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Leaching of selected heavy metals from electronic waste in the presence of the *At. ferrooxidans* bacteria

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ABSTRACT

Purpose: This paper presents the experimental work carried out to evaluate the leaching efficiency of zinc, nickel and lead from printed circuit boards (PCBs) using biological leaching with different quantities of acidophilic bacteria as inoculum.

Design/methodology/approach: Bioleaching was conducted using periodic method in Erlenmneyer flasks, with pure cultures of At. ferrooxidans. Some conditional parameters: oxidation-reduction potential, pH were taken into account.

Findings: The results demonstrate that a greater quantity of inoculum conduces the extraction of metals from the solid into solution only in the initial stage of the bioleaching. 57% and 51% of the available Zn and Ni were leached from PCBs in the presence of At. ferrooxidans bacteria. No Pb was detected in the leachate during bioleaching.

Research limitations/implications: Further research is needed to determine the influence of various conditions and parameters on activity of microorganisms and efficiency of metals bioleaching from waste materials.

Practical implications: Presented study is a continuation of research conducted on the possibility of metals recovery from waste by biological methods.

Originality/value: The paper could be an interesting source of information for researchers who apply bioleaching methods.

Keywords: Bioleaching; Acidithiobacillus ferrooxidans; PCBs

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1. Introduction

Bioleaching processes are based on the ability of microorganisms to transform solid compounds into soluble and extractable elements which can be recovered. Acidophilic microorganisms play a crucial role in the biohydrometallurgical techniques. Among major groups of bacteria, most commonly used are acidophilic and chemolithotrophic microorganisms of: *Acidithiobacillus ferrooxidans*, *Acidithiobacillus thiooxidans*, *Leptospirillum ferrooxidans* and heterotrophy for example *Sulfolobus*. In addition, fungi such as *Penicillium* and *Aspergillus Niger* are examples of some eukaryotic microorganisms used in bioleaching during metal recovery from industrial wastes [1].

Studies on the extraction of metals using microorganisms has been carried out for many types of wastes. Bioleaching has been applied for the removal metals from fly ash [2], tannery sludge [3], lithium batteries [4], sewage sludge [5] spent catalysts [6,7] or electronic scraps [8]. These wastes are often complex in terms of material, which contains in its composition, basic and precious metals as well as hazardous substances. An example of a heterogeneous material are electronic waste, a mixture of various metals (especially Cu, Al, Fe, Ni) and their alloys, which elements are covered or laminated with plastics and ceramics. The main carrier of valuable metals in the waste are electronic printed circuit boards (PCBs) elements consisting of multiple components which are constantly evolving in mass and form. Among these components a significant amount represent metals. For example, metal content in these elements of mobile phones is about 28%, including 10-20% of copper, 1-5% of lead, 1-3% of nickel, content of precious metals (Ag, Pt, Au) about 0.3-0.4%, and the rest are plastics (19%), bromine (4%), glass and ceramics (49%) [9]. Despite the significant interest in recent times, in biohydrometallurgical methods still a small number of publications are devoted to research into the possibility of recovery of valuable metals from electronic waste with bioleaching method. Among available studies most are focused on copper, which is the dominant metal in electronic waste. However, the presence of other minor metals in the waste material e.g. Ni, Pb, Sn, Zn, Al, should be regarded. Determination of the effectiveness of their transition from the solid into solution in the presence of bacteria and to identify the impact of these metals on the metabolic activity of microorganisms is an essential element of a complementary knowledge in the range of metal recovery from waste by biological methods.

The purpose of this study was to determine the efficiency of Zn, Ni and Pb extraction during bacterial leaching of PCBs. In all experiments pure culture of acidophilic bacteria *Acidithiobacillus ferrooxidans* were used at 20-22°C, a temperature lower than implied by the optimal conditions for growth and activity of *At. ferrooxidans* bacteria [10].

2. Bioleaching of minor metals from PCBs

Researches into the possibility of microbiological leaching of Cu and also Al, Ni, Zn, Pb and Sn from electronic waste were conducted by Brandl et al. [8]. With the mixture of *At. ferrooxidans* and *At. thiooxidans* cultures, bacteria were able to leach more than 90% of available Cu, Zn, Ni, and Al at scrap concentrations of 5-10 g/l at 30˚C. With respect to Pb and Sn, precipitation of these metals were observed as $PbSO_4$ while Sn precipitated probably as SnO. Material heterogeneity of waste, in particular the presence of alkaline particulate components of the solid phase might hinder the bioleaching process and slow down its dynamics [8,11]. This phenomenon was observed by Brandl et al. [8]. When the concentration of scrap in the medium exceeded 10 g/l experiments showed that bacterial growth was inhibited. Although *Acidithiobacillus* are characterized by highly developed adaptability to extreme environmental conditions (e.g. high concentrations of metals [12]), the toxic influence of waste on microorganisms can be observed. It is believed that high Al concentration (and the alkaline character of the non-metallic components) in the environment inhibits the growth of bacteria. Therefore for more efficient metal mobilization a two-step leaching process was proposed where biomass growth is separated from metal leaching. Also Wang et al. [13] showed that pure culture of *At. ferrooxidans, At. thiooxidans* and their mixture can not only efficiently bioleach the main metal (copper) but also bioleach other minor metals such as lead or zinc. Various percentages of metals were leached depending on the sieve fractions of experimental samples and PCBs concentration at 28˚C. Percentage of solubility of examined metals into the leaching solution basically increased with decrease of sieve fraction of sample, and decrease of PWBs concentration. Copper, lead and zinc were extracted in amount higher than 88.9% at <0.35mm of the sieve fractions of sample at 5 days of leaching time by the above three kinds of cultures. Liang et al. [14] investigated the influence of printed circuit boards addition amounts and times on bacterial growth and Cu, Zn, Pb, Ni recovery, in variable PCBs concentrations added separately within next few days. Bacterial growth and metals recovery were closely related to PCBs amounts and times. Novel strategies in the process of bioleaching of Cu, Ni, Zn and Pb from waste using multiple PCBs additions (4 g/l at 48 h, 6 g/l at 96 h and 8 g/l at 144 h) were proposed. High level of Al, Zn and Pb transition into the solution was also obtained using acidophilic mixed culture of bacteria in the bioleaching [15]. 88.2% Al, 91.6% Zn, 86% Pb were leached within 96 h. Experiments with *S. thermosulfidooxidans* and acidophilic heterotroph were conducted by Ilyas et al. [16]. During bioleaching of electronic waste using a static method at 45˚C, 81% Ni, 89% Cu, 79% Al, 83% Zn were leached. Pb and Sn were detected in precipitates.

3. Materials and methods of research

Electronic waste in the form of PCBs obtained from spent mobile phones were used in the experiments. The scraps of PCBs were shredded and then crushed by cutting mill. The fraction of <0.5 mm particle size was used in all bioleaching experiments. Concentrations of metals in this fraction were determined by Atomic Absorption Spectrophotometer (AAS - Solaar M6-UNICA Atomic Absorption) and were as follows: 35.9 % Cu, 0.2% Zn, 0.6% Pb, 1.4% Ni.

In the study pure culture of *At. ferrooxidans* were used. The strain were isolated from the source of mineral water coming from Głębokie and Łomnica (Poland, Nowy Sącz county) [17]. *At. ferrooxidans* were cultured on Silverman/Lundgren (9K) medium consisting of (g/l): $(NH_4)_2SO_4$ - 3.0; KCl - 0.1; K_2HPO_4 - 0.5; $MgSO_4{\cdot}7H_2O$ - 0.5; $Ca(NO_3)_2$ - 0.01; $FeSO_4{\cdot}$7H2O - 44.2 with the initial concentration Fe(II) – 9,0 g/l.

Bioleaching experiments were conducted in 300 ml Erlenmeyer flasks containing 1g of waste and 100 ml of solution. Flasks were maintained on a rotary shaker (130 rpm) at 20-22˚C. Samples were inoculated with a different quantity of microorganisms: 10%, 20%, 50% and 100% v/v. pH was adjusted with sulfuric acid to 1.7. Growth of *At. ferrooxidans* was monitored by measuring pH and oxidation–reduction potential (ORP). Chemical leaching processes were also conducted using 9K medium with pH adjusted to 1.7. Metal concentrations in the samples were measured using AAS.

4. Results and discussion

Changes in pH and ORP during bioleaching of metals from PCBs with variable quantities of bacteria culture are shown in Fig. 1a and 1b. In biological samples as well as in sterile ones pH values were adjusted to 1.7. Control samples required constant adjustments to the specified pH value within 21 days of bioleaching. For biological samples the correction time depended on the quantities of inoculum in solutions - systems with 10% and 20% of bacteria dose needed a longer adjustment respectively to 16 and 12 days, compared to the samples inoculated with 50% and 100% of bacteria (Figs. 1a, 1b - filled points indicate the last day of adjustment). An increase in pH in the initial stage of process has been observed for samples with the lowest quantities of bacteria. The value rose from 1.8-2.0 to about 2.2-2.4, and was accompanied by slowing growth of the bacteria with apparent low ORP values. In the following days of bioleaching initially adjusted pH gradually decreased and underwent acidification in the presence of bacteria and reached at 21st day the value of 1.5-1.6. The increase in ORP (due to the oxidation of Fe^{2+} to Fe^{3+}) in combination with the low pH value during leaching is an indicator of substantial growth of microorganisms and was attributed to bioleaching stage (instead of acid leaching) [18]. The dynamics of solution acidification with 50% and 100% of bacteria is much higher. ORP reached a maximum of 374 mV from an initial value of 326 mV in the control test. While in biological systems rapid increase of ORP in the range of 600-606 mV has been observed.

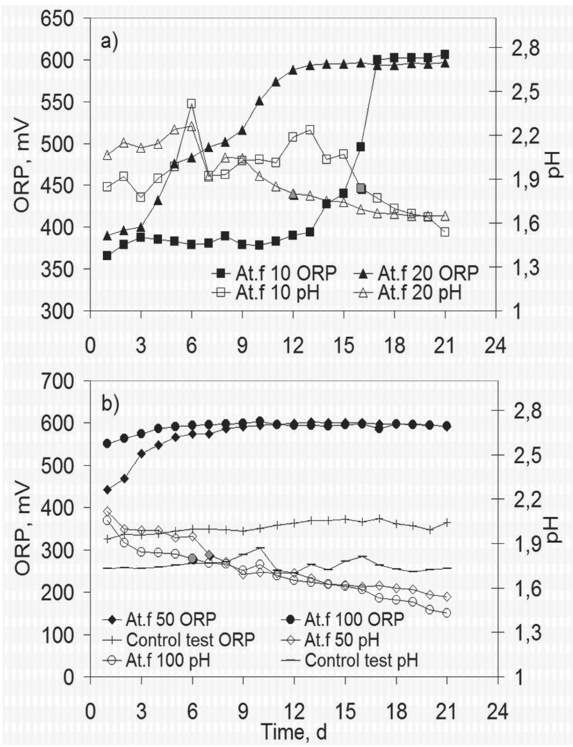

Fig. 1. Changes of ORP and pH during bioleaching with different quantities of pure *At. ferrooxidans*: a) 10%, 20%; b) 50%, 100% and control test. For pH - filled points indicate the last day of adjustment of pH

The effectiveness of Zn and Ni extraction during 21 days of leaching in the presence of variable doses of *At. ferrooxidans* bacteria and in the control test are shown in Figures 2 and 3.

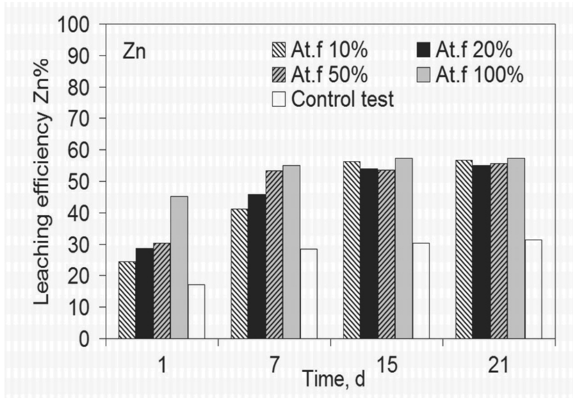

Fig. 2. Efficiency of zinc leaching with variable quantities of *At. ferrooxidans*.

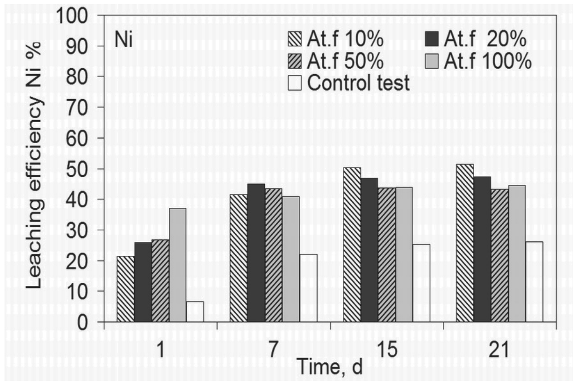

Fig. 3. Efficiency of nickel leaching with variable quantities of *At. ferrooxidans*.

Higher dose of bacteria cultures conduce leaching of zinc and nickel from the waste, in the early stage of the process. Within 21 days 57.3% of Zn was leached with quantity 100% of bacteria culture. For samples with a lower dose of inoculum comparable degree of Zn leaching was achieved in the range 55.1-56.7%. Nickel was leached in an amount of 51.4% with the presence of 10% of bacteria in solutions and for other systems efficiency was >41%. The leaching of Zn and Ni in the control condition was slower - within 21 days 31.3% 26.1% were mobilized respectively. For all the samples with variable quantities of bacteria, the presence of lead in leachate was observed only at the first day of initiated bioleaching process (Table 1). Over the next 21 days no Pb was detected in the leachate. Leaching of Pb with sulfur-oxidizing bacteria like members of the genus *Thiobacillus* is not very effective, because of the low solubility of $PbSO_4$ in aqueous solutions [19]. Sulfate was present in the medium at high levels, because ferrous sulfate was added as an energy source for *At. ferrooxidans*. Therefore, mobilized Pb was precipitated as $PbSO_4$ and probably remained in the precipitate in the leachate. Similar observations can be found in [8,16,20].

Table 1.
Efficiency of Pb leaching during experiment

Leaching time, 1st day	Quantity of inoculum, %				
	0	10	20	50	100
Pb, %	3.3	5.3	2.7	4.8	-

5. Conclusions

The Zn, Ni and Pb extraction from printed circuit boards was studied using biological leaching with *At. ferrooxidans* bacteria. The experimental results demonstrate that a greater quantity of inoculum conduces the extraction of metals from the solid into the solution only in the initial stage of the bioleaching. Within 21 days *At. ferrooxidans* were able to leach 57% and 51% of the available Zn and Ni from PCBs during bioleaching. No Pb was detected in the leachate, which was probably precipitated as sulphate.

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