H^+ + O_2 \xrightarrow{A.ferrooxidans} 4Fe^{3+} + 2H_2O \quad (1)$$

$$Cu + 2Fe^{3+} \rightarrow Cu^{2+} + 2Fe^{2+} \quad (2)$$

With rapid increase of the WPCBs as an electronic waste and worldwide environment awareness, an effective industrial methods is necessary to treatment WPCBs (Wu and Qiu, 2014). Bio-heap leaching processes are commercially used especially for the recovery of copper from low-grade ores and mineral concentrates (Brierley, 2001; Olson et al., 2003). Therefore, the recycling of WPCBs by bio-heap could be of an great importance in industrial operation. Column leaching is used as a simulating model for heap or dump leaching processes, which gives information about what could be expected in heap or dump leaching and how leaching conditions can be optimized (Ilyas et al., 2013; Muñoz et al., 1995; Qiu et al., 2011). Ilyas et al. (2010) recently employed column reactors for bioleaching of WPCBs by moderately thermophilic bacteria, which exhibited a recovery of copper (85%) in 300 d.

Many researches indicate that the information of kinetic is very important to optimize the leaching parameters and to improve column bioleaching performance (Olson et al., 2003; Rohwerder et al., 2003). However, up to now, no data on kinetic are available using acidophilic microorganisms (such as *A. ferrooxidans*) in column metal bioleaching of from WPCBs. Moreover, some papers show that maintaining pH of leaching solution can achieves higher copper extraction efficiency in a shaking flask experiment (Yang et al., 2009; Zhu et al., 2011). Whether this method can apply to a column bioleaching and what is the effects on bioleaching of sulfuric acid are questions need to be investigated.

The purpose of this study is to answer above questions, analyze the kinetics of column bioleaching of copper and evaluate the performance of *A. ferrooxidans* in such a reactor.

2. Materials and methods

2.1. Chemicals

All chemicals were of analytical grade (AR) and were used without further purification. All aqueous solutions were prepared using deionized water (Milli-Q Integral 5).

2.2. WPCBs sample

WPCBs used throughout this study were obtained from a local electronic waste supplier in Mianyang, China. For the column leaching experimental use, the scraps were crushed and screened to size range of 4–10 mm after manually removing the main electronic components (e.g. capacitors, batteries and resistors). The analytical results of selected elements of the WPCB sample is listed in Table 1.

Because WPCBs contain some metallic oxides and alkaline substances, they were washed with dilute sulfuric acid (pH = 2.0) before used in column leaching. 250 g of pre-washed WPCBs samples was soaked in 5.00 L of dilute sulfuric acid (pH = 2.0). The pH of effluent was monitored continuously and an appropriate amount of 5.0 mol L^{-1} of H_2SO_4 was added gradually. After the stabilization of pH, the samples, which settled down at the bottom of every sample, was separated, then washed and dried to constant weight. The sample was digested in aqua regia and the concentration of Cu in this sample is 24.5% ± 0.041.

2.3. Bacteria and culture conditions

The bacterium used in this study was *A. ferrooxidans SW-02* (*A. ferrooxidans*) (Yang et al., 2014). This bacterium was provided by the Key Laboratory of Solid Waste Treatment and Resource Recycle, Ministry of Education (Southwest University of Science and Technology). After isolation, purification, 16S rDNA gene amplification, its sequencing and checking homology by NCBI blast search, it was submitted to GenBank for accession number (KJ094412).

The bacterium was incubated in optimized 4.5 K medium salt media (Fu et al., 2011). The optimized 4.5 K medium was composed of mineral salts [$(NH_4)_2SO_4$ 2.0 g L^{-1}, K_2HPO_4 0.25 g L^{-1}, $MgSO_4{\cdot}7H_2O$ 0.25 g L^{-1}, KCl 0.1 g L^{-1}, $Ca(NO_3)_2$ 0.01 g L^{-1}] and 22.2 g L^{-1} of $FeSO_4{\cdot}7H_2O$. Medium components for further experiment were the same as described here. The culture of *A. ferrooxidans* was incubated in 250 mL Erlenmeyer flasks each containing 100 mL of the medium and 1% (v/v) inoculum, on a rotary shaker at 170 rpm and 30 °C. The initial pH of the cultural medium was adjusted to pH 2.0 using a 5.0 M H_2SO_4 solution After several successive incubation steps, bacterial concentration in the late logarithmic phase) reached to approximately 20×10^7 cells mL^{-1} and the pH of bacterial cultures was 2.25 ± 0.05 at this time. To acclimatize the bacteria, 1.00 mL of the inoculum was added to a 250 mL Erlenmeyer flask containing 100.0 mL of the prepared 4.5 K medium. The flasks were agitated in a rotary shaker at 170 rpm and 30 °C. When the solution turned red and the pH of the solution reached 2.25 ± 0.05, 0.2 g WPCBs chips was placed into the solution and leached for two days. The bacteria was accustomed to WPCB substrate by gradually increasing the quantity of WPCBs, started from 0.2 g and ended at 3.5 g, at which no bacteria could grow any more. At each step, a 1% (v/v) inoculation was performed using a sample obtained from the previous step. Finally, cells were harvested by centrifugation at 12,000*g* for 20 min. Cell pellets were washed twice with deionized water and then incubated in the prepared 4.5 K medium until the lag phase was reached.

2.4. Column leaching experiments

Four column reactors (height 20 cm, internal diameter 6.0 cm, Fig. 1) were used for column bioleaching tests. First, every column was filled with 250 g washed sample. In the tests with columns A and B, a 4.95 L of prepared 4.5 K medium (initial pH = 2.0) and 0.05 L of *A. ferrooxidans* culture were added into a graduated incubator whereas in the tests with column C and D, while only 5.00 L 4.5 K cultural medium was added in the incubator (initial pH = 2.25 ± 0.05). To maintain the feed at 30 °C, the column reactor and the incubator were placed in a thermotank. Clean air was provided through an air compressor with the flow rate of 20 L min^{-1}. All columns was fed with the leaching solution using a peristaltic pump at the rate of 40 mL min^{-1} after bacterial cultures in the late logarithmic (the pH of bacterial cultures was 2.25 (±0.05) at this time) phase in columns A and B. During the leaching process, the pH of solution of columns A and C was maintained at 2.25

Table 1
Chemical analysis the representative sample of the WPCBs.

Component	Cu	Ca	Al	Pb	Fe
%(w/w)	24.8 ± 0.045	7.1 ± 0.037	2.5 ± 0.041	0.57 ± 0.033	0.18 ± 0.047

The values represent means of those obtained from triplicate experiments.

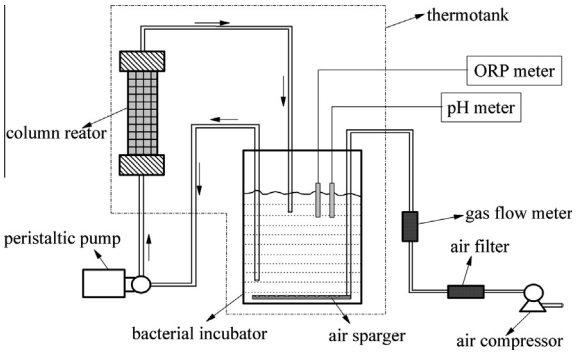

Fig. 1. Sketch of column bioleaching unit.

(±0.05) by adding an appropriate amount of 5.0 M H_2SO_4. Supernatant of 5.00 mL were collected, filtered, and acidified every 24 h to analyze the concentrations of Cu^{2+}, Fe^{2+}, Fe^{3+} and the pH in the culture medium. Evaporation losses of leaching solution were supplemented by an equal amount of distilled water. When analysis of leaching solution indicated that bioleaching had reached to in lag phase in column A, the leaching solution of all columns was allowed to drain off completely. The column charge was rinsed with distilled water. The residues were then dried and prepared for final analysis.

2.5. Analytical procedure and methods

For metal content analysis in the original WPCBs, the pulverized samples (0.5 g) were added into a 20.00 mL aqua regia in a tight sealed vessel and heated at 160 °C for 6 h to dissolve. The solution was then cooled to room temperature and the volume was adjusted to 50.00 mL for metal determination (Cu, Ca, Al, Pb, Fe) by inductively coupled plasma atomic emission spectrometry (ICP–OES, ThermoFisher iCAP6500, USA).

The concentrations of Cu^{2+} and total iron (T-Fe) in cultural medium were measured by an atomic absorption spectrophotometry (PerkinElmer AA700, USA) during bioleaching process, whereas Fe^{2+} was analyzed by titration, using 4.903 g L^{-1} potassium dichromate as an titrant. pH of the solution w measured using a digital pH meter (Mettler Toledo SevenMult S40, Germany) and Oxidation Reduction Potential (ORP) was monitored by a 501 ORP Meter (Shanghai Precision & Scientific instrument, China). The number of bacteria was counted during acclimatization of bacteria using a Helber bacteria counting chamber. SEM–EDX analysis was performed with a field emission scanning electron microscope (Carl Zeiss Ultra 55, Germany).

3. Results and discussion

3.1. Copper recovery on column bioleaching

Many researches (Wang et al., 2009; Zhu et al., 2011) have demonstrated that copper can be leached efficiently using *A. ferrooxidans* in shake flasks. However, insufficient data are available on the use of *A. ferrooxidans* in a column Cu bioleaching from WPCBs and its potential for commercial exploitation. In order to find the behavior of *A. ferrooxidans* on the column bioleaching of WPCBs, the concentrations of Cu^{2+} in the cultural medium was analyzed regularly.

Fig. 2 showed Cu^{2+} concentration in the bacterial culture and its recovery during the leaching process, which reflects the bioleaching activity. The recovery was calculated based the following equation:

$$\text{Cu recovery } \% = \text{Wt Cu}_{\text{leach.soln}}/\text{Wt Cu}_{\text{clips}}$$

where Wt $Cu_{leach.soln}$ = $[Cu^{2+}]_{soln}$ × V_soln.

Wt Cu_{clips} = Multiply Wt of clips by percent of Cu contained in the clips used fill in the leaching column.

In groups C and D (abiotic systems), copper recovery was very low and no evidence of any significant metal leaching and no any difference produced in incubated systems. This indicates that without bacteria copper leaching was nil is unaffected even though the pH of leaching solution is adjusted by adding sulfuric acid (column C). In addition, in column B (without acid adjusting), only about 42.8% of copper was extracted in 28 d. The maximum copper extraction was observed in column A, and about 94.8% of copper was extracted in 28 d. Compared with column B, the bioleaching solution pH in column A was maintained at 2.25 (±0.05) with adjustment with 5.0 M H_2SO_4. The result shows that maintaining pH is very important to column bioleaching WPCBs. The results showed that copper leaching is greatly influenced by both the presence of the bacteria and an adequate pH.

3.2. The mechanism of sulfuric acid addition

Sulfuric acid was added to adjust the solution pH and achieve a higher copper extraction efficiency (Chen et al., 2011). The copper recovery with *A. ferrooxidans* is affected significantly by adding H_2SO_4 as showed in Section 3.1. Further study of this phenomenon is necessary.

In groups B and D, the pH of leaching solution was not adjusted by H_2SO_4. Figs. 3 and 4 show the changes in pH, Fe^{2+} and Fe^{3+} concentration during 28 d of bioleaching period. The pH in column D increased quickly during the first 10 d of leaching, and then rose

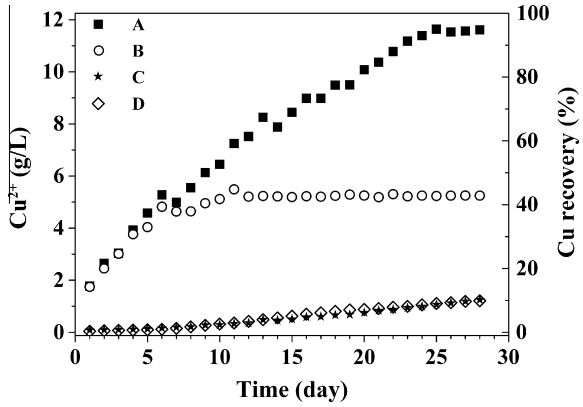

Fig. 2. The concentration and recovery of copper on column leaching. ((A) Column A, bacteria, adding acid; (B) column B, bacteria, without adding acid; (C) column C, without bacteria, adding acid; and (D) column D, without bacteria, without adding acid).

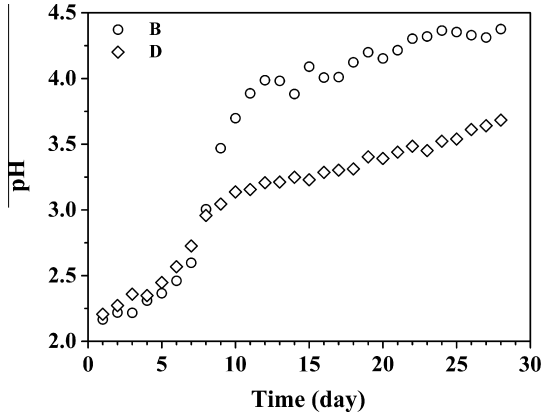

Fig. 3. The changes of pH in column leaching. ((B) Column B, bacteria, without adding acid and (D) column D, without bacteria, without adding acid).

slowly from 11 d. Oxidization rate of ferrous by O_2 in the leaching process (Eq. (3)) remained stable in D column after 11 d, due to the constant flow rate of clean air. This indicates that biochemical leaching occurs in the early phase which led the pH increase quickly. Moreover, the changing trend in Fe^{3+} in groups C and D was constant (Fig. 4), this indicates that Fe^{2+} oxidation by O_2 in column leaching process is unaffected when the pH of leaching solution is adjusted by adding 5.0 M H_2SO_4. And it explains why copper recovery in groups C and D has no difference.

$$4Fe^{2+} + 4H^+ + O_2 \rightarrow 4Fe^{3+} + 2H_2O \quad (3)$$

In column B, comparing with groups C and D, the consumption of H^+ is mostly contributed to ferrous ions oxidation by *A. ferrooxidans* (Eq. (1)). However, the changing trend of pH in groups B and D has no significant differences during the first 7 d. The T-Fe ions (the total Fe^{2+} and Fe^{3+}) concentration (Fig. 4) in group D changed from 4.49 g L^{-1} to 4.55 g L^{-1}, while in group B the T-Fe ions concentration changed from 4.31 g L^{-1} to 0.26 g L^{-1}. The experiment result indicates that the hydrolysis of Fe^{3+} (Eq. (4)) (Sasaki et al., 1998) provides plenty of H^+ to buffer the pH in group B. The oxidation of copper by Fe^{3+} in solution was the reaction mechanism of the bioleaching process (Eq. (2)). However due to the hydrolysis of Fe^{3+} and formation of jarosite precipitation reduced large quantity of Fe^{3+}. Therefore, a lower bioleaching rate in B is expected. In addition, a pH that was not low enough also caused a reduced bacterial activity, consequently lower leaching rate.

$$3Fe^{3+} + 2SO_4^{2-} + R^+ + 6H_2O \leftrightarrow KFe_3(SO_4)_2(OH)_6 + 6H^+ \quad (4)$$

In the aforementioned equation, R^+ represents K^+ and NH_4^+.

In group A, comparing with group B, the T-Fe ions concentration changed from 4.31 g L^{-1} to 0.53 g L^{-1} in the during the first 7 d, and its concentration remained at above 0.4 g L^{-1} after column bioleaching 7 d, while in group B the T-Fe ions concentration reduced to almost 0 g L^{-1}. This indicate that the hydrolysis process of Fe^{3+} (Eq. (4)) can be inhibited by adding 5.0 M H_2SO_4 to maintain a constant low pH in the leaching solution. Moreover, the Fe^{2+}–Fe^{3+} cycle (Eqs. (1) and (2)) was kept and more copper could be effectively leached. This explains why the copper recovery increased significantly when the pH was adjusted by adding 5 M H_2SO_4 (in Section 3.1).

3.3. Kinetics of column bioleaching

Bioleaching kinetics is very important to analyze the mechanism of metal leaching from WPCBs. To determine a suitable kinetic model, the following processes needed to be analyzed

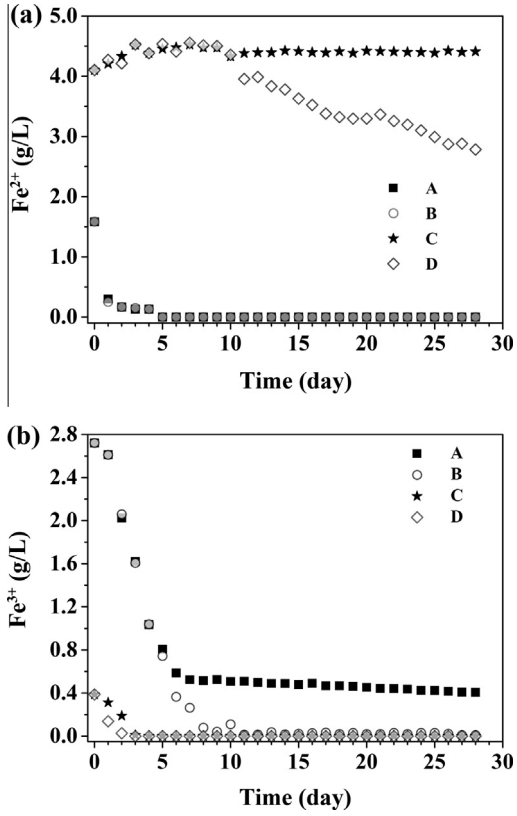

Fig. 4. The changes of Fe^{2+} and Fe^{3+} in column leaching. (The figure caption of columns A, B, C and D refers to Fig. 2 legend. (a) The concentration of Fe^{2+} during leaching period and (b) the concentration of Fe^{3+} during leaching period).

(Mishra et al., 2009): (1) the diffusion of a reactants from a liquid boundary layer to a solid product; (2) the diffusion of the reactant through the solid product layer; (3) a chemical reaction in the studied system; (4) the transfer of the resultant though the layer of the solid phase; (5) diffusion of the resultants from the liquid boundary layer to the solution.

The results of previous studies believed that leaching or bioleaching kinetics are controlled by diffusion mass transfer of either reactant or product ions through a liquid boundary layer or a product metal deposit (Mishra et al., 2008). If the reaction rate is controlled by a solid product layer diffusion, it can be described by application of shrinking core model theory (Eq. (5)) (Goto et al., 1996). When the leaching rate is controlled by a chemical reaction at the particle's surface, the leaching kinetics process can be represented by Eq. (6) (This equation describes a linear plot of gradient k (the first-order rate constant for the surface reaction.)) (Mishra et al., 2008). Because the progress of the leaching would be unaffected by the presence of any product layer, the quantity of reacting material is proportional to the available surface of the unreacted core. When no product layer is formed on the solid phase, the reacting particle would be shrinked during the reaction, finally the solid phase disappears. For small particle, this can be explained by a Stokes regime (Eq. (7)) (Mishra et al., 2008). The applicability of each kinetic model was derived using the metal leaching data from Fig. 2. Results for each model are plotted in Fig. 5(a, c and e).

$$kt = 1 - 2/3F_t - (1 - F_t)^{2/3} \quad (5)$$

$$kt = 1 - (1 - F_t)^{1/3} \quad (6)$$

$$kt = 1 - (1 - F_t)^{2/3} \quad (7)$$

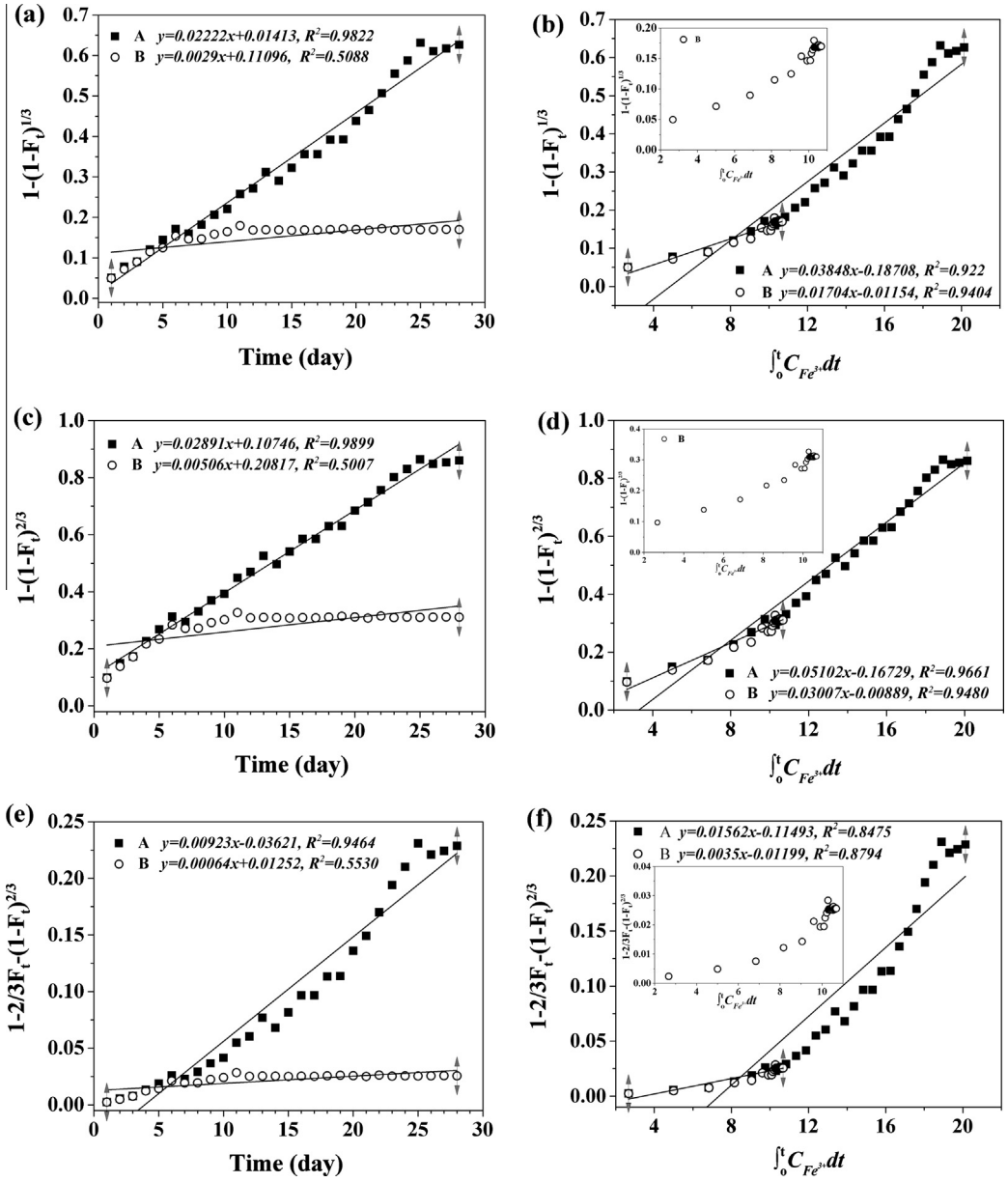

Fig. 5. The kinetics of copper leaching. (F_t represents the fraction of metal mobilized; columns A and B refer to Fig. 2 legend. (a) The rate control by chemical reaction of leaching in columns A and B. (b) The rate control by modified chemical reaction of leaching in columns A and B. (c) The Stokes regime model of leaching Cu in columns A and B. (d) The modified Stokes regime model of leaching Cu in columns A and B. (e) The shrinking core model of bioleaching Cu in columns A and B. (f) The modified shrinking core model of bioleaching Cu in columns A and B. Detailed data of column B was shown in the inserted figure (b), (d) and (f)).

In the aforementioned equation, t represents the leaching time; F_t represents the fraction of metal mobilized; k represents the rate constant.

In kinetic studies of bioleaching systems, generally, it is assumed that the concentration of the leaching agent (such as Fe^{3+}) is constant (da Silva, 2004; Giaveno et al., 2007). However, the concentration of Fe^{3+} can vary significantly during a bioleaching process (Fig. 4). This assumption may lead to inaccurate simulation of the bioleaching process using conventional kinetic models (Eqs. (5)–(7)). Accordingly, the conventional kinetics models for a bioleaching process should be modified by considering the variation of Fe^{3+} concentration in the column bioleaching solution. The following equations was applied as the new rate-controlling equations (Haghshenas et al., 2009). Among them, Eqs. (8)–(10) showed the bioleaching rate is controlled by solid product layer diffusion, chemical reaction and liquid boundary layer diffusion, respectively. The applicability of each new kinetic model was derived using the metal leaching data from Figs. 2 and 4. Results for each model are plotted in Fig. 5(b, d and f).

$$k\int_0^t C_{Fe^{3+}}dt = 1 - 2/3F_t - (1-F_t)^{2/3} \tag{8}$$

$$k\int_0^t C_{Fe^{3+}}dt = 1 - (1-F_t)^{1/3} \tag{9}$$

$$k\int_0^t C_{Fe^{3+}}dt = 1 - (1-F_t)^{2/3} \tag{10}$$

In the aforementioned equation, t represents the leaching time; F_t represents the fraction of metal mobilized; k represents the rate constant; $C_{Fe^{3+}}$ represents the Fe^{3+} concentration in the solution.

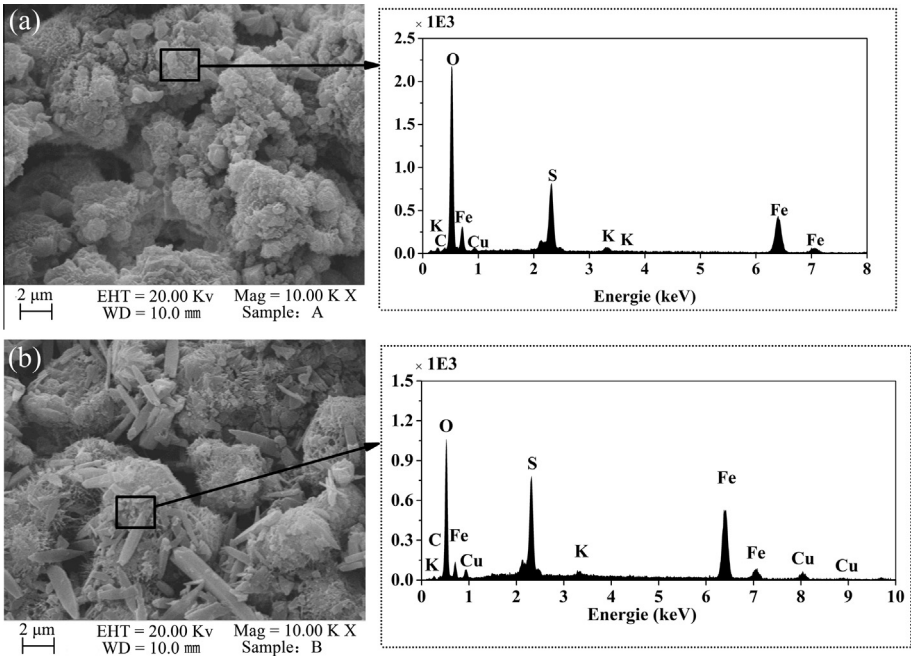

Fig. 6. The SEM of precipitates. ((A) Column A, bacteria, adding acid and (B) column B, bacteria, without adding acid).

In column B, using conventional kinetic models, the shrinking core model of Cu recovery (Fig. 5(e)) fits better than the Stokes regime model (Fig. 5(c)) and the chemical reaction model (Fig. 5(a)). However, using modified kinetic models, the Stokes regime model of Cu recovery fit better than the shrink core model and chemical reaction model. Further, the kinetic model in which the variation of Fe^{3+} with time is taken into account predicts the experimental data much better than the model in which variation of Fe^{3+} with time is negligible. These results indicate that it is feasible to use modified kinetic models to analyze in column B, and the liquid boundary layer diffusion is the controlling step of the bioleaching.

However, in column A, the data analysis based on conventional kinetic models are better than using modified kinetic models., Both conventional and modified kinetics models showed that the liquid boundary layer is the controlling step of the leaching process. In columns A and B, the concentration of Fe^{3+} has a notable difference after bioleaching for 6 d (Fig. 4(b)). The variation of Fe^{3+} with time is assumed negligible due to the concentration of Fe^{3+} was kept above 0.4 g L^{-1} in column A. This explained why conventional kinetic models are better than modified kinetic models. In addition, the kinetic process using modified models has a good compatibility when the concentration of Fe^{3+} is significantly reduce to under 0.4 g L^{-1}.

The copper bioleaching rates in groups A and B were also controlled by the external diffusion. This shows that the kinetic of column bioleaching copper from WPCBs is unaffected by the precipitation layer. However, shake flask level experiments reveal that the production precipitations such as jarosite is not conducive to bioleaching (Xiang et al., 2010). Thus it is necessary to analyze the precipitation layer.

Fig. 6 shows the SEM–EDX analysis of precipitation on WPCBs sample surface. The result shows that precipitates composition and morphology have not significant difference between column A and B by SEM–EDX. This shows that the precipitates composition and morphology is unaffected by adding 5.0 M H_2SO_4. Also in columns A and B, the structure of precipitates are loose and the size of precipitates are less than or equal to 3 μm. So the precipitation layer has little effect to the transfer process of iron ions or copper ions. This indicates that the transfer process of iron ions or copper ions in leaching process is unaffected by the precipitation layer comparing with the liquid boundary layer. This explains why the kinetics of column bioleaching copper in groups A and B also are controlled by an external diffusion.

4. Conclusions

The copper recovery from WPCBs by *A. ferrooxidans* the column reactors has been well demonstrated. Experiment results show that the rate of copper dissolution is controlled by external diffusion rather than internal diffusion. The kinetics of column bioleaching WPCBs remain unchanged because the size and morphology of precipitates would be unaffected by maintaining the solution pH. In the leaching process, the precipitation reaction could be restrained under a constant pH maintained by adding dilute sulfuric acid. Thus the Fe^{2+}–Fe^{3+} cycle process can be kept continue and promotes copper recovery. Based on the obtained result, column bioleaching copper from WPCBs by *A. ferrooxidans* is feasible and increasing the concentration Fe^{3+} and the velocity of leaching solution cycling may accelerate the kinetics of copper bioleaching in column reactor.

Acknowledgments

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