

SELECTIVE RECOVERY OF COPPER FROM SOLUTIONS AFTER BIOLEACHING ELECTRONIC WASTE

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Abstract: Research on selective extraction of copper from solution after bioleaching grounded printed circuit boards (PCBs) using LIX 860N-IC were conducted. The effect of LIX 860N-IC concentration, phase ratio and influence of initial pH value of aqueous phase on the extraction of copper and iron was examined. It was found that the extraction rate of copper increases with the LIX 860N-IC concentration. Best results of Cu extraction (98 %) were achieved with extractant concentration of 5 % and pH 1.9. Higher pH value of aqueous phase (pH=2.4) is conducive to the simultaneous effect of Fe co-extraction.

Key words: solvent extraction, copper, solution after bioleaching, electronic waste.

1. Introduction

Over the past decades, there has been an increasing interest in biological methods and possibilities of their applications in metals recovery. Biological leaching has been conducted in the presence of variety of microorganisms and in a wide range of waste-carrying base, precious metals as well as hazardous substances, such as: fly ashes (Zn, Al, Cd, Cu, Ni, Cr, Pb, Mn, Fe), tannery sludge (Cr), jewellery waste and automobile catalytic converter (Au, Ag, Pt) spent lithium-ion or Ni-Cd batteries (Li, Co, Ni, Cd). Much attention is paid to the growing group of electronic waste, which are examples of complex material, containing a mixture of various metals, their alloys and also plastics and ceramics (CUI and ZHANG, 2008; PANT *et al.*, 2012; WILLNER and FORNALCZYK, 2012; VELGOSOVA *et al.*, 2013; WILLNER and FORNALCZYK, 2013). As a result of bioleaching electronic waste, a multi-component solution is obtained, containing various metal ions, of which copper is a predominant component. Due to the presence of additional metal cations, especially iron cations, direct recovery of copper (i.e. by electrolysis) is much more hindered. In this case, an effective method that allows the separation of desired metal (Cu) from their mixture may be solvent extraction (PANDA *et al.*, 2012; GOTFRYD and PIETEK, 2013). Over the past few years (bio)leaching–solvent extraction–electrowinning (BL–SX–EW) process has been conducted in hydrometallurgical production of copper from low grade ores. About 20–25 % of the world's total copper production is obtained through solvent extraction followed by electrowinning processes (MUNOZ and DREISINGER, 2007; PANDA *et al.*, 2012). In practice during hydrometallurgical process of copper production, sulfuric acid solution for leaching raw material is used. Post-extraction of

the raffinate is subjected to solid/liquid separation (sedimentation and filtration) and final extractive treatment of the solution is conducted. Next copper is recovered as a stripped liquor (moderately acidic copper sulfate) and is intended for electrolysis to obtain copper cathodes. Simultaneously, acid regeneration is carried out and the received regenerated electrolyte is used again in cycles as a stripping factor (GOTFRYD and PIETEK, 2013). There are very few publications that refer to recovery of metals from solutions after bioleaching e-waste (CHENGLONG *et al.*, 2010). The purpose of the study was to identify the selectivity and efficiency of LIX 860N-IC relatively to copper from polymetallic solution after bioleaching electronic waste.

2. Materials and methods

Bioleaching was conducted on printed circuit boards (PCBs) derived from spent mobile phones. PCBs were shredded with the cutting mill to a particle size < 0.5 mm. The strain of *Acidithiobacillus ferrooxidans* bacteria, isolated from ferruginous mineral waters in Poland was used in the study (PACHOLEWSKI and PACHOLEWSKA, 2001). The culture was maintained in Silverman/Lundgren (9K) medium, containing (g/L): $(\text{NH}_4)_2\text{SO}_4$ - 3.0; KCl - 0.1; K_2HPO_4 - 0.5; $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ - 0.5; $\text{Ca}(\text{NO}_3)_2$ - 0.01; $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ - 44.2; Fe(II) – 9,0 g/L. Bioleaching was 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 10 % (v/v) in experiments. Solutions were filtered, combined and then subjected to solvent extraction. Content of metals in sample was determined by atomic adsorption spectrometry (AAS, Solaar M6-Unicam). Composition of post-bioleaching solution is presented in Table 1.

Table 1. Concentration of metals in solution after bioleaching PCBs.

Metal	Cu	Fe	Sn	Pb	Ni
Concentration (g/L)	4.525	3.437	0.061	0.0005	0.0695

The reagents from the hydroxy oxime group have exceptional selectivity of copper extraction from acidic sulphate solutions in the presence of iron (III) (GOTFRYD *et al.* 2002; SZYMANOWSKI, 2003). Therefore the organic solvent such as LIX 860N-IC (5-nonilsalicylaldoxime) obtained from the supplier (BASF, Ireland), was used in studies. The extractant was diluted in the range 2.5-20 % with Exxsol D80 (dissolvent). Experiments were carried out in separatory funnel by contacting desired volume of the organic (O) and aqueous phase (A) by manual mixing for 5 and 10 minutes. Different phase ratios O:A were used from 1:3 to 3:1, and initial pH of aqueous solutions was 2.4 and 1.9. Concentration of Cu and Fe ions was determined by AAS. Stages of studies are illustrated in Figure 1. The metal ion concentration in the organic phase was determined from the difference between concentration of metal before and after extraction. The efficiency of metal ions extraction process (E) was expressed in the following way:

$$E = \frac{C_o \cdot V_o}{C_{w0} \cdot V_w} \cdot 100\% \quad (1)$$

where: C_o – concentration of metal ions after extraction in organic phase, g/L;
 C_{w0} – initial concentration of metal ions in the aqueous phase, g/L;
 V_o – the volumes of the organic phase, mL;
 V_w – the volumes of the aqueous phase, mL.

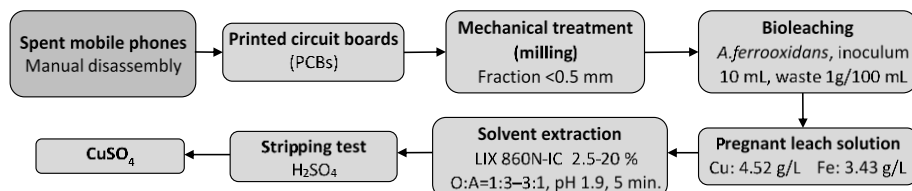


Fig. 1. Schematic diagram of experimental stages during solvent extraction of copper from solution after bioleaching PCBs.

3. Results and discussion

A preliminary study was carried out due to the possibility of extractant reaction with other cations present in the solution and the progress of solvent extraction in a non-specific manner. The aim was to initially determine used extractant selectivity towards copper extraction from multi-component solution after bioleaching electronic waste. Preliminary tests of extraction copper from polymetallic solutions were conducted for 5 and 10 min at pH 2.4 and phase ratio O:A = 1. The results of these tests (data not illustrated) showed that the process of extraction of Cu occurred very quickly. Within 5 minutes, 99.6 % of Cu was extracted to the organic phase. Increasing the mixing time up to 10 minutes had not improved the efficiency of this process. Due to the presence of iron ions in solution and possibility of its transition from the aqueous to the organic phase, phenomenon of co-extraction of iron was traced. Within 5 minutes, 14 % extraction rate of Fe from aqueous to the organic phase was recorded. The amount of iron in the organic phase was greater when the mixing time of phases lasted 10 minutes. Together with copper, 24.9 % of Fe was co-extracted to organic phase. This effect combined with the lack of efficiency of copper extraction, confirmed the need to shorten the time of mixing and reducing the pH of aqueous solution. Further studies on identifying efficiency of selective extraction of copper were carried out in shorter time (5 minutes) and at lower pH.

Copper extraction was carried out at different concentrations of LIX 860N-IC (2.5-20 %) and at pH 1.9, phase ratio O:A = 1 and contact time 5 min. As shown in Fig. 2, copper rate extraction increased from 58.0 % to 98.3 % as the concentration of LIX 860N-IC increased from 2.5 % to 5.0 %. Beyond 5.0 % extraction of Cu seems to be plateau. Simultaneously co-extraction of Fe was observed when concentration of extractive reagent raised. The optimal concentration of LIX 860N-IC is suggested to be about 5.0 %. Accompanying co-extraction of iron (14.6 % in preliminary tests) is a result of pH solution, which value was 2.4. Effect of co-extraction of Fe (in the range

1.9 % - 5.2 %) was significantly reduced at pH=1.9. Similar observations of elimination (or reduction) of the iron effect co-extraction at lower pH value was observed by PANDA *et al.* (2012) and CHENGLONG *et al.* (2010). At this stage of the study the pH value of the aqueous phase (pH = 1.9) as a result of acidification of solution during bioleaching, was adopted as initial pH value and intended for further solvent extraction. However, further research on the influence of the pH on extraction efficiency and Fe co-extraction should be carried out.

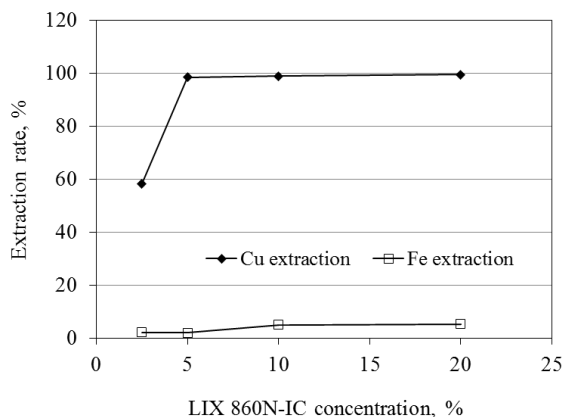


Fig. 2. Effect of LIX 860N-IC concentration on copper and iron extraction rate (pH = 1.9, O:A = 1, contact time 5 min).

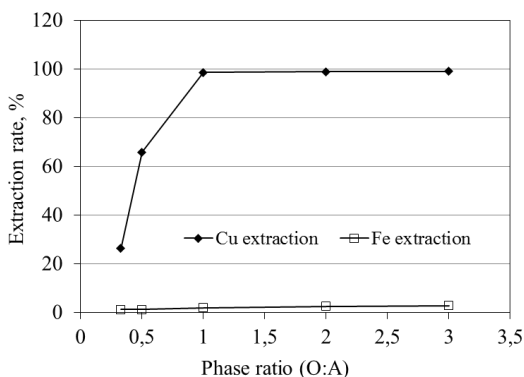


Fig. 3. Influence of phase ratio (O:A) on copper and iron extraction rate (pH = 1.9, LIX 860N-IC 5 %, contact time 5 min).

Fig. 3 presents influence of phase ratio (O:A) on the Cu and Fe extraction. Extraction rates of copper increased from 26.4 % to 98.3 % with phase ratio in the range of 1:3 to 1:1. Above the ratio O:A = 1 extraction of Cu maintained a slight increase. Simultaneously with copper, a slight increase of iron was observed in the adopted phase ratios (A:O = 1:3 to 3:1).

4. Conclusions

On the basis of conducted research involving the solvent extraction of copper from solutions after bioleaching electronic waste, it was found that: (i) the extraction rate of copper increases with the LIX 860N-IC concentration; (ii) in the adopted experimental conditions best results were achieved when concentration of reagent was 5 % and proper phase ratio was O:A = 1:1; (iii) the increase of pH aqueous phase (pH = 2.4) was accompanied by the effect of Fe co-extraction (24.9 %) and (iv) extraction of Cu at the level of 98.3 % was obtained at pH = 1.9. At the same time, the lowest degree transition into the organic phase of Fe amounting 1.9 % was simultaneously achieved.

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