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Recycling of metals from pretreated waste printed circuit boards effectively in stirred tank reactor by a moderately thermophilic culture

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To seek a feasible technique for processing waste printed circuit boards (PCBs), pretreatment of PCBs by table separation and further bioleached by moderate thermophiles in a stirred tank reactor were investigated. The shaking table separation, conducted after grinding and sieving of PCBs, produced two fractions: metal-rich parts (RPCBs), which is more suitable for pyrometallurgy process than untreated PCBs, and metal-poor parts (PPCBs) with only 8.83% metals was then bioleached by a mixed culture of moderate thermophiles effectively. After adaptation, the mixed culture could tolerate 80 g/L PPCBs. The bioleaching results showed that metals recovery was 85.23% Zn, 76.59% Cu and 70.16% Al in only 7 days. Trace Pb and Sn were detected in the leachate because of precipitating. The microorganism community structure was analyzed by amplified ribosomal DNA restriction analysis. Two moderately thermophilic bacteria species were identified as *Leptospirillum ferriphilum* and *Acidithiobacillus caldus*. Furthermore, uncultured *Thermoplasmatales archaeon* was also detected in the leaching system. It was also shown that moderate thermophiles revealed best bioleaching ability when compared with mesophiles and the mixture of mesophiles and moderate thermophiles. Finally, we designed a two-stage process model according to the present study to achieve semi-industrial waste PCBs recycling and economic feasibility analysis indicated that the process was profitable.

[**Key words:** Waste printed circuit boards; Table separation; Bioleaching; Moderate thermophiles; Community structure; Amplified ribosomal DNA restriction analysis]

Electronic waste (e-waste) is one of the fast growing streams in the world. Relatively short life-span and high eliminated rate of electron and electronic equipment has resulted in increasing amount of e-waste and threatening the environment and human health due to its hazardous components. Printed circuit boards (PCBs), as typical e-waste, its recycling has attracted attentions not only from perspective of waste treatment but also valuable metals (1). It was demonstrated that the metal content in PCBs is around 28%, of which the percent of copper was up to 20%. Precious metals like silver, platinum and gold also presenting in the electronic scrap accounted for 0.3–0.4%. The content of rest materials was plastics 19%, bromine 4%, glass and ceramics 49% (2). Provided that a suitable treatment and recovery process is applied, waste PCBs might serve as a secondary metal resource.

Traditional methods, such as pyrometallurgical, hydrometallurgical and mechanical processes, of recycling metals from PCBs (3,4), to some extent, cause secondary pollution and require high investments and high energy consumption. Currently the main industrial-scale treatment and metal recovery method for PCBs is the combination of mechanical separation and pyrometallurgy. Mechanical separation, for example, table separation, conducted after grinding and sieving, produced two fractions: metal-rich (RPCBs) and metal-poor (PPCBs) parts. After mechanical separation, RPCBs with high metal contents meeting the request of advanced pyrometallurgy was sent to metallurgical plant to obtain pure metal, while PPCBs was used as building materials or discarded directly (5). However, PPCBs, a spare fraction produced by sharking table separation, may still contain residual metals and other harmful compounds in quantities that may prevent further utilization or disposal according to legislation. Unfortunately, to reduce costs, some factories even used these parts directly as building materials, which will result in long term ecology and health problems (6,7). In addition, it is also a waste of resource to discard PPCBs directly with valuable metals in it.

Consequently, searching for a simple, low-cost and environmentally friendly approach to recycle metals from PPCBs is an urgent issue. Biohydrometallurgy may be a promising technology in the recycling of PCBs (8). It depends on naturally biological attachment and their metabolites in extracting valuable metals from the waste (9). Furthermore, it has exhibited great success in the leaching of low-grade ores (10). In recent years, bioleaching has been applied in recovering metals from e-waste and show great potential. Based on the research by Brandl et al. (11), during bioleaching of metals from e-waste at concentrations of 5–10 g/L,

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more than 90% copper could be leached by *Thiobacillus*. Similar phenomenon was observed in the research by Yang et al. (12), when the PCBs concentration was 15 g/L, Cu (96.8%), Zn (83.8%), and Al (75.4%) were recovered after 72 h by *Acidithiobacillus ferrooxidans*. Furthermore, due to the high toxicity of PCBs itself, microbial growth was obviously inhibited with PCBs concentration increasing. Therefore, the reports about bioleaching of PCBs were always carried out under low concentration (10,13,14). However, industrial-scale waste PCBs recycling by biohydrometallurgy will be required high level PCBs concentration.

In this paper, powdered PCBs was separated by shaking table separator firstly, and the PPCBs was then bioleached by a mixed culture of moderate thermophiles in the stirred tank reactor. To increase the tolerance of microorganism and bioleaching efficiency in high concentration of PPCBs, the mixed culture was adapted for a long time. Finally, at 80 g/L PPCBs, the culture grew well, meanwhile, achieving relatively high metals recovery, and the community structure was analyzed by amplified ribosomal DNA restriction analysis (ARDRA). We also compared metals recovery by different mixed culture applied in bioleaching PCBs. Then a two-stage leaching model and its economic feasibility was constructed to simulate semi-industrial waste PCBs processing. This study would provide some valuable information for finding a new and feasible way for recycling waste PCBs.

MATERIALS AND METHODS

A brief procedure description for this study The main experimental design is shown in Fig. 1. Firstly, powdered PCBs is divided to RPCBs and PPCBs by shaking table separation, and the former containing metal concentrates can be processed by pyrometallurgy directly. Then PPCBs as low-grade material will be bioleached to extract residual metals at a relatively high pulp density by adapted moderate thermophiles.

Pretreatment of PCBs by sharking table separation The waste printed circuit mother boards were obtained from electronics shop in Changsha, China. No physical or mechanical separation process was used before transportation to the laboratory. The scraps were directly cut into small pieces (diameter <40 mm), then pulverized into granules by a vibratory mill, and the PCBs powder between 74 μm and 1 mm was collected and subjected to homogenizing by the agitator, and sorting by a shaking table finally.

Table separation was operated on a sloping bed to separate particles according to specific gravity and particle size in water media (5). The powdered PCBs entered into the classifier through a feed well at the upper end of the bed. With the effect of gravity, lateral flow force from water, the inertial and friction force generated by asymmetric reciprocating motion of shaking bed, the particles were made longitudinal and lateral movement along the inclined surface of the bed. Finally, according to the proportion and granularity hierarchical, the particles were discharged from different areas of sharking bed, with metal-rich parts at the bottom and metal-poor parts at the central or upper. Both of the metal-rich parts and metal-poor parts were then dried to constant weight in a vacuum drying oven at 45°C.

The enrichment and adaptation of bioleaching microorganisms Acid mine drainages (AMD) sample was taken from Dexing Copper Mine, which is the biggest copper mine in China and located at E117°43.258′, N29°13.449′. Biogeochemical properties of AMD sample are shown in Table 1. There are various heavy metals with different levels and relatively low pH but high redox potential, also element S^0 appearing. Then the sample was inoculated into the medium, which contained (g/L) $(NH_4)_2SO_4$ 3.0, Na_2SO_4 2.1, $MgSO_4 \cdot 7H_2O$ 0.5, K_2HPO_4 0.05, KCl 0.1, Ca $(NO_3)_2$ 0.01, $FeSO_4 \cdot 7H_2O$ 30, S^0 4, and cultured at 45°C for enrichment of moderate thermophiles. The medium pH was initially adjusted to 2.0 with 5.0 mol/L H_2SO_4 solution. The above enrichment culture was then acclimated by increasing PPCBs quantities (10 g/L, 30 g/L, 50 g/L, and 80 g/L, respectively). For each step, 10% (v/v) culture, obtained from the previous step, was inoculated. The adaptation experiments were performed in a 3 L glass cylindrical reactor with a mechanic stirrer operating at 400 r/min and 45°C. The recovery rate of metals was estimated from the ratio of dissolved metal ions to the original metal content in the powdered PPCBs. After being cultured for several days, aliquots of bioleaching liquid were sampled periodically to analyze the concentration of metals.

Bioleaching experiments The bioleaching experiments were performed in a 3 L glass cylindrical reactor, placed in a thermostatic bath to keep the constant temperature at 45 ± 0.2°C, and equipped with a top-entered mechanic agitator operating at 400 r/min. Aeration was supplied from the bottom of the reactor at a flow rate of 400 mL/min. The acclimatized culture from the final stage of adaptation experiments was inoculated into 1800 mL modified 9 K medium (g/L): $(NH_4)_2SO_4$ 3.0, Na_2SO_4 2.1, $MgSO_4 \cdot 7H_2O$ 0.5, K_2HPO_4 0.05, KCl 0.1, Ca $(NO_3)_2$ 0.01, with additional 25 g $FeSO_4 \cdot 7H_2O$ and 3 g S^0. The initial pH was adjusted to 2.0. The acid consumption was compensated by 5 mol/L H_2SO_4 to keep pH value around 2.0 at the initial period of bioleaching. Distilled water was supplemented for evaporation losses regularly.

Analysis methods Metal contents in the PCBs and the elements contained in AMD sample were determined by inductively coupled plasma–atomic emission spectrometer (ICP–MS). Metal ions and total iron concentrations in solution were determined by atomic absorption spectrophotometer (AAS). Ferrous iron concentration in solution was assayed by titration with potassium dichromate. The pH value was measured with pH S-3C acid meter. The redox potential was measured using a platinum electrode with an Ag/AgCl reference electrode. Free cells in solution were observed and counted under an optical microscope. The surface morphology of PPCBs before and after bioleaching was observed by scanning electron microscope (SEM) (Tescan Vega3).

Preparation of total DNA and PCR amplification The bioleaching solution was sampled at 4-day intervals for extracting total DNA as described previously (15). Amplification of 16S rRNA of bacteria from positions 27 to 1492 and 16S rRNA of archaea from positions 21F to 958R was performed as described, respectively (16). When the PCR program finished, the PCR product was separated by gel electrophoresis on a 1% agar gel in Tris/acetate-buffer and analyzed by staining with ethidium bromide (EB) under UV light. The band of the expected size (1500 bp and 900 bp) was cut-off and purified with a commercial kit (Gel Extraction Kit, Promega, USA), then stored at −20°C.

Cloning and amplified rDNA restriction analysis The purified amplicons were cloned using the pGEM-T Easy Vector System (Promega). The detailed process for cloning and amplified rDNA restriction analysis was performed as described (17,18). ARDRA banding patterns, which were identified, were grouped into an

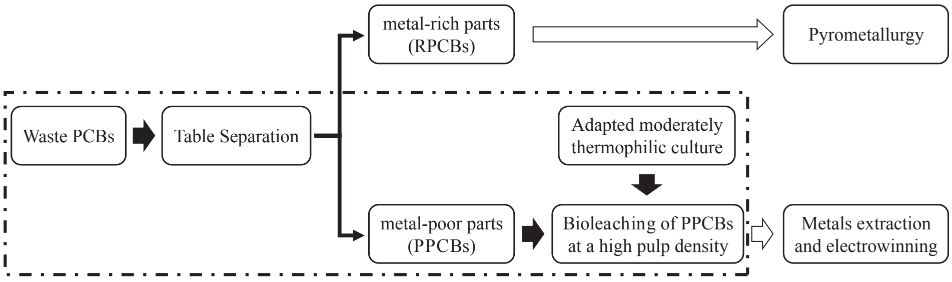

FIG. 1. The schematic treatment process of waste PCBs (main experiment conducted was marked in dotted box)

TABLE 1. Analysis of biogeochemical properties for AMD sample.

Sample	ρ/(mg/L)										Redox potential (mV)
	Cu	Zn	Pb	Mn	S	Mg	Fe	Hg	Ni	Al	
AMD	100.19	3.18	1.89	156.66	4401	1102	981.83	1.07	4.02	944	699

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