BIOLEACHING OF COPPER FROM ELECTRONIC WASTE USING ASPERGILLUS NIGER AND ACIDITHIOBACILLUS

M. Saidan, M. Valix

Material and Mineral Processing Research Unit,
School of Chemical and Biomolecular Engineering
The University of Sydney, NSW, 2006, Australia
Email: marjorie.valix@sydney.edu.au

ABSTRACT

The main concern of this study is to establish a feasible and an economical method of extracting copper from electronic waste using Aspergillus Niger and Acidithiobacillus Thioxidans. Both Aspergillus Niger and Acidithiobacillus Thioxidans are known to exhibit efficient generation of organic acid and sulfuric acid respectively. To establish their leaching potential, chemical leaching tests using their specific bio-acids (citric acid and sulfuric acid) were tested. In this study, concentrated copper waste was used as the test case material. Optimum conditions for leaching were found to depend on leaching pH, types of metabolic products including ferric ions and temperature of leaching. The maximum solubilisation of copper is 82% over 24 hours of leaching, which demonstrates the potential for bioleaching as a process for recovering metals from e-waste.

Introduction

In recent decades the world has witnessed a technological boom, fuelled by continual and unprecedented consumer demand for the latest gadgets and devices. It is estimated that growth in the electronics sector alone has increased by almost 23% per year in recent years (Brandl, 2001a). Even in the current economic climate it is a trend that seems almost certain to continue. This astounding development has brought with it huge technical benefits to society; creating jobs, wealth and generally increasing living standards across the globe. However, in the process large amounts of electric and electronic wastes (e-wastes) have been generated. Although there is no agreed definition of what constitutes e-waste, it has been defined (Schafer et al., 2003) as any equipment that is dependent on electric currents or electromagnetic fields in order to work properly, including equipment for the generation, transfer, and measurement of current. The problem with e-waste is its growing volume, its toxicity and its content of valuable resources (e.g., gold) which are lost when e-waste is disposed. Incineration and landfilling of e-waste has created ‘toxic time bombs’ that threaten the ecology and human health and represent a significant loss of valuable resources. [e.g., Environment Victoria 2005]. The response by various countries, including the EU, Japan and US, to implement legislations and directives to reduce the disposal and promote the recycling of e-waste constitute a significant step in addressing this huge issue (2002/96/EC(a), 2002/96/EC(b), Victoria, 2005). These legislations, on their own, however will not solve this problem as they simply order the diversion of e-waste from landfills and incinerators without proposing technological solutions (Antrekowitsch et al., 2006). The challenge in managing e-waste will be in developing sustainable recycling technologies that are able to address the volume and complexity of this waste using cost effective and ecologically sensitive methods.
The possibility of a solution that is both economically feasible and also environmentally sustainable has encouraged a variety of active research into the area in recent years. Perhaps the most promising of these technologies is through the use of naturally occurring biological micro-organisms and their metabolic products in extracting valuable metals from the waste (Bosecker, 1986, Ilyas et al., 2007, Le et al., 2006, Valix et al., 2001b). The increase in interest in the use of biohydrometallurgical route for re-processing wastes is driven by the fact that this method is environmentally sound with a huge potential to lower operational cost and energy requirements.

A key factor in developing this technology is matching the potency of the organisms with the requirements for dissolving the metallic fractions of e-wastes. Traditionally chemolithoautotrophs bacteria (e.g., Acidithiobacillus ferrooxidans and Acidithiobacillus thiooxidans) have been applied in leaching sulphide minerals and fungi (e.g., Aspergillus niger) have been used in dissolving oxide minerals and waste (Jain & Sharma, 2004, Watling, 2006). The objective of this study is to examine the roles of the metabolic acidic products of autotrophic bacteria and heterotrophic fungi organisms in extraction of metals from e-wastes. Included in this study is the examination of using the oxidising properties of ferric ions in the dissolution of copper. In this study sulphuric and citric acids were used as the test case acids for leaching copper metals from a copper rich e-waste fraction.

**Experimental**

**Materials**

Copper rich waste was obtained from a shredding process. A fraction with a particle size range of 40 to 104 µm was collected and used throughout all experiments. Concentration of metals in this fraction has been measured by acid digestion in aqua-regia followed by analysis of dissolved metals using Varian Vista AX CCD Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) employing standard procedures. The results are shown in Table 1.

<table>
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<tr>
<th>Elements</th>
<th>Content (g.kg⁻¹)</th>
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<tr>
<td>Al</td>
<td>1.3</td>
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<tr>
<td>Cu</td>
<td>851.3</td>
</tr>
<tr>
<td>Mg</td>
<td>0.6</td>
</tr>
<tr>
<td>Zn</td>
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**Leaching Tests**

Chemical leaching tests were carried out with 1% (w/v) pulp density of waste at temperatures from 70 and 90°C whilst shaken at 800 rpm. The copper rich was leached in reagent grade citric and sulphuric acids. Leaching was performed for 6-24 hours, after which the solution were filtered and analysed for dissolved metals using Varian Vista AX CCD Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES)
using standard procedures. The pH was monitored during leaching with a dedicated pH-mV-temp meter TPS WP-80D.

Results

Secondary Reactions

Secondary reactions are reactions other than metal leaching which can influence the dissolution or stability of the metals solution (Valix et al., 2001a). These can include the adsorption of the metal complexes on the epoxy waste and precipitation of the dissolved metals. Occurrence of these reactions during leaching can veil the true potential of the acids to dissolve the metallic fractions of the waste. Conditions that are chosen to assess the activity of the acids must therefore overcome or reduce the effects of these reactions. Brown (Brown, 2009) has shown that leaching at pH below 4.5 allows the epoxy fractions of the waste can overcome metal complex adsorption and these conditions also avoided metal hydroxyl precipitation and passivation. All leaching tests were conducted at pH from 1.5 to 2.0.

Leaching with Organic and Mineral Acids

Metals can be dissolved directly with organism contact with the metal or indirectly through the action of the metabolic products (Brandl et al., 2001b). Organisms bioleaching efficiency is based on their ability to generate various metabolic products that solubilise metal fractions. Fungi micro-organisms generate various metabolic products including exopolysaccharides, amino acids and proteins with the ability to dissolve the metallic fractions from e-wastes (Welch et al., 1999). However organic acids are considered to have a central role in dissolving metals through their supply of protons and ligands (Gadd, 1999). Chemolithoautotrophic bacteria such as Acidithiobacillus thiooxidans is able to metabolise sulfur based compounds to sulphuric acid.

The acidic media dissolves the metallic fractions of e-wastes by various mechanisms including acidification, reduction/oxidation and complexation reactions. Dissolution of copper involves a series of electrochemical reactions. The reduction of the acid ion provides the cathodic reaction to oxidise the metallic copper to Cu$^{2+}$.

\[
\begin{align*}
\text{H}_3\text{O}^+ + \text{e}^- & \rightarrow \text{H}_2 + \text{H}_2\text{O} & (1) \\
\text{Cu} & \rightarrow \text{Cu}^{2+} + 2\text{e}^- & (2)
\end{align*}
\]

The oxidised copper solubilises by reacting with any solvating agents (e.g., H$_2$O) and ligands that are present during leaching. The simplest product for example is the hydrolysed hexaaquacopper (II) solution [Cu(H$_2$O)$_6$]$^{2+}$ in equation 3. In the presence of stronger anions (e.g., SO$_4^{2-}$) and complexing agents such as citrate (C$_3$it) ligand, copper sulphate and copper complexes will form preferentially (see equations 4-7) promoting the dissolution of copper.

\[
\begin{align*}
\text{Cu}^{2+} + 6 \text{H}_2\text{O} & \rightarrow [\text{Cu}(\text{H}_2\text{O})_6]^{2+} & (3) \\
\text{Cu}^{2+} + \text{SO}_4^{2-} & \rightarrow \text{CuSO}_4 & (4) \\
\text{Cu}^{2+} + \text{H}_3\text{C}_{\text{it}} = \text{CuH}_2\text{C}_{\text{it}}^{1+} + \text{H}^+ & (5) \\
\text{Cu}^{2+} + \text{H}_2\text{C}_{\text{it}}^{-1} = \text{CuHC}_{\text{it}}^{0} + \text{H}^+ & (6)
\end{align*}
\]
A comparison of copper dissolution, the test case metal in this study, from copper rich e-waste by acidification and complexation was considered by using sulphuric and citric acid.

Up until 2005, there had been no previous work published on the leaching of metals from electronic scrap using moderately thermophilic bacteria. The advantage of using thermophilic organisms in the leaching process is that at the higher temperatures, the reaction kinetics are expected to increase and thus the required recoveries can be achieved in a minimal time period (Ilyas et al., 2007). Ilyas et. al., (Ilyas et al., 2007) selected both a moderately thermophilic strain of acidophilic \( S. \) thermosulfidooxidans and an unidentified, acidophilic, heterotrophic bacteria (code A1TSB) to carry out their investigations. Although metal bioleaching was also studied at lower (5% w/v) and higher (20% w/v) electronic scrap concentrations, the results were presented for a scrap concentration of 10%, which exhibited the highest metal bioleaching rates. For this study, a high temperature leaching was chosen to reflect the potential actions of thermophilic bacteria and to achieve optimum dissolution. The copper rich waste was leached for 6 and 24 hours at 90°C. The copper dissolved after 6 and 24 hours of leaching as a function of pH are shown in Figures 1 and 2 respectively.

Figure 1 shows at high pH (above pH 1.9) citric acid provided higher Cu dissolution to sulphuric acid, whereas at lower pH sulphuric acid provided higher Cu dissolution. This trend persisted after 24 hours of leaching. These results demonstrate the dominant effect of complexation at the higher pH with 72% Cu recovery in comparison to acidification alone with 11% Cu recovery. It is apparent that increasing the proton concentration provided a higher acid activity from sulphuric acid with 83% Cu recovery, whereas the effect of increasing the proton concentration had the opposite effect in citric acid with only 36% Cu recovery. The copper recovered with sulphuric acid is consistent with the optimum obtained by Ilyas et. al., (Ilyas et al., 2007) of 89% Cu with mixed consortium of acidophiles, however over a longer period of 18 days. These results reveal the rate limiting step in the bioleaching of metals is likely to be the generation of the metabolic products rather than the chemical leaching step.

The acid and copper citrate predominance diagrams in Figure 3 and 4 respectively shows that in the presence of excess H\(^+\), the citrate is fully protonated. This has direct consequences on the formation of copper complexes – at this low pH there are no free citrate ions to complex with copper, so it remains as Cu\(^{2+}\). The copper solubility induced by the complexation reaction is therefore reduced at the lower pH for citric acid. The higher copper recovery at the lower pH is consistent with the higher reactivity of acidophiles at the lower pH (Brandl et al., 2001b).

These results demonstrate the dependence on the leaching effectiveness of Acidithiobacillus thiooxidans and fungi metabolites on solution pH. This in turn reflects the difficulty in often using pure cultures of the acidophilic heterotrophs in leaching available metals in the scrap (Ilyas et al., 2007). Whereas enhancement of metal leaching appeared possible when combinations of organisms are used. The synergy of combining both the complexation and acidification reaction was examined
by leaching with an equimolar quantities of sulphuric acid and citric. Copper recoveries after 24 hours of leaching are shown in Figure 5. As shown, the addition of

![Figure 1](image1.jpg)

**Figure 1.** Copper dissolution as a function of pH after 6 hours leaching in citric and sulphuric acid at 90°C, 800 rpm and 1% pulp density.

![Figure 2](image2.jpg)

**Figure 2.** Copper dissolution as a function of pH after 24 hours leaching in citric and sulphuric acid at 90°C, 800 rpm and 1% pulp density.
Figure 3. Predominance diagram for citric acid (L), total ligand activity = 0.5M, $T = 298K$.

Figure 4. Predominance diagram for copper citrate complexes, total copper activity = 0.01M, $T = 298K$, (citrate = L).
Both acids stabilised the copper dissolution over a wider range of pH, enabling high recoveries of copper to be achieved from 1.15 to 3.0.

**Effect of Ferric Ions**

Bacterial oxidation of Fe\(^{2+}\) to Fe\(^{3+}\) is achieved by *Acidithiobacillus ferrooxidans*. The reduction of ferric ions (Fe\(^{3+}\)) can catalyse the oxidation of copper thus promoting its dissolution (see equation 2).

\[
Fe^{3+} + e^- \rightarrow Fe^{2+}
\]  

(8)

The effect of adding ferric ion (7g/L) in the sulphuric acid leaching of copper is shown in Figure 6. It appears that adding ferric ions does improve the solubility of copper particularly at the more acidic conditions. This is consistent with Choi et al., (Choi et al., 2004), where the actions of ferric ion was also shown to increase at the lower pH. Studies of the system pH revealed that a lower pH corresponded to a faster copper mobilisation rate. At a pH of 1.5 the mobilisation rate reached 99% after 48 hours. It took 72 hours for the same mobilisation rate to be achieved at a pH of 2.0. This study demonstrated the ferric ions and the leaching pH were significant factors in the mobilisation of copper from e-wastes.
Figure 6. Catalytic effect of ferric ion in dissolving copper for 6 hours 90°C, 800 rpm, 1% pulp density.

**Conclusions**

This study has revealed some facets for the use of bacteria and fungi in dissolving copper from e-wastes. Based on this study, it can be concluded that it is indeed possible to leach valuable metals from electric and electronic waste products using suitable micro-organisms. This study demonstrated the effectiveness of bioleaching as a technology for recovering copper metals from e-wastes. The metabolic products from organisms including *Aspergillus Niger* and *Acidithiobacillus Thioxidans* and *Acidithiobacillus ferrooxidans* are capable of dissolving copper effectively. The metabolic products used in this study included sulphuric acid, citric acid and ferric ions. Copper is dissolved by the acids through various reactions involving electrochemical anodic reduction of copper catalysed by the cathodic reduction of protons and/or ferric ions. The presence of complexing citrate ligands was shown to stabilize and promote the solubility of copper at the less acidic conditions (pH 2-3). Excess protons at low pH promoted dissolution of copper in sulphuric acid and ferric ions. At these conditions, the citrate ligand, however, was preferentially protonated leading to poorer copper recovery. At the higher pH, the complexation reaction of citrate ligand was shown to dominate the dissolution of copper. Synergy in leaching copper was achieved by combining the acidification and complexation properties of sulphuric and citric acid enabling optimum recovery of copper to be achieved over a wider pH range of 1.15-3.0.

**REFERENCES**


**BRIEF BIOGRAPHY OF PRESENTER**

M. Saidan

<table>
<thead>
<tr>
<th>Degree</th>
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<tr>
<td>Postgraduate student from</td>
<td>Sydney University</td>
</tr>
<tr>
<td>Master of Chemical Engineering</td>
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