Chemical Engineering Journal 324 (2017) 122–129

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Enhanced bioleaching efficiency of copper from waste printed circuit board driven by nitrogen-doped carbon nanotubes modified electrode

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HIGHLIGHTS

- NCNTs modified electrode can enhance the bioleaching rate of copper from waste printed circuit board.
- The role of NCNTs modified electrode on bioleaching process is positive effect.
- NCNTs modified electrode can be recycled on bioleaching process.

ARTICLE INFO

Article history:
Received 4 March 2017
Received in revised form 2 May 2017
Accepted 3 May 2017
Available online 5 May 2017

Keywords:
Electronic waste
Acidithiobacillus ferrooxidans
Modified electrode
Nitrogen-doped carbon nanotubes
Bioleaching

ABSTRACT

To improve the copper bioleaching efficiency from waste printed circuit board (WPCB) by *Acidithiobacillus ferrooxidans* (*A. ferrooxidans*), a novel simplified material (nitrogen-doped carbon nanotubes (NCNTs) modified electrode) was used in this paper. Experiments mainly including the exploration of NCNTs optimal concentration and recycling effect of NCNTs modified electrode were investigated. The variations of pH, ORP, Fe^{2+} concentration and Cu^{2+} concentration were studied in detail, and the mechanism of the modified electrode was also analyzed in this study. Conclusions were obtained that the optimal experimental conditions were: bacteria inoculation 10%, initial pH 2.0, WPCB powder 1 g, solid/liquid (w/v) ratio 1/50, temperature 28 °C, rotational speed 125 r/min and modified electrode 2.5 mg/cm^2. The copper bioleaching rate reached 99% after 9 days reaction, and it was 20% higher than that of the group which was only added *A. ferrooxidans*. With the analysis of XRD, the precipitate formed $(NH_4)Fe_3(SO_4)_2(OH)_6$ at the end of the reaction, and the modified electrode didn't affect the formation of the yellow precipitate. Meanwhile, the modified electrode could be recycled, and the positive effect wasn't weakened obviously on these processes. The results may provide a reference for enhancing the copper bioleaching efficiency from WPCBs and expand the application of NCNTs in hydrometallurgy field.

1. Introduction

Continuously economic development and improvement of people's living standard has been accompanied by daily growth of waste electrical and electronic equipment (WEEE) around the world [1,2]. According to the statistics by Solving the Electronic Waste (e-waste) Problem (StEP), the total generated WEEE in the global was approximately 48.9 million tons and China had 7.25 million tons of WEEE in 2012. By 2017, the production of e-waste will reach 65.4 million tons, and 80% of the e-waste will be shipped to Asia [3]. The printed circuit board (PCB) is an important part of electrical and electronic equipment. Large amount of WEEE will generate numerous waste printed circuit board (WPCB) [4]. Statistics showed that more than 0.5 million tons of WPCB need to be disposed per year, and continuous growth of WPCB has been accompanied by environmental pollution [5]. Usually, the contents of PCB are 30% polymer materials, 30% inert oxides, and 40% metals, respectively [6]. Copper is one of the predominant metals, followed by iron, nickel, and precious metals. WPCB which is known as "secondary resources" because of its high value, is a hot spot in present studies. Meanwhile, it

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http://dx.doi.org/10.1016/j.cej.2017.05.024
1385-8947/

also has some heavy metals and organic pollutants. When informal treatment is adopted to remove these contamination, it is harmful to both environment and human health [7,8].

To date, there were many approaches for extracting metals from WPCB, such as thermal treatment, mechanical, chemical, and biological methods [9–11]. Incineration will produce dioxins which belong to the toxic substances. Although pyrolysis can suppress the generation of harmful gases, but its industrial application costs high [12]. Mechanical method mainly contains pretreatment, crush, and separation, it has high energy consumption, and the dust produced in the processing of mechanical disruption will lead to pollute the work environment [13]. Chemical method mainly exists large consumption of reagents, and lots of waste acids are produced at the end of reactions [11]. Biological method refers to the use of oxidation, adsorption and acid dissolution in bioleaching metals from WPCB by microorganisms or their metabolites. Microorganisms including *Acidithiobacillus ferrooxidans*, *Acidithiobacillus thiooxidans* and *Leptospirillum ferrooxidans* are commonly used in laboratory [14–16]. Due to less consumption of reagents and pollution to the environment, biological method is considered as a green leaching technology. Unfortunately, the bioleaching efficiency is low, and measures have been taken to improve it, such as surfactants, electric field, carbon nanomaterials were participated to improve the bioleaching efficiency. Tween 80 could promote sulfur metabolism in the growth of *A. ferrooxidans* [17]. Cao [18] investigated the effect of electric field to bioleaching copper from WPCB by *A. ferrooxidans,* and results showed that an appropriately direct current could control the concentration of Cu^{2+} in solution, then improve the bioleaching efficiency of copper.

As a nano-material, NCNTs has an enormous surface area, favorable selectivity and stability, excellent conductivity. These characteristics make it commonly used in the catalysis field, especially in the field of fuel cell and heterogeneous catalysis [19,20]. The effect of nitrogen-doped carbon nanotubes (NCNTs) in bioleaching copper from WPCB was researched by Bai [21], and results indicated that NCNTs could improve the bioleaching efficiency of copper, and it could be recycled. However, the mechanism of catalysis about NCNTs wasn't analyzed in this research. To date, there was no study about using NCNTs modified electrode to bioleaching copper from WPCB.

Accordingly, the objective of this study was to explore the effect of NCNTs modified electrode in bioleaching copper from WPCB by *A. ferrooxidans,* to optimize the conditions of bioleaching reaction and provide a foundation of the further pilot test. The mechanism of NCNTs modified electrode was also investigated. Finally, the recycling feasibility of modified electrode was studied. Meanwhile, the applications of modified electrode in the field of hydrometallurgy were expanded definitely.

2. Materials and method

2.1. Characterization of circuit board from spent phones

Generally PCB without components is consist of some heavy metals like gold, copper, stannum, nickel and some other organic substances, and the compositions also vary slightly with different manufacturers and years definitely. In this study, PCB was collected from an e-waste recycling company in Shanghai. The material was ground by grinder (DF-40, Bilon, China) and sieved to obtain a mesh size of <1 mm. This powder was dissolved by aqua regia ($HCl:HNO_3$ = 3:1, Analytical grade) and analyzed by ICP-AES (A6300, Thermo, USA), and the main metals in circuit boards from spent phones are shown in Table 1.

2.2. Manufacture of NCNTs modified electrode

Carbon cloth was soaked in HNO_3 solution for 4 h with the purpose of removing impurities and increasing the content of nitrogen. Then using deionized water to wash it until the pH in the solution rose to 7.0, and drying it in 120 °C oven for 2 h [22]. As the anode material, the carbon cloth was cut into 4 cm × 2 cm prior to the experiment.

The diffusion layer in cathode was made as follows: First, 30% of PTFE was painted on both sides of the carbon cloth, and after 2 h of natural drying, the carbon cloth was heated in the muffle furnace at 370 °C for 20 min. Second, the black carbon was dissolved by 40% PTFE, and painted on one side of the carbon cloth, then the carbon cloth was heated in furnace at 370 °C for 20 min again after its 2 h of natural drying. Third, 60% PTFE was painted on the side which was already painted black carbon, then heated in furnace at 370 °C for 10 min. All of these steps were repeated four times. Finally, the diffusion layer in cathode was obtained from these steps, and it had the best diffusion effect of oxygen.

The catalyst layer in cathode was painted with NCNTs. A concentration gradient like 0, 1.0, 1.5, 2.0, 2.5, 3.0 mg/cm^2 of NCNTs was adopted to paint the other side of carbon cloth. Deionized water, nafion and iso-propanol were mixtured and added into small beaker which the NCNTs was already in it. Then treated with ultrasound in order to make sure the NCNTs was fully dispersed, and the catalyst layer was formed after 24 h of natural drying. The brief flow of modified electrode is shown in Fig. 1.

2.3. Source and adaptation of bacteria

A pure culture of *A. ferrooxidans* was isolated from acidic mine drainage taken from the copper mine, Dexing, Jiangxi province, China [6,23]. The bacteria was grown in 9 K medium with its components: $(NH_4)_2SO_4$ 3.0 g, KCL 0.1 g, $MgSO_4{\cdot}7H_20$ 0.5 g, K_2HPO_4 0.5 g, $FeSO_4{\cdot}7H_20$ 44 g, $Ca(NO_3)_2$ 0.01 g, 1000 ml deionized water. 20% H_2SO_4 was used to adjust pH value.

The growth cultures of *A. ferrooxidans* on modified electrode were investigated with the increase of NCNTs under the 28 °C and 125 r/min condition. The concentration of copper ions was also increased with the purpose of improving the *A. ferrooxidans*' resistance. The cell number was continuously monitored during the growth period, and the number of bacteria remained almost constant after one week, then 10% bacteria was inoculated into fresh culture for another domestication. This adapted strain was used in next bioleaching experiment.

2.4. Bioleaching experiment

Bioleaching studies were carried out in 150 ml conical flasks, there were about 50 ml 9 K culture medium in each of them, and the initial pH was adjusted to 2.0 by 20% H_2SO_4. PCB powder 1 g, bacterial inoculation 10% and the solid to liquid ratio 1:50 were performed in these experiments. A wire was used to connect the anode and cathode, which was called modified electrode system in this present study. Series of different modified electrode experiments are shown in Table 2. Using a group of inoculating *A. ferrooxidans* but free of carbon cloth and NCNTs as control, three parallels were set up in each experiment (Seen from Table 3). After 9 days bioleaching, the modified electrode was washed 2–3 times by deionized water, when it was dried naturally, the same experiment was carried out to confirm the possibility of recycling towards the modified electrode.