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THE EFFECT OF SPECIFIC CONDITIONS ON Cu, Ni, Zn AND Al RECOVERY FROM PCBs WASTE USING ACIDOPHILIC BACTERIAL STRAINS

The objective of this work was to evaluate the influence of static, stirring and shaking conditions on copper, zinc, nickel and aluminium dissolution from printed circuit boards (PCBs) using the mixed acidophilic bacterial culture of Acidithiobacillus ferrooxidans and Acidithiobacillus thiooxidans. The results revealed that static conditions were the most effective in zinc and aluminium dissolution. Zinc was removed almost completely under static conditions, whereas maximum of nickel dissolution was reached under the stirring conditions. The highest copper recovery (36%) was reached under stirring conditions. The shaking conditions appeared to be the least suitable. The relative importance of these systems for the bioleaching of copper and nickel decreased in the order: stirring, static conditions, shaking.

Keywords: bioleaching, metals, electronic waste, PCBs

1. Introduction

Nowadays, recycling of electronic waste has become an important subject of many studies not only from the waste treatment point of view, but also from valuable metal recovery. In the printed circuit boards (PCBs), metals content is around 28-30 mass % (copper: 10-20 %, lead: 1-5 %, nickel: 1-3% and precious metals like silver, platinum and gold are also present in the electronic scrap to a total of 0.3-0.4%) [1]. The quantity of metals, especially copper, turns the electronic scrap into an interesting raw material according to the economic point of view. Electronic waste is not only important source of valuable metals, but also it is a potential environmental contaminant, namely Cd, Ni, Pb, Sb, Hg, polybrominated diphenyl ethers and polychlorinated biphenyls represent a real environmental threat [2]. Serious problems occurred in China due to relatively primitive technologies used to process the e-waste. Dangerous levels of polychlorinated biphenyls and polybrominated diphenyl ethers have been observed in various environmental matrices, such as the atmosphere, sediment, water and soil, and in biological samples, including human serum, cord blood, breast milk, placenta and hair from many Chinese e-waste dismantling sites [3].

In order to avoid such problems, the purpose of [4] is recycling and other forms of recovery of such wastes so as to reduce the disposal of waste and to contribute to the efficient use of resources and the retrieval of valuable secondary raw materials. It also seeks to improve the environmental performance of all operators involved in the life cycle of electrical and electronic equipment (EEE).

In the last years, hydrometallurgical treatment of PCBs became so important that it significantly exceeded the pyrometallurgical processing. Nowadays, majority of studies concentrate on hydrometallurgical processes and improving the wide variety of reagent systems in the presence of suitable oxidant. In the previous study [5], various reagent systems e.g. sulphate, chloride, nitrate, iodide, ammonia, cyanide thiourea and thiosulphate have been confirmed as the most effective for leaching of base and precious metals from PCBs. But those systems suffer from relatively high reagent costs, high corrosivity and high temperatures. It was also confirmed that ferric iron in acidic sulphate media is a low-cost and suitable oxidant for leaching of metals from PCBs [6-8]. Ferric iron is a strong oxidant (0.77 V) capable of oxidising majority of metals from ores or electronic waste, in which metals are present in metallic form [9-11]. Mathews and Robins in 1972 described the formation rate of Fe(III) (M min-1) in acidic sulphate solutions as directly proportional to the concentration of dissolved $[O_2]$ and $[Fe(II)]^2$, but inversely proportional to $[H+]^{0.25}$ (Eq 1) [12].

$$\frac{d[Fe(III)]}{dt} = k \frac{[Fe(II)]^{-2}[O_2]}{[H+]^{0.25}} e^{\left(-\frac{E}{RT}\right)} \qquad (1)$$

Bioleaching is a specialized biohydrometallurgical process, which utilizes either metabolic activities or products of microorganisms. Microorganisms (bacteria and fungi) used in this process are able to transform solid compounds into soluble and extractable elements that can be recovered [13].
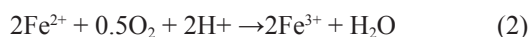
Bacterial consortium composed of *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans* can grow and utilize ferrous iron or elemental sulphur and thus produce ferric ions (Eq. 1) or sulphuric acid (Eq. 2) that are of a great

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importance as leaching agents in metal recovery from primary and secondary sources (Eq. 3, 4, 5) [14-16].

$$2Fe^{2+} + 0.5O_2 + 2H+ \rightarrow 2Fe^{3+} + H_2O \qquad (2)$$

$$S^0 + 1.5O_2 + H_2O \rightarrow SO_4^{2-} + 2H+ \qquad (3)$$

$$MS + 2Fe^{3+} \rightarrow M^{2+} + 2Fe^{2+} + S^0 \qquad (4)$$

$$MS + 2O_2 \rightarrow M^{2+} + SO_4^2 \qquad (5)$$

$$M (Cu, Ni, Zn, Co, Al) + Fe_2(SO_4)_3 \rightarrow MSO_4 + 2FeSO_4 \qquad (6)$$

The mixed culture of *A. ferrooxidans* and *A. thiooxidans* appear to be more effective in metal recovery from PCBs than separated culture [17]. As majority of acidophilic bacteria are aerobic, we assumed that providing the continuous agitation of leaching material could increase the bioleaching efficiency by enhancing the bacterial metabolism.

The present studies were undertaken to evaluate the effect of chosen process parameters namely shaking, stirring and static conditions on Cu, Ni, Zn and Al recovery from PCBs using acidophilic bacterial strains and thus determine the main parameter responsible for faster diffusion of leaching agents.

2. Experimental method

PCBs sample. Electronic scrap, in the form of printed circuit boards, was crushed to particle size of 1- 1000 mm. Analysis of the electronic scrap before bioleaching revealed the presence of Cu (19.21%), Zn (1.17%), Ni (0.32%), Al (1.73%). Metal concentrations of PCBs were determined by atomic absorption spectrophotometer (Perkin Elmer 3100), its composition is shown in Table 1.

TABLE 1

Content of basic metals in analysed MSC sample

Metal	Cu	Ni	Zn	Al
Content, mass %	19.2	0.32	1.2	1.7

Microorganisms. Bacterial culture formed by *A. ferrooxidans* and *A. thiooxidans* originating from Smolnik mine drainage obtained from Institute of Geotechnics SAS in Kosice was used in the experiments.

Adaptation of microorganisms. Adaptation of bacteria was carried out in 500 ml Erlenmeyer flask containing 230 ml of nutrient medium proposed for the mixed bacterial culture [18] and 50 ml mixture of the bacteria and 2g PCBs. Metal adaptation of bacteria took place in an incubator at 30°C and lasted for 14 days.

Bioleaching experiments. Bioleaching experiments were carried out in sterile 500 ml Erlenmeyer flasks at temperature of 30°C. 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 1000 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 shaking, flasks were put into a shaker bath (150 rpm) to keep the content in homogenous form at 30°C. To investigate the effect of stirring a magnetic stirrer was used. All experiments were conducted in duplicates. The samples (5 ml) were regularly withdrawn on days: 1; 3; 7; 14; 21 and 28. During our experiment, the pH of each experimental solution was adjusted using sulphuric acid and monitored using a pH meter (Gryf 209). Memmert shaker bath, model WB 14 with SV 1422 was used to keep the content in homogenous form at 30°C. To ensure stirring the solution was used IKA lab-disc compact magnetic stirrer. For the metals concentration analyses a Perkin Elmer 3100 atomic absorption spectrometer was used.

3. Results and discussion

The influence of stirring and shaking on metal bioleaching from spent PCBs was compared to static conditions. The time-courses of Cu, Ni, Zn and Al dissolution in all three bioleaching systems are presented in Fig. 1. Copper exhibited the highest bioleaching efficiency in the stirring system. The dissolution of Cu (Fig. 1(a)) was very low within the first 14 days, when only 7% of Cu dissolved. After that time the bioleaching rate of Cu increased rapidly and on 28th day Cu bioleaching efficiency reached value of 36%. In the case of shaking and static conditions, dissolution rates of Cu did not exhibit evident differences. Unlike the stirring system, the Cu dissolution rates in those two systems were very low and stable up to day 21.
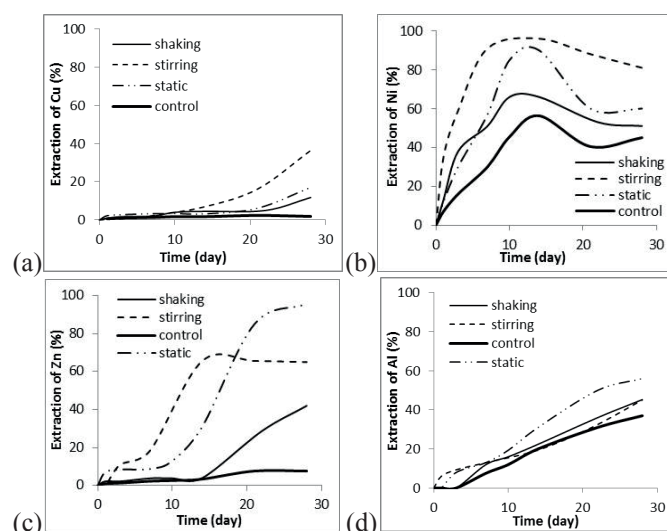

Fig. 1. Percentage of metals solubilized under shaking, stirring and static conditions from PCBs: (a) copper, (b) nickel, (c) zinc, (d) aluminium.

The stirring system also attained the highest extraction of Ni (Fig. 1(b)). The yield of 35% was reached during the first day of the process and within the next 14 days a majority of Ni (96%) was dissolved. In the case of shaking the metal

bioleaching rate was lower. Only 66% of Ni was dissolved during the 2 weeks of the bioleaching.

Regarding zinc, the highest bioleaching rate was observed from day 7th to 14th when majority of Zn was dissolved, while under the shaking condition Zn dissolution started later (Fig. 1(c)). However, a much higher Zn bioleaching efficiency was reached under the static condition (95%) compared to that under the stirring condition (64%).

There was almost no difference in dissolution performance of aluminium in the three bioleaching systems (Fig. 1(d)). Under all three studied conditions the Al bioleaching process performance was very similar. However, a higher percentage of Al dissolved was reached under the static condition (56%) compared to that under the shaking and stirring systems, when 45% of Al dissolved.

Fig. 2(a) shows the pH changes over the bioleaching time. In the stirring systems the pH rapidly increased in the first 7 days up to pH=2 and consequently the pH slightly decreased and remained stable around pH 1.7 until the end of the experimental period. On contrary, the pH changes under the static conditions were not so significant in the first 14 days of the bioleaching.
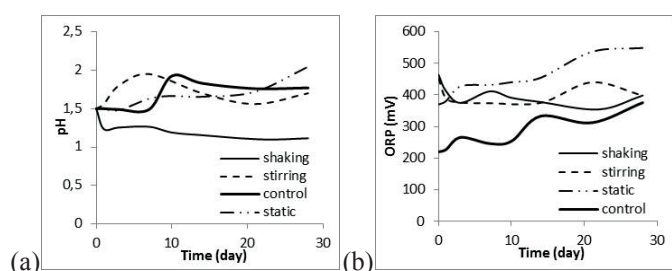

Fig. 2. (a) The pH changes over the leaching time, (b) Changes in oxidation-reduction potential during bioleaching study.

According to the process chemistry, fast biooxidation of Fe^{2+} ions under stirring conditions led to proton consumption (Eq.2), which was accompanied by a pH increase (Fig. 2(a)) [19]. Consequently hydrolysis of Fe^{3+} ions and jarosite formation resulted in the pH decrease and its stabilization. The fast pH increase in the first days promoted ferric ion as well as jarosite precipitation which resulted in the inhibition of bacterial iron oxidation due to the formation of a precipitate layer around the bacterial cells. According to Daoud and Karamanev [20] jarosite formation hinders leaching agent diffusion at pH above 1.8.

Based on the very low concentration of ferric ions (Fig. 3) in the leach liquor and constant oxidation-reduction potential (ORP) (Fig. 2(b)) values in the 20 days of bioleaching under the stirring condition it may be assumed that there was a balance between the simultaneous consumption of Fe^{3+} ions during the oxidation of metals and release of Fe^{3+} ions during the biooxidation of Fe^{2+} ions.

In the shaking system the pH was relatively steady and low (around 1.2) throughout the whole experimental period (Fig. 2(a)). The ORP decreased first and then slightly increased (Fig. 2(b)), followed by fluctuations on a low-level (420 mV – 380 mV). The ferric iron concentration in the leaching solution was very low and unlike the static condition, no Fe^{3+} concentration increase was observed (Fig. 3). It may be assumed that by the use of shaking the leaching material was not adequately

agitated and even compaction of the material covered by a sulphur layer was observed. Low pH values pointed out a good metabolic activity of *A. thiooxidans* and also indicated that proton consumption was limited through the kinetic barriers. Low ORP values and concentration of ferric iron, as well, showed that due to creation of the zone the bacteria of *A. ferrooxidans* were not able to obtain energy directly from the leaching material. It may explain the inhibition of bioleaching process and slower dissolution of the metals from PCBs, as well.
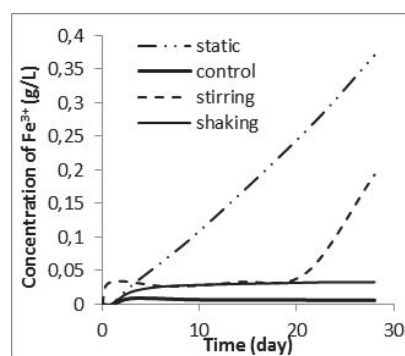

Fig. 3. Changes of Fe^{3+} concentration with time on leaching PCBs.

The experimental results showed that the fastest bioleaching kinetics was observed under the stirring condition, however, after about 14 days the bioleaching process slowed down and this fact negatively influenced the overall metal bioleaching efficiency reached at the end of the process (Fig. 4(b)). The metal bioleaching efficiency calculated for the 14th day (Fig. 4(a)) suggests that bioleaching under stirring conditions was faster and higher efficiency could be reached if precipitation layer formation was prevented.
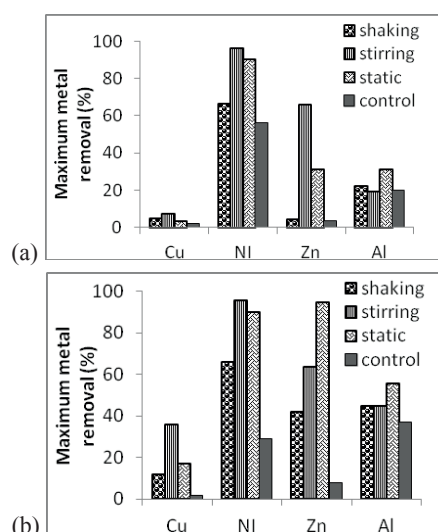

Fig. 4. The percentage of copper, nickel, zinc and aluminium solubilized from PCBs: (a) calculated for the 14th day, (b) at the end of the process.

A higher pH values measured under stirring conditions indicated that precipitation reaction occurred and limited diffusion of the leaching agents led to a lower bioleaching efficiency of the metals compared to the static conditions. It may be suggested that maintaining a low and relatively

constant pH throughout the whole bioleaching process could result in higher bioleaching efficiency of the metals under stirring conditions.

4. Conclusion

Although the stirring system allowed to highest dissolution of the metals, the presence of jarosite significantly lowered the metal bioleaching efficiency. Jarosite formation is known to have negative effect on metal bioleaching process because of a kinetic barriers formation leading to the slow diffusion of reactants and products through this zone. But according to the process kinetics stirring was the most suitable for metal recovery from waste PCBs, however, the maintaining of low pH is necessary for a high bioleaching efficiency of the metals.

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