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Column bioleaching of metals from electronic scrap

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ABSTRACT

The present work was aimed at studying the column bioleaching feasibility of metals from electronic scrap by the selected moderately thermophilic strains of mixed adapted consortium of acidophilic chemolothotrophic and acidophilic heterotrophic bacteria. These included *Sulfobacilllus thermosulfidooxidans* and *Thermoplasma acidophilum*. The tolerance of bacterial cultures to mixed metal ions (Ag^{+}, Al^{3+}, Cu^{2+}, Fe^{3+}, Ni^{2+}, Pb^{2+}, $Sn^{2+}$and Zn^{2+}) could be improved markedly after nearly two year adaptation from 12 g/L to 20 g/L. During whole leaching process included acid pre-leaching operation of 27 days and bioleaching operation of 280 days about 80% Zn, 64% Al, 86% Cu and 74% Ni was leached out.

1. Introduction

Electric and electronic products continue to revolutionize communication, entertainment, transportation, education and health care around the world. There is no sign that this revolution will abate soon. Technical innovation will continue to be a cornerstone of social progress and advanced electronics are leading the way (Fisher et al., 2005). Terazono et al. (2006) have reviewed the data on electronic waste generation in different parts of the world. Studies by Bertram et al. (2002), Jirang and Lifeng (2008) also affirm that wastes from electrical and electronic equipment are the fastest growing waste category; this finding emphasizes the need for their efficient recycling strategies.

Recycling of electronic waste is an important subject not only from the point of waste treatment but also from the recovery aspect of valuable materials. However, recycling of electronic scrap is still quite limited due to the heterogeneity of the materials present in the products and the complexity of the production of this equipment (Veit et al., 2005). From the point of material composition, electronic waste can be defined as a mixture of various metals, particularly copper, aluminum, nickel, iron and steel, attached to, covered with, or mixed with various types of plastics and ceramics (Hoffmann, 1992). Precious metals have a wide application in the manufacture of electronic appliances, serving as contact materials due to their high chemical stability and their good conducting properties. Among electronic wastes, printed circuit boards have quite diverse composition, containing polymers, ceramics and metals. The metal content is around 28-30% (copper: 10–20%, lead: 1–5%, nickel: 1–3% precious metals like silver, platinum and gold are also present in the electronic scrap to a total of 0.3–0.4%). The content of the other important materials remaining; plastics 19%, bromine 4%, glass and ceramics 49%. Besides these inorganic elements, the other important organic compounds are also found in circuit boards like isocyanates, phosgene, acrylic and phenolic resins (Ludwig et al., 2003).

Mechanical and pyrometallurgical recycling of electronic waste have been investigated by different researchers (Noakes, 1999; Veit et al., 2007, Li et al., 2007). But such processes requiring high consumption of energy, cannot efficiently recover precious metals and contain halogenated flame retardants in the smelter feed that can lead to the formation of dioxins and furans. Traditional smelters designed for the treatment of mining concentrates or simple copper scrap encounter some challenges for electronic waste treatment. However, state-of-the-art smelters are highly dependent on investments (Krebs et al., 1997, Menad et al., 1998).

Use of microorganisms for the recovery of metals from wastes could be an economical alternate to these processes. Though, this process has been successfully applied for the leaching of metals from ores (Olson et al., 2003), data pertaining to its application for the extraction of electronic waste material is still scanty. Recently, a few studies have been undertaken for the extraction of metals from electronic scrap/printed circuit boards (Brandl et al., 2001; Faramarzi et al., 2004; Choi et al., 2004). These studies were conducted with mesophilic chemolithotrophic (*Acidithiobacillus ferooxidans* and *Acidithiobacillus thiooxidans*) or cyanogenic bacteria (*Chromobacterium violaceum*). The rates of bioleaching of metals from ores by moderate

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thermophiles have been demonstrated to be higher than mesophiles and in another case even higher than extreme thermophiles (Das et al. 1999; Deveci et al., 2004).

However, no data is available on the use of moderately thermophilic bacteria for column bioleaching of metals from electronic scrap particularly from printed circuit boards except some optimization studies have been carried out at shake flask level (Ilyas et al., 2007). To further develop column bioleaching research of the electronic scrap and to comprehensively up scale the process, a series of experiments were carried out in our lab and some results were achieved as follows (Ilyas et al., 2007):

- The non metallic portion of scrap also contributes toward alkalinity of it and that can be minimized by washing treatment without the alteration of concentration of metals.
- The mixed culture of acidophilic chemolithotrophic bacteria and acidophilic heterotrophic bacteria exhibited greater bioleaching potential than individual cultures.

So the present studies were undertaken to evaluate the potential of mixed metal-adapted cultures of moderately thermophilic acidophilic chemolithmixootrophs and moderately thermophilic, acidophilic heterotrophs to solubilize metals from printed circuit boards in a column reactor.

2. Materials and methods

2.1. Microorganisms

Acidophilic moderately thermophilic bacteria were used in these studies. These included *Sulfobacilllus thermosulfidooxidans* and *Thermoplasma acidophilum*. *Sulfobacilllus thermosulfidooxidans* was collected from Reko Diq copper ore deposits, Pakistan. After isolation, purification, 16S rDNA gene amplification, its sequencing and checking homology (98%) by NCBI blast search, it was submitted to GenBank for accession number (GQ228448) while *T. acidophilum* was obtained from culture collection of Wuhan Institute of Technology, Wuhan, China and its origin was Xinjing coal deposits in China.

2.2. Culture conditions

Iron-tryptone soya broth (FeTSB) medium, developed by Johnson et al. (1987), was used, with some modifications, to obtain and maintain the growth of *S. thermosulfidooxidans*. The FeTSB medium composed of (g/L): $MgSO_4.7H_2O$, 0.50; $(NH_4)_2SO_4$, 0.15; KCl, 0.05; KH_2PO_4, 0.05; $Ca(NO_3)_2$, 0.01 and TSB, 0.25. The solution pH was adjusted to 2.0 using sulfuric acid and autoclaved at 121 °C and 15 psi for 15 min. Filter sterilized ferrous sulfate solution was added to the solution to a final concentration of 50 mM, before inoculation. After obtaining rich growth, the cell mass of cultures was harvested by centrifugation at 10,000 rpm for 20 min. The cell pellet was washed twice with autoclaved distilled water having pH adjusted at 2.0 with 2.0 M sulfuric acid and finally it was suspended in sterilized distilled water and preserved at 4 °C for inoculation in the further experiments. The acidophilic heterotrophs were grown in the same medium but supplemented with glucose (1% w/v) instead of ferrous sulfate, as energy source at pH 2.0. The above mentioned liquid media were supplemented with 0.5% (w/v) agarose to prepare solid media.

The adaptation of moderately thermophilic cultures to mixed metal ions (Ag^+, Al^{3+}, Cu^{2+}, Fe^{3+}, Ni^{2+}, Pb^{2+}, $Sn^{2+}$and Zn^{2+}) was performed through serial sub-culturing in the logarithmical phase of growth and by gradually increasing the concentration of mixed metal ions at the same time. Finally, the cells were harvested by centrifugation and inoculum was prepared as described earlier in this section.

2.3. Source and description of electronic scrap

Electronic scrap, in the form of printed circuit boards, was obtained from local electronic waste supplier, Wuhan, China. No physical/mechanical separation process was used before its transportation to the laboratory. For experimental use, the scrap was crushed and then ground to fine powder of 100 to 120 μm particle size by using ring mill grinder.

2.4. Analysis of electronic scrap samples

For metal analysis, the electronic scrap (1.0 g) was dissolved in100 mL of aqua regia by refluxing in a round bottom flask for 1 h. The solution was allowed to cool and the volume was made up to 100 mL. The concentrations of dissolved metal ions (i.e. Ag^+, Al^{3+}, Cu^{2+}, Fe^{3+}, Ni^{2+}, Pb^{2+}, $Sn^{2+}$and Zn^{2+}) were determined by atomic absorption spectrophotometer (Varian AA-400) and the data were analyzed for calculating the concentrations of different metal ions in the electronic scrap.

2.5. Preparation of electronic scrap for bioleaching studies

Finely ground washed samples of electronic scrap were used in the bioleaching experiments. Washed samples of electronic scrap were prepared by suspending 50 g of electronic scrap in 500 mL of saturated solution of sodium chloride. The mixture was stirred for 10 min and allowed to stand till heavier particles settled down at the bottom. The floating material was decanted off and the denser part, which settled down at the bottom of every sample, was separated, washed and dried to constant weight. Then the samples were sterilized by Tyndalization and homogenized prior to bioleaching. The samples treated in this way were referred to as “Washed charge” and this washed charge was used in further column bioleaching studies.

2.6. Metal bioleaching studies

Two columns of height 58 cm and an internal diameter of 13 cm were used in the bioleaching studies that were fabricated locally. A HDPE support plate with multiple 10 mm holes was used for allowing air to be injected below the plate and dispersed uniformly over the washed charge in columns. A layer of support scrap sized at 10–15 mm was placed in the bottom of the column before 10 kg washed charge was loaded .Temperature of column was maintained at 45 °C with water jacket around the column and thermocouple installed inside the charge.

Because scrap was alkaline in nature so before inoculation the charge was pre treated with sulfuric acid for pH stabilization. Each column was fed with two liters autoclaved distilled water of pH 2.0 that was applied to the surface of the column charge by using a garden sprinkler head and was allowed to pass through the washed charge by gravity and recirculated through a side pipe with a peristaltic pump, pH of effluent was monitored continuously and concentrated sulfuric acid was added gradually. After stabilization of pH in columns, pre-leaching was stopped. Effluent in the column was allowed to drain off and the column contents were rinsed with dilute sulfuric acid and autoclaved distilled water of pH 2. Finally, all the solution was removed to perform bioleaching.

During bioleaching studies each column was fed with two liters of autoclaved FeTSB medium having pH 2.0, adjusted with sulfuric acid. Then column B was inoculated with respective inocula 10% (v/v) with a cell density of about 10^7 cells/mL and the rate of flow was adjusted to 50 mL/min while column A was considered as aseptic control. Solution level in both columns was maintained at a sufficient height and clean air was provided through a rotameter with the flow rate of 150–200 L/h. Effluents from both pre-leaching and bioleaching were