The Effect of Aeration and Stirring on Metal Recovery from Printed Circuit Boards

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Abstract

The present research was aimed at studying the bioleaching processes used to mobilize non-ferrous metals (Cu, Ni, Zn and Al) from waste printed circuit boards (PCBs) with biologically generated ferric iron-containing sulphuric acid solutions. The used bacterial strains Acidithiobacillus ferrooxidans and Acidithiobacillus thiooxidans were recovered from an acidic mine drainage. These bacteria were sub-cultured and acclimated in medium containing PCBs. Biologically oxidized Fe^{3+} from Fe^{2+} in presence of A. ferrooxidans caused the mobilization of metals. This study evaluated the influence of three different conditions on Cu, Zn, Ni and Al bioleaching from PCBs by metal-adapted mixed bacterial culture of Acidithiobacillus ferrooxidans and A. thiooxidans. The experimental results demonstrate, that aeration and stirring had pronounced effect on copper, nickel and zinc bioleaching. It was revealed that the highest Zn (76%) and Cu (40%) recovery was obtained under combined conditions of both stirring and aeration. For nickel recovery (63%) aeration was found to be the most effective. On the other hand, no investigated condition was effective for Al bioleaching. The pH changes in all three different conditions during bioleaching were very similar and on day 7 reached pH over 2. It is concluded, that mixed bacterial culture of A. ferrooxidans and A. thiooxidans were able to grow in the presence of electronic waste. The results also pointed out the importance of Fe^{3+} on Cu, Zn and Ni recovery. Our experiments confirmed significant influence of different conditions on ferric ions concentration. Aeration had the most pronounced effect on the rapidly increase of Fe^{3+} concentrations after 12th day and reached the highest concentrations at the end of experiment.

Keywords: bioleaching, electronic scrap, metals, Acidithiobacillus ferrooxidans, Acidithiobacillus thiooxidans

Introduction

Nowadays, the world is facing primary resources shortage thereby waste has become very interesting source. Among different kinds of wastes, spent electronic devices represent important source of many metals involving precious metals. Approximately 20–60 million Mg of this kind of waste is produced each year. This amount is three times higher than other types of waste (Karwowska et al., 2013). Spent printed circuit boards (PCBs) seem to be the most promising resource of valuable metals. Especially their high contents of copper (10–20%), nickel (1–3%), lead (1–5%) and also precious metals (0.3–0.4%) made them reasonable and economically convenient choice (Ilyas, 2010). As far as electronic scrap is land-filled or incinerated, metals such as copper, lead, nickel or halogenated- resisting burned materials might disperse into environment causing serious problems (Saidan et al., 2012). There are several ways of electronic scrap treatment among them, biohydrometallurgical approach is very promising. This environmentally friendlier method often achieves higher efficiencies comparing to conventional hydrometallurgical and pyrometallurgical methods (Wang et al., 2009). Main advantages of bioleaching are low operation costs, less chemical and energy consumption, thus minimizing pollution (Willner, 2013). Bioleaching consortium is formed by chemoautotrophic, mesophilic, acidophilic bacteria, mainly A. ferrooxidans, providing oxidising agent Fe^{3+}, and A. thiooxidans, providing H^+ which keeps pH at low rates (Eq. 1,2). Ferric ion and sulphuric acid consequently mobilize metals from primary and secondary sources (Eq. 3, 4, 5) (Lee and Pandey, 2011, Luptáková, 2012).

$$2Fe^{2+} + 0{,}5O_2 + 2H_2+ \rightarrow 2Fe^{3+} + H_2O \quad (1)$$
$$S^0 + 1{,}5O_2 + H_2O \rightarrow SO_4^{2-} + 2H^+ \quad (2)$$
$$MS + 2Fe^{3+} \rightarrow M^{2+} + 2Fe^{2+} + S^0 \quad (3)$$
$$MS + 2O_2 \rightarrow M^{2+} + SO_4^{2} \quad (4)$$

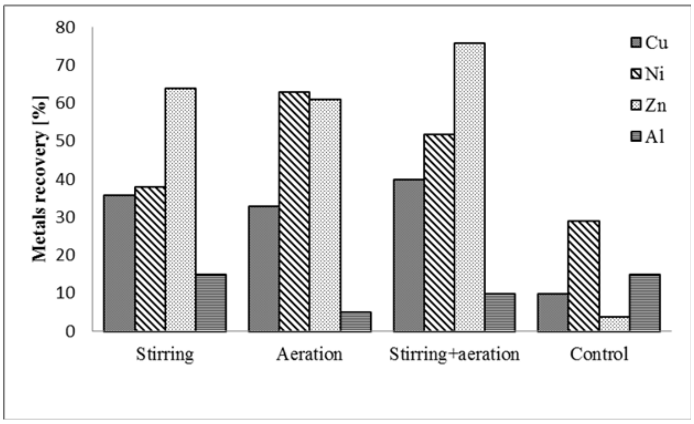

Fig. 1. Percentages of solubilised Cu, Ni, Zn, Al, by bioleaching under different conditions during 28 days

Rys. 1. Uzysk Cu, Ni, Zn, Al w procesie bioługowania w różnych warunkach, w czasie 28 dni

$$M(Cu, Ni, Zn, Co, Al) + Fe_2(SO_4)_3 \rightarrow MSO_4 + 2FeSO_4 \quad (5)$$

Majority of bioleaching is performed by autotrophic aerobic bacteria. Oxygen is essential nutrient for growth and survival. As an electron acceptor, oxygen is re-oxidising ferrous into ferric ion, thereby aeration was expected to be the key factor boosting metal mobilization (Ilyas et al., 2014). Also, stirring was applied to enhance diffusion of oxidising agents. Combination of these two effects was expected to be ideal option intensifying bioleaching. On the other hand, stirring may be harmful for bacteria mechanically damaging their cell integrity.

The present study aimed to investigate the influence of aeration, stirring and combination of both on metal bioleaching rates and yield of metals and also to determine the most suitable conditions for bacterial activity and metal mobilization from spent PCBs.

Materials and methods

Bacterial culture formed by *A. ferrooxidans* and *A. thiooxidans* originating from Smolnik mine drainage obtained from Institute of Geotechnics was used in the experiments. Adaptation of bacteria was carried out in 500 ml Erlenmeyer flask containing 230 ml of nutrient medium proposed for the mixed bacterial culture (Kaduková et al., 2012) and 50 ml mixture of the bacteria and 2 g PCBs. Metal adaptation of bacteria took place in an incubator at 30°C and lasted for 14 days.

Bioleaching experiments were carried out in sterile 500 ml Erlenmeyer flasks. Each flask contained 470 ml of diluted sulphuric acid, 30 ml of the metal-adapted mixed bacterial culture, 5 g PCBs (particle size from 1 to 5 mm) and 2 g of elemental sulphur. The pH values were adjusted to 1.5 with 10 M H_2SO_4. To investigate the effect of aeration, air influx was provided into solutions via pump. To investigate the effect of stirring a magnetic stirrer was used. All experiments and abiotic control leaching were conducted in duplicates. The samples (5 ml) were regularly withdrawn on days: 1; 3; 7; 14; 21 and 28.

Results and discussion

The results of copper, nickel, zinc and aluminium extraction by the metal adapted consortium of *A. ferrooxidans* and *A. thiooxidans*, under three conditions of bioleaching – aeration, stirring and combination of both are presented in Fig. 1. During bioleaching study under stirring condition, approximately 36% Cu, 38% Ni, 64% Zn and 15% Al were leached out. During bioleaching under aeration conditions 33% Cu, 63% Ni, 61% Zn and 5% Al were extracted. Metal bioleaching efficiency under combined conditions was 40% Cu, 52% Ni, 76% Zn and 10% Al. In abiotic control leaching only 10% Cu, 29% Ni, 4% Zn and 15% Al were extracted.

The pH changes over the leaching under aeration, stirring and combined conditions are plotted in Fig. 2. Within the first three days of the bioleaching the pH dropped from the initial pH of 1.5 up to 1. This fact indicated a high metabolic activity of A. thiooxidans (Eq.2). After this first period the pH began rapidly to increase, and on day 7 reached pH over 2. It may be assumed that the pH increase was owing to alkaline nature of electronic waste. Metal dissolution and ferrous ions oxidation also contributed to sulphuric acid consumption resulting in the pH increase. After day 7 the pH slightly decreased and remained relatively stable until the end of the bioleaching processes. This third period indicated that hydrolysis reaction of Fe^{3+} and jarosite formation occurred (Daoud and Karamanev, 2014 Velgosova et al., 2014). Authors Daoud and Karamanev (2006) claimed that overcoming pH limit 1,8,

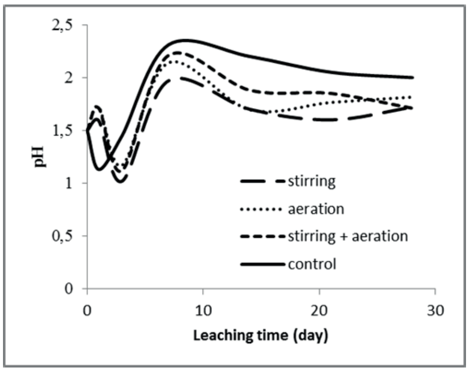

Fig. 2. Comparison of changes of pH between effects of aeration, stirring, combined aeration with stirring and abiotic control leaching, during 28 days

Rys. 2. Zmiana pH w czasie w zależności od aeracji, mieszania, kombinowanych warunków mieszania i aeracji, abiotyczne ługowania w czasie 28 dni

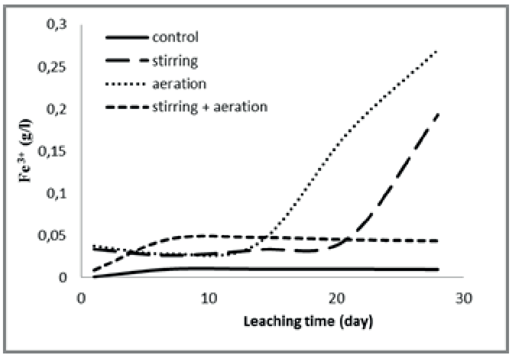

Fig. 3. Changes of Fe^{3+} concentratios under different conditions

Fig. 3. Zmiana koncentracji Fe3+ w różnych warunkach

jarosite was formed and could have negative effect on metal dissolution. In abiotic control leaching the pH changes were very similar to those in bioleaching. However, the higher bioleaching efficiency of the metals pointed out the significant influence of ferric irons generated by bacterial strains.

Given oxidation of ferrous ions by mixed bacterial culture, this reaction is influenced by temperature, pH, cell and oxygen concentrations (Daoud and Karamanev, 2006). In case of our experiments, ferric ions concentrations were significantly influenced by different conditions (Fig. 2). At the beginning of the experiment, combination of aeration and stirring enhanced Fe^{3+} concentrations, which may led to inhibition of bacterial growth. Following constant concentrations predicting balance between Fe^{3+} and PCBs metals mobilization (Eq. 1, 3). In the case, where only aeration was provided, Fe^{3+} concentrations started to increase rapidly after 12th day and reached the highest concentrations at the end of experiment. That was possibly caused by fast growth of bacteria and low metals solubilisation, except for nickel.

Results revealed that bioleaching efficiency of Cu, Zn and Al (except for Ni) was almost the same under both stirring and aeration conditions. Combined aeration and stirring had significant effect only on zinc solubilisation. It seems that the most suitable condition for Ni recovery was aeration.

Conclusions

The results from this work demonstrate that aeration, stirring and combination of both influenced bacterial activities resulting in a higher Fe^{3+} formation. Based on the results, combination of both stirring and aeration seems to be the optimal condition for zinc and copper mobilization. For nickel recovery aeration was the most effective. The total Al bioleaching efficiency in all three cases was very low. According to our results it is obvious that for particular metals specific conditions are needed. This might be related to mechanisms of metal dissolution, which has not been explained completely, so far.

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Wpływ napowietrzania i mieszania na odzysk metalu z obwodów drukowanych

Obecnie prowadzone badania mają na celu sprawdzenie wyników zastosowania procesów bioługowania do mobilizacji metali nieżelaznych (Cu, Ni, Zn oraz Al) pochodzących z obwodów drukowanych (ang. skrót PCBs) z biologicznie wytwarzanymi żelazowymi roztworami kwasu siarkowego zawierającego żelazo. Użyto w tym celu szczepy bakterii Acidithiobacillus Ferrooxidans *oraz* Acidithiobacillus Thiooxidans*, bakterie wydzielono z kwaśnego drenażu kopalnianego. Bakterie wyhodowano i przystosowano do medium zawierającego elementy obwodu drukowanego. W obecności bakterii* A. ferroxidsans *biologicznie utleniono Fe^{2+} do Fe^{3+}, co spowodowało mobilizację metali. W trakcie badań oceniono wpływ trzech różnych warunków bioługowania Cu, Zn, Ni oraz Al pochodzących z obwodów drukowanych, przy pomocy mieszanych kultur bakterii z rodziny* Acidithiobacillus ferrooxidans *oraz* A. Thiooxidans *przystosowanych do warunków panujących w roztworze. Wyniki eksperymentu wykazały, że napowietrzanie oraz mieszanie mają znaczący wpływ na bioługownie miedzi, niklu oraz cynku. Odkryto, że największy udzysk Zn (76%) oraz Cu (40%) uzyskano dzięki połączeniu procesów zarówno mieszania, jak i napowietrzania. Największy wpływ na uzysk niklu (63%) miało napowietrzanie. Jednakże, nie odkryto żadnego warunku mającego wpływ na bioługowanie Al. Zmiany pH podczas bioługowania były porównywalne we wszystkich trzech przypadkach i podczas siódmego dnia ługowania pH wzrosło powyżej 2. Wywnioskowano, że mieszane kultury bakterii* A. ferroxidans *oraz* A. thiooxidans *są w stanie wzrastać w obecności odpadów elektronicznych. Wyniki również wykazały potrzebę obecności Fe^{3+} w procesie odzysku Cu, Zn oraz Ni. Przeprowadzone badania potwierdziły istotny wpływ różnych warunków na stężenie jonów żelazowych. Najbardziej zauważalny wpływ na dynamiczny wzrost stężenia Fe^{3+} po dwunastym dniu procesu miało napowietrzanie, stężenie Fe^{3+} osiągnęło największe stężenie pod koniec eksperymentu.*

Słowa kluczowe: bioługowanie, złom elektryczny, metale, Acidithiobacillus ferrooxidans, Acidithiobacillus thiooxidans