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INFLUENCE OF PHYSICAL AND CHEMICAL FACTORS ON BIOLOGICAL LEACHING PROCESS OF COPPER FROM PRINTED CIRCUIT BOARDS

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The article presents the results of the research regarding the biological leaching of this metal from electronic wastes components in the form of printed circuit boards. The purpose of the study was to evaluate the influence of some physical and chemical factors (e.g. pH, oxidation-reduction potential) on bioleaching process and efficiency of copper transfer from solid phase into solution. Bioleaching experiments were carried out with pure cultures of *Acidithiobacillus ferrooxidans*. The obtained results were discussed.

Key words: biological leaching, *Acidithiobacillus ferrooxidans,* PCBs, copper

INTRODUCTION

In addition to traditional methods of metal-bearing waste processing including electronic scrap (pyro- and hydrometallurgical) [1-3], the new solutions aimed at improving the technology (already used) or development of new methods for efficient metals recovery (with fulfilled environmental protection) are being looked for. Works in this direction are also conducted with biohydrometallurgical methods, which utilize the potential and the biochemical activity of microorganisms in the leaching process.

Experimental work using bacterial leaching for the extraction of some base (Cu, Zn, Pb, Ni, Sn, Al) or precious metals (Ag, Au) from electronic waste was carried out with the participation of microorganisms such as *Acidithiobacillus*, *Acidiphilium acidophilum*, *Sulfobacillus thermosulphidooxidans* bacteria, fungi [4-9] or cyanogenic bacteria *Chromobacterium violaceum*, *Pseudomonas fluorescens* [10-12].

In this paper, pure culture of acidophilic bacteria *Acidithiobacillus. ferr ooxidans* was used to recover copper from printed circuit boards (PCBs). The purpose of this study was to evaluate the influence of some physical and chemical factors (pH, oxidation-reduction potential, quantities of bacteria) on bioleaching process and determine efficiency of copper transfer from solid phase into solution.

FACTORS INFLUENCING BIOLEACHING PROCESS

Process of metals bioleaching from electronic waste is a complex process, determined by many factors. Main parameters which affect the bioleaching kinetics [4,5,8-10] and metabolic activity of microorganisms are pH, concentration of Fe^{2+} in the system, qualitative and quantitative composition of waste, the toxicity of the ingredients (for microorganisms) and the degree of grinding material, temperature and time.

It is considered [13,14] that the biological leaching of copper from waste (PCBs) is implemented primarily through an indirect mechanism. $Fe_2(SO_4)_3$ created by *At. ferr ooxidans* in the leaching process oxidizes elemental copper (contained in the waste) to the copper ion, according to the reaction:

$$Cu + Fe_2(SO_4)_3 \rightarrow Cu^{2+} + 2\,Fe^{2+} + 3\,SO_4^{2-} \quad (1)$$

$$2\,FeSO_4 + H_2SO_4 + 0{,}5\,O_2 + bacteria \rightarrow \rightarrow Fe_2(SO_4)_3 + H_2O \quad (2)$$

Dynamics of bioleaching process can be disrupted (slowed down) by the presence of alkali contents in the solid phase. The toxic influence of waste on microorganisms whose growth was significantly inhibited during the bioleaching process has been shown [4]. It is believed that high Al concentration (and the alkaline character of the non-metallic components) in the environment inhibits the growth of bacteria. Gradual adaptation of bacteria to the environment and the addition of acidifying agent can improve efficiency of the process.

The concentration of Fe^{3+} ions, pH and the quantity of used microorganisms play the major role in the leaching of metals from waste into solution. Introducing the higher dose of *At. ferr ooxidans,* iron ions Fe^{2+} to the system and ensuring pH of $1{,}5 < pH < 2{,}0$ (adjusted with H_2SO_4) can improve the efficiency of metals extraction from the waste [5].

Temperature is an important parameter that guarantees the activity of microorganisms. The optimal tem-

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perature of *Acidithiobacillus* bacteria activity is 28-37 °C [15]. For the electronic waste, most bioleaching experiments were carried out at 30 °C [4,5,9,12]. However the effectiveness of process in the temperature range of 22-25 °C was also noted. [16,17].

Experiments in this work were done at the lower temperature 20-22 ºC using *At. ferrooxidans* bacteria.

EXPERIMETAL WORK

Materials. The research work was made on the PCBs obtained from used cell phones. PCBs were shredded using the cutting mill to a particle size < 0,5 mm. The metal content in the sample was determined by atomic adsorption spectrometry (SOLAAR M6-UNICAM Atomic Absorption) and was as follows: 35,9 % Cu; 0,6 % Fe; 0,2 % Zn; 0,6 % Pb.

Applied microorganisms. In this study *Acidithiobacillus ferr ooxidans* strain was used. Bacteria were isolated from the source of mineral water coming from Łomnica (Nowy Sącz county, Poland) [18]. The culture was maintained in a standard Silverman/Lundgren (9K) medium.

Bioleaching were carried out in Erlenmeyer flasks (300 mL) by using a rotary shaker (130 rpm) at 20-22 ˚C. The samples of the waste were 1 g, the volume of solution was 100 mL, whereas the quantities of bacteria culture were variable: 10 %, 20 %, 50 % and 100 % (v/v). Parallelly, the chemical leaching processes in control systems were carried out. Experiments were carried out with the daily regulation of leaching solution pH of 2,0 by adding H_2SO_4 for the bacterial samples as well as for sterile variants. The changes of copper concentration, the oxidation-reduction potential (ORP), and pH have been analysed in the solution. All experiments were carried out within 21 days.

RESULTS AND DISCUSSION

Figure 1 shows the dynamics of pH changes during the 21 days of leaching process in biological systems and the control test, carried out with the adjustment of pH to 2,0. Samples inoculated with the smallest quantity of bacteria (10 %, 20 %) required more frequent adjustment of pH, compared to systems containing 50 % and 100 % v / v inoculum. For these samples major fluctuations in adjusted pH values have also been observed. The initial value of this parameter for the solution with 10 % of bacteria on 1st day was 2,32 and reached a value of 2,75 on 13 th day of the leaching.

The fluctuation range of adjusted pH values is about half as long for the 20 % systems (correction to 7 th day) and 50 % (correction to 6th day), whereas the leaching solution containing 100 % of the inoculum did not require additional acidification. In the following days of leaching, adjusted pH initially was maintained at a level of about 2,0 and then was gradually decreased on 21st day to the pH 1,7-1,8. Solutions inoculated with

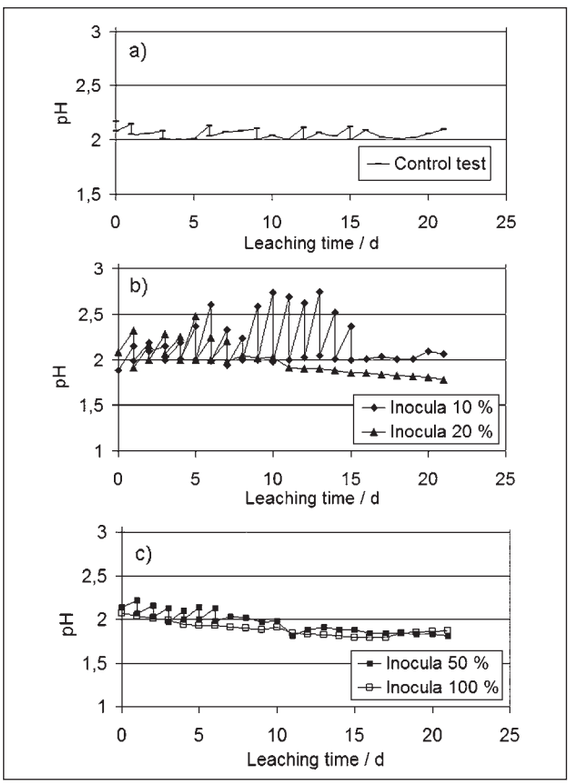

Figure 1 Variation of pH during leaching process with variable quantities of *At. Ferrooxidans*: a) control test (0 %); b) 10 % and 20 %; c) 50 % and 100 % of inolcula

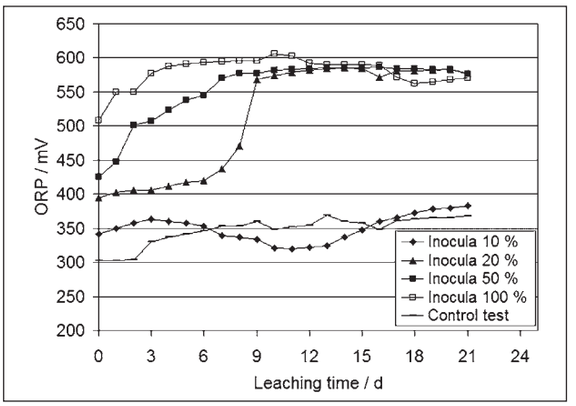

Figure 2 Variation of ORP during leaching process with variable quantities of *At. ferrooxidans* and for control test

bacteria under influence of biological oxidation of Fe^{2+} ions were gradually acidified. This is explained by the reactions of ferric iron precipitation as sulphate, iron hydroxides or jarosite [19].

The exception was a system with 10 % inoculum, in which regrowth of pH was observed at the end of the process. The control system required constant adjustment pH to 2,0. The increase in pH visible for all biological samples in the initial stage of the process is associated with the presence in material of alkaline components. [4]. It is accompanyed with delayed growth of

bacteria in the environment, which found reflection in the changes of ORP recorded during the experiment (Figure 2). For example, for a sample containing 20 % of the inoculum during the first 7 days there was observed a small increase in the value of ORP from 395 to 437 mV. As the reaction proceeded and activity of microorganisms increased, within the next 2 days a sharp increase of ORP to 568 mV was observed and then the maximum value of 585 mV was reached on 14th day. This trend (with high value of redox potential) was attributed to bioleaching stage (instead of acid leaching), bacterial oxidation and regeneration of Fe^{2+} to Fe^{3+}. The growth dynamics of the ORP value (at the beginning) is greater when the quantity of bacteria in the leaching system is higher.

A gradual decrease in the ORP value (for a system of 20 %, 50 %, 100 %) observed at the end of the process, indicated the regressive phase of bioleaching and slowing down the activity of bacteria in solutions. The different character of changes in ORP (in relation to other biological systems) demonstrated the system which was inoculated with lowest quantity of bacteria – 10 %. The value of ORP remained in the range 320-383 mV and was comparable with the control system, kept in the range of 303 to 369 mV. Probably the extreme conditions (high pH) affect adversely the microorganisms, causing reduction in the growth of biomass and reduce their oxidative activity. It is well known that ferrous iron oxidation by *A. ferrooxidans* rapidly decreases at pH values greater than 2,5 [20,21].

In Figure 3 the efficiency of Cu extraction during the 21 days of leaching in the presence of variable quantities of *At. ferrooxidans* and in the control test are presented.

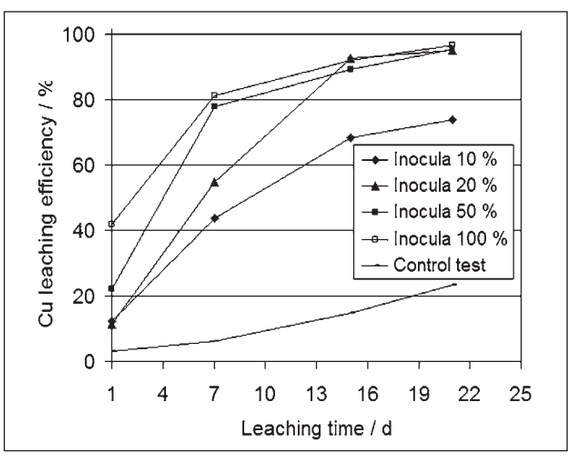

Figure 3 Efficiency of copper leaching with different quantities of bacteria and in control test

It can be observed that a higher dose of bacteria cultures accelerates the leaching of copper from waste, which is the result of increased concentrations of Fe^{3+} ions in solution. Within 7 days 43,6 %, 54,8 %, 78,0 %, 81,3 % copper was mobilized, when flasks were inoculated with 10 %, 20 %, 50 % and 100 % of *At. ferrooxidans*, respectively. Despite the limited activity of bacteria in the system inoculated with 10 % of culture (low ORP value), it was observed that the efficiency of copper extraction with respect to the control test, was much higher. Maximally (21st day), 96,7 %, 95,6 %, 95,2 %, 74,0 % Cu was leached in systems 100 %, 50 %, 20 % and 10%, respectively. The leaching of copper in the control condition was significantly slower - within 21 days 23,3 % Cu was transfered into solution.

SUMMARY

Researches on bioleaching of electronic waste by the static method at a temperature lower than implied by the optimal conditions for growth and activity of *At. ferrooxidans* bacteria were carried out. It was shown that copper can be effectively mobilized and the efficiency of Cu leaching from the waste with *At. ferrooxidans* is more efficient than chemical leaching efficiency.

One of the parameters determining the efficiency of the leaching process is the presence of Fe^{3+} ion and acidic pH. The recovery of copper in the adopted experimental conditions rises with increasing quantity of microorganisms in leaching systems. Ascending efficiency of the Cu transition to a solution is accompanied by decrease pH, which (after an initial adjustment) is the effect of the metabolic activity of bacteria, causing acidification of the environment.

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Note: Nowak P is responsible for English language, Katowice, Poland