Effect of carbonaceous matter on copper behavior in bioleaching from waste printed circuit boards

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Abstract: In this paper, the effects of humic acid, activated carbon and graphite on the bioleaching behavior of copper from waste printed circuit boards (WPCBs) with HQ0211 bacteria strain have been investigated. The compatibility test and the optimal additive amount of carbonaceous matter and the mechanism analysis were studied. It was demonstrated that humic acid has good compatibility with microorganisms. Humic acid can significantly promote the dissolution rate of copper with appropriate amount. The addition of activated carbon and graphite could inhibit the growth of bacteria. And the inhibition was weakened on the bioleaching process. The optimal condition of bioleaching copper was WPCBs 50 g L−1, initial pH 1.5, bacterial leaching time 7 days, the leaching rate of copper increased by 11.08%, 8.71% and 6.84% respectively in the experimental group with proper dosage of humic acid, activated carbon and graphite.

1. Introduction
With the rapid development of economy, the update speed of electrical and electronic equipments (EEEs) is accelerating, the quality of people's life is gradually improving, and the service life of household appliances and office electronic products is shortening at the same time. This phenomenon has lead to the generation of electronic waste[1,2]. As a necessary component of electronic products, waste printed circuit boards (WPCBs) is increasing gradually.

At present, the existing methods of metal resource utilization in WCMBs include pyrometallurgy, hydrometallurgy, mechanical physics and microbial method, etc[3-6]. Bioleaching technology has attracted more and more attention and research in the field of resource utilization of WPCBs due to its advantages of low cost, low energy consumption, simple operation and environmental friendliness [7]. Activated carbon, graphite, and humic acid (collectively referred to as carbon) are widely used in various fields because of their large specific surface area, adsorbability, high conductivity and environmental friendliness[8-11]. Many researchers began to apply carbonaceous matter to bioleaching, such as Mehrabani, J.V. etc [9]. in bioleaching pyrite and sphalerite, it was found that graphite as catalyst can improve the bioleaching rate of pyrite, while bioleaching sphalerite, graphite can increase the microbial population. Liuwei[12] found that the increase of cobalt ion leaching rate in bioleaching of cobalt ores was attributed to the electrochemical interaction between activated carbon and cobalt ores.

The use of the above carbonaceous matter in bioleaching of WPCBs has rarely been studied. In this paper, the effects of humic acid, graphite and activated carbon on microbial leaching of copper from
WPCBs were studied. The feasibility of carbon catalyzed bacterial leaching of copper was discussed, and the leaching conditions were optimized to provide basis for further experiments.

2. Experiments

2.1 Materials

WPCBs used in this study was purchased from an e-waste recycling company in Shanghai, China. The chemical composition is shown in Table 1, in which the content of copper is about 23.41%. Carbonaceous matter purchased from Shenyang Fifth Reagent Company.

| Component | Si  | Cu  | Ca  | Br  | Al  | Sn  | Ti  | Mg  | Pb  | Sr  | Zn  |
|-----------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Content   | 33.07 | 23.41 | 19.11 | 12.13 | 7.32 | 1.02 | 0.42 | 0.39 | 0.28 | 0.13 | 0.11 |

2.2 Microorganisms and cultivation

The HQ0211 bacterial strain used in this study is a mixture of Acidithiobacillus ferrooxidans, Ferroplasma acidiphilum, Leptospirillum ferriphilum. The bacterial strain was cultured in 9K medium, which contained 3.0 g (NH₄)₂SO₄, 0.1 g KCl, 0.5 g K₂HPO₄, 0.5 g MgSO₄•7H₂O, 0.01 g Ca(NO₃)₂, 44.2 g FeSO₄•7H₂O and 1L distilled water. All reagents were analytical grade (AR).

2.3 Compatibility test of carbonaceous matter with bacteria

Weigh 0.12 g of humic acid, graphite and activated carbon in an Erlenmeyer flask, respectively. Then the suspension of bacteria was transferred to the above Erlenmeyer flask containing 200 mL 9K medium in 10%(V/V) and cultured in orbital shaker at 45 ℃ and 170 rpm for 9 days. In addition, a blank control group without carbonaceous matter was set up, and other conditions remained unchanged.

2.4 Bioleaching

200 mL activated bacterial suspension, 10 g WPCBs and a certain amount of carbonaceous were taken into 500 mL erlenmeyer flask, then was placed in orbital shaker at 45 ℃ and 170 rpm. During the biological leaching process, redox potential (Eₗ), pH, Fe²⁺ concentration and copper ion concentration of the leaching solution were measured regularly.

2.5 Analytical methods

The morphology of leaching residue was analyzed by scanning electron microscopy (SEM, FEI-Quanta250FEG). The pH value of solution was measured by pHS−25 digital display pH meter (Shanghai, China), and TM39 potentiometer (Beijing, China) was used for solution potential measurement. Fe²⁺ concentration was measured by potassium dichromate titration. The concentration of Cu²⁺ was measured by iodometry and the leaching rate of copper was calculated by the following formula (1):

\[ \text{copper leaching percent} = \frac{C_1}{C_2} \times 100\% \]  

Which \( C_1 \) is the leaching concentration of copper from leachate solution in Erlenmeyer flask, and \( C_2 \) is the initial copper concentration of WPCBs.

3. Results and discussion

3.1 compatibility test

Before the copper reaction in bioleaching WPCBs was started, the compatibility test of mixed acidophilic bacteria HQ0211 with carbonaceous matter was carried out. The number of bacterial cells, redox potential (Eₗ), pH value and concentration of Fe²⁺ in the culture medium were used as indicators of the compatibility between bacteria and carbonaceous matter in bioleaching copper from WPCBs. The number of bacterial cells can directly reflect the growth of bacteria. Fig. 1 (a) showed that the mixed...
Acidophilic bacteria HQ0211 had good compatibility with humic acid, and the number of bacterial cells in the liquid was more than $1.0 \times 10^8$ cells per mL after 2 days of culture. Activated carbon and graphite inhibited the growth of bacteria to a certain extent, and entered logarithmic phase after cultured 4 and 8 days of culture, respectively, and stable phase on the 6th and 9th days. The change of pH value during the growth of bacteria was shown in Fig. 1(b). Mixed acidophilic bacteria HQ0211 is an autotrophic microorganism with good oxidation energy, which can oxidize Fe$^{2+}$ to Fe$^{3+}$ under aerobic conditions. In this process, a part of H$^+$ in the solution will be consumed resulting in a rise in the initial pH of the culture solution. After a period of reaction, the hydrolysis of Fe$^{3+}$ will lead to the production of H$^+$. Therefore, the pH of all the experimental groups decreased slowly in the following culture growth. The potentiometric value of HQ0211 solution depends on the relative amount of Fe$^{3+}$ and Fe$^{2+}$ and the more Fe$^{3+}$ the higher the potentiometric value when TFe is fixed [13]. Fig. 1 (c) shows that the change of $E_h$ in culture medium is contrary to the change of pH in Fig. 1 (b) and the change of Fe$^{2+}$ concentration in Fig. 1 (d). Under different carbonaceous matter concentration gradients, the potential value change gradually increase, and the Fe$^{2+}$ concentration showed a gradual decrease trend. This process can be explained by formula (2), and its basic reaction formula is as follows [14]:

$$4\text{Fe}^{2+} + 4\text{H}^+ + \text{O}_2 \rightarrow \text{HQ0211}^{2+} + 4\text{Fe}^{3+} + 2\text{H}_2\text{O}$$

Figure 1. Effects of carbonaceous matter on the number of growth bacteria (a), $E_h$ (b), pH (c) and concentration of Fe$^{2+}$(d).
3.2 Bioleaching

Fig. 2 shows the effects of humic acid on the redox potential ($E_h$), pH value, ferrous ion concentration and copper leaching percent in WPCBs leached by bacteria. In the presence of different concentrations of humic acid, the leaching behavior of WPCBs by mixed acidophilic bacteria HQ0211 is shown in Fig. 2a-d, respectively. Fig. 2d shows that the copper leaching percent were 76.07%, 87.15%, 84.86% and 80.71% respectively in the presence of 0 g/L, 0.2 g/L, 0.4 g/L and 0.6 g/L of humic acid. The results showed that humic acid significantly accelerated copper leaching. The optimum concentration of humic acid enhanced copper leaching was 0.2 g/L, and the leaching rate of copper increased by 11.08% compared with the control group. With the increase of humic acid content, the improvement of copper ion leaching rate is not obvious, which may be because excessive humic acid can chelate with metal ions and reduce the concentration of copper ion in leaching solution[15]. Fig. 2a and 2b show that $E_h$ and pH value decrease rapidly in first day, then gradually increase as the extension of leaching time and the change of pH into the opposite trend. From Fig. 2c, it can be seen that the main reason is that leaching reaction proceeds rapidly in the early stage of leaching. And Fe$^{3+}$ oxidizes copper to Cu$^{2+}$, so that copper can be quickly leached. The formation of Fe$^{2+}$, resulting in the rapid reduction of $E_h$. At the middle stage of leaching, mixed acidophilic bacteria converted Fe$^{3+}$ to Fe$^{2+}$ faster than Fe$^{3+}$ oxidized copper to Cu$^{2+}$, so the concentration of Fe$^{3+}$ increased slowly and the potential value increased slowly. Since WPCBs are alkaline, when WPCBs powder is added to the bioleaching system, the pH value increases rapidly, and the addition of humic acid alleviates the increase of pH in the leaching process to a certain extent. With the progress of bioleaching, the pH value decreases gradually due to the consumption of H$^+$ by bacterial oxidation Fe$^{2+}$[16].

![Figure 2. Effects of humic acid on leaching efficiency of $E_h$(a), pH(b), ferrous ion concentration(c) and copper leaching percent(d).]
Fig. 3a and 3b show the effect of the amount of activated carbon and graphite additives on the concentration of copper ions in WPCBs leached by bacteria. As shown in Fig. 3a, the leaching rate of copper increases gradually with the increase of the dosage of activated carbon. Finally, the leaching rate of copper increases from 75.19% to 84.78% under the condition of the addition of 0.6 g/L of activated carbon, and the leaching rate increases by 8.99%. From Fig. 3b, the leaching rate of copper increased from 75.19% to 82.13% when graphite content was 0.6 g/L. The reason may be that activated carbon and graphite have huge specific surface area, which can significantly improve the surface area of the carrier, increase the adhesion area of the carrier, effectively reduce the adhesion of jarosite on the surface of WPCBs, and thereby increasing the bioleaching rate[17].

![Figure 3a and 3b](image_url)

**Figure 3.** Effects of activated carbon (a) and graphite (b) on copper leaching efficiency.

3.3 SEM analysis
In order to study the effect of carbonaceous matter on bioleaching, the leaching residues were selected for scanning electron microscope (SEM) under the conditions of adding 0.2g /L humic acid, 0.6g /L activated carbon and 0.6g /L graphite, respectively.. Fig. 4 shows the SEM images of the samples before and after bioleaching. The results show that the surface morphology of WPCBs powder has significant difference before and after bioleaching. It can be seen that the original WPCBs powder surface is smooth, a large number of metals are evenly distributed or wrapped by plastic. According to the SEM photographs of bioleaching residues, compared with the biolithol residues without carbonaceous substances, the surface porosity of the residue samples increased after the addition of carbonaceous matter, the particle size decreased, and no jarosite attachment was found. In fact, in the acidic medium, the oxidation-reduction reaction and bacterial metabolites erode the surface of WPCBs particles, resulting in more reactive surfaces on the surface of samples due to corrosive chemical effects, thus increasing the dissolution rate of copper[18].
In this paper, the catalysis of carbonaceous matter in bioleaching process was studied. The results show that: (1) The addition of activated carbon and graphite can inhibit the growth of bacteria, but in the process of bioleaching, the addition of activated carbon and graphite increases the surface area of carrier, which can effectively reduce the formation of jarosite and promote the bioleaching rate. (2) Humic acid has good compatibility with mixed acidophilic bacteria HQ0211. (3) The addition of humic acid promotes the leaching rate of copper. The addition of humic acid increases the biomass of the leaching system, accelerates the oxidation rate of Fe^{2+} and keeps the concentration of Fe^{3+} in the leaching process at a higher level, thus increasing the leaching rate of copper. However, with the increase of the addition amount, the leaching rate did not increase significantly, and the final leaching rate of Cu^{2+} reached 87.15%.

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