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Bioleaching of indium and tin from used LCD panels

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Abstract: The demand for indium is increasing every year. This metal is mainly used as indium tin oxide (ITO) in the production of transparent conductive coatings for liquid crystal displays (LCD). This paper focuses on biohydrometallurgical methods used for the recovery of indium and tin from LCD sourced from spent mobile phones. Bioleaching experiments were carried out in two different leaching media: 9K medium and H_2SO_4 solution, using mixed, adapted bacteria *Acidothiobacillus ferrooxidans* and *Acidothiobacillus thiooxidans*. The main aim of this study was to evaluate the potential and efficiency of indium and tin extraction in the presence of acidophilic microorganisms. Within 35 days, using 9K medium, 55.6% of indium was bioleached, whereas the chemical leaching resulted in a value of 3.4%. Leaching efficiency of tin was 90.2% on the 14th day of the experiment for the biological system (9K) and 93.4% on 21st day of control leaching.

Keywords: *bioleaching, ITO, indium recovery, tin recovery, LCD panels*

1. Introduction

Nowadays mass consumption and a short life-cycle of electronic goods (due to breakdown, slow-down, or just the availability of a newer model) cause a lot discarded waste. This waste material could have a second life due to being a rich source of metals such as gold, silver, copper, iron, indium, gallium, rare earth metals, etc. (Willner and Fornalczyk, 2012; Saternus et al., 2017). Aside from computers and televisions, devices with high global demand and a short life cycle are cell phones. One of the main element of these products is Liquid Crystal Display (LCD). It is estimated that newly sold LCD will likely to be found in the waste stream in less than five years (Yang, 2012). Material used in LCD, and interesting from the point of view of recycling process, is indium.

Indium is relatively rare metal. Its electrical and optical properties make it interesting for technology firms. Additionally, indium has a low melting point (430 K) and high boiling point (2353 K) and becomes superconducting at 3.37 K (Alfantazi and Moskalyk, 2003). As ITO it is used in manufacturing of flat-panel screens (about 70% of all indium production). 25% of indium production is applied in LED lighting (Gibson and Hayes, 2011). There is also a growing demand for indium in manufacturing of photovoltaic (PV) systems used in solar panel construction (Pongracz, 2014). Indium is obtained as a result of processing zinc, bauxite, tin and silver ores. South America, Canada, South Korea and Japan are the main producers of primary indium, whereas China is the leading one. Taking into account the consumption, Japan occupies the first place. Because of indium's scarcity it appears to be very important to focus on the secondary source of indium - recycling. The most attractive material seems to be spent ITO (90% In_2O_3, 10% SnO_2, the contents of other elements are less than 20 ppm), which is applied onto LCD glass as thin conductive films (thickness about 150 nm) (Wang, 2009; Silveira et. al, 2015).

Depending on the type and manufacturer, the composition of LCD panels may vary. The most abundant elements in LCD panels are silicon, aluminium and calcium present as SiO_2, Al_2O_3, CaO,

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respectively and constituting the glass of LCD. Besides indium, variety of other metals (Zn, Fe, Cu) can be present in LCD. However, the most desirable metal in terms of recovery is indium, whose content in LCD waste is greater compared to other minerals. The concentration of indium in sphalerite and chalcopyrite is between 10 and 20 mg/kg, while the amount of indium in LCD screens is in the range of 100 – 300 mg In/kg glass (Wang, 2009; Yang, 2012; Zhang et al., 2015). This value can be higher (even to 1400 mg In/kg) when the polymer film attached to the LCD screen is previously removed (Silveira et al., 2015). The recovery process of indium is under investigation by many researchers which have tested different methods. One of the most important processes of indium extraction from LCD is acid leaching. The leaching efficiency was tested against various acid media using HCl, H_2SO_4, HNO_3 and their combinations. By using the mentioned media, it is possible to leach indium efficiently from the ITO. However, the presence of minor metals and their ability to simultaneously move to a solution should be considered during the selection of leaching agents and the development of the strategy for recycling of LCD panels (Alfantazi and Moskalyk, 2003; Zhang et al., 2015).

Apart from hydrometallurgical methods of indium recovery from waste LCD, it is also possible to test the bioleaching method. Until now, this method was only under investigation when considering indium-bearing sphalerite (minerals) (Eisen et al., 2016) or material from the flotation tailings dams (Martin et al. 2015), while analysis of the composition of the waste LCD panels indicates the possibility of testing this raw material for the use of the bioleaching method for the extraction of indium and tin.

There are many works regarding bioleaching of various types of waste containing valuable metals (e.g. electronic waste, spent Ni-Cd batteries, savage sludge, red mud). These wastes are often complex mixtures of different materials and contain basic, precious metals as well as hazardous substances. Key microorganisms which were studied extensively and applied widely both in industrial biomining and laboratory scale are bacteria *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans* (Brandl et al., 2001; Willner 2013; Willner et al., 2015). Bioleaching of indium from sphalerite was conducted, likewise, with acidophilic ferrous iron-oxidising and sulfur-oxidising species (Eisen et al., 2016) or with indigenous microorganisms originating directly from mine-waters adapted to low temperatures (11 °C) (Martin et al., 2015).

In this study, an adapted, mixed culture of *A. ferrooxidans* and *A. thiooxidans* was used in bioleaching experiments. The main aim was to evaluate the potential and efficiency of indium and tin extraction from used LCD panels, in the presence of acidophilic microorganisms.

2. Material and methods

LCD panels used in experiments were received from spent mobile phones of different models and manufacturers (Fig. 1). LCD panels were manually dismantled by separating the individual layers from the specific matrix - the carrier of indium tin oxide (ITO). In the first step separated layer of glass with ITO was crushed, milled and sievied to obtain a mesh size of less than 1.0 mm. Part of layer with ITO was strongly bonded with plastic layer. To avoid loss of ITO material, this part of adhered raw material was milled and sievied (mesh < 0.5 mm), to separate ground ITO material from milled plastic film residue (Fig. 1C). Recovered fraction of ITO was added to the milled material from first step, then mixed and homogenized. The content of indium and tin in the sample was determined by the Microwave Plasma Atomic Emission Spectroscopy (MPAES) (Agilent MP-AES 4200). The composition was 0.1% of In and 0.025% of Sn. The scanning electron microscope (SEM) equipped with a Hitachi S 4200 and microanalysis method (EDS) were carried out to identify the qualitative composition of LCD material during experiment.

Cells of *A. ferrooxidans* and *A. thiooxidans* bacteria were used in the experiments. *A. ferrooxidans* was separated from ferruginous mineral water (Piwniczna-Lomnica, Poland) (Pacholewski and Pacholewska, 2001). *A. thiooxidans* was isolated from the mixed culture obtained from the mine water (the shaft Pech, the locality Smolnik, Eastern Slovakia) (Luptakova et al., 2009) and received from the Institute of Geotechnics of Slovak Academy of Science, Kosice, Slovakia. The microorganisms were incubated at 30 °C in a thermostat, in Erlenmeyer flask containing 9K medium. The Silverman – Lundgren (9K) medium was composed of (g/dm^3) $(NH_4)_2SO_4$-2.0; KCl-0.1; $MgSO_4 \cdot 7H_2O$-0.25; KH_2PO_4-0.5; $FeSO_4 \cdot 7H_2O$-44.2, S^0-10. In order to increase the activity of the cells before the inoculation of samples, bacteria was transferred several times with fresh 9K medium. A mixed culture of *A. ferrooxidans* and *A.*

thiooxidans was initially adapted to be with indium compounds. Adaptation was carried out over 4 weeks, with a dose (≤ 0.1 g) of ground LCD material into medium added every 3 days.

The experiment was carried out in Erlenmeyer flasks containing leaching solution with mixed bacteria at 30 °C in a thermostat. The pulp density was 2.5% (w/v), whereas the mixed strain of bacteria was 10 cm^3. Experiments were carried out in two different leaching media, with initial pH=1.9: a) the 9K medium with S^0 (2 g) and b) solution of H_2SO_4 with S^0 (2 g). The control tests under sterile conditions were conducted in parallel. Regular measurements of pH, the oxidation-reduction potential (ORP) and metals concentration were taken. Experiments were carried out in two series lasting 35 days. To quantify amount of metals dissolved in the leaching media, 5 cm^3 sample was filtered and the filtrate was analysed by the MPAES (Agilent MP-AES 4200).

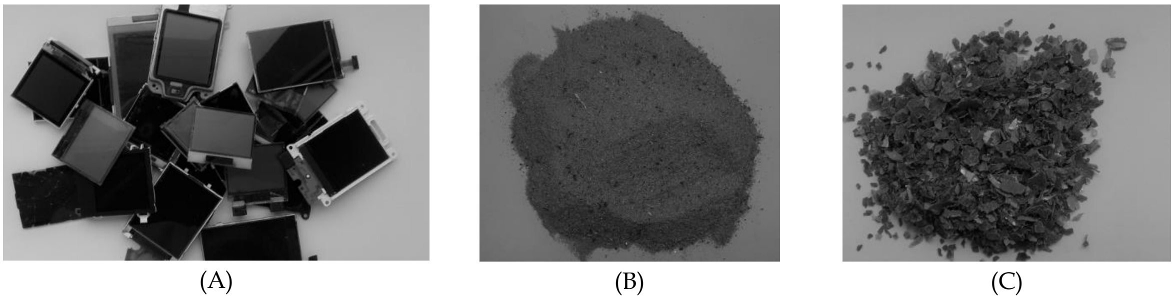
(A) (B) (C)

Fig. 1. Materials used in the tests: (A) used LCD panels, (B) ground material to be tested, (C) milling residue

3. Results and discussion

3.1 pH and ORP effect

Changes in pH and ORP of leaching solutions during application of the mixed culture of *A. ferrooxidans* and *A. thiooxidans* are shown in Fig. 2.

The course of pH changes in biological and chemical leaching solutions is different from each other. Explanation for the effects of pH changes observed in samples containing H_2SO_4 or 9K medium inoculated with bacteria, is a different course of reactions occurring in both systems. In the H_2SO_4 test, chemical leaching process may occur. The persistent low pH is the result of the systematic supply of sulfuric acid to this system with the participation of bacteria that promotes the oxidation of S^0 to H_2SO_4 (which also promotes releasing indium from waste – Fig. 4). In the case of LCD leaching in 9K bacterial medium containing 9 g/dm^3 of Fe^{2+}, the sulfuric acid could be consumed in the first instance by the chemical oxidation of Fe^{2+} to Fe^{3+} (progressive increase of ORP – Fig. 2) and additionally by metal dissolution, which both contributed to acid deficit in this system and likewise increase in pH. Then the formed Fe^{3+} ion could act on the LCD material as an effective oxidant (causing dissolution of indium – Fig. 4). Gradual acidification of 9K medium, inoculated with bacteria, which starts at day 10 is attributable not only to the presence of bacteria (promoting the oxidation of S^0 to H_2SO_4), but also to hydrolysis reactions and precipitation of iron(III) compounds (jarosite) and it explains the effect of self-acidification and decrease of pH (Molaei et al., 2011).

In the control sample with H_2SO_4, pH increase was observed which is probably related to the continuous acid consumption for chemical metal dissolution, and the lack of regeneration of this leaching agent in the presence of bacteria. For the 9K medium, after initial pH rise (day 1 to day 14), there was a decrease in this parameter also associated with the precipitation of iron Fe^{3+} in the form of iron(III) compounds in the presence of oxygen.

The oxidation process of Fe(II) to Fe(III) by *A. ferrooxidans* in biological systems with 9K medium is reflected in the course of ORP variation (Fig. 2). ORP potential increased from 400 mV to 550 mV after 14 days of bioleaching. The ORP value in the 9K control medium was 369 mV over the same time period, and a slight increase was due to the oxidation of Fe(II) spontaneously due to atmospheric oxygen. For control processes conducted with H_2SO_4 ORP values were in the range of 355-375 mV.

Oxidation of ferrous iron in the bioleaching process causes precipitates of various types of jarosite ((K,Na,NH_4,H_2O)-$Fe_3(SO_4)_2(OH)_6$) minerals. The precipitation of jarosite was visually observed (yellowish-brown phase) in the leaching systems with 9K medium, both for biological and control samples. The SEM-EDS solid residue patterns confirmed the presence of jarosites – Fig. 3 and Table 1.

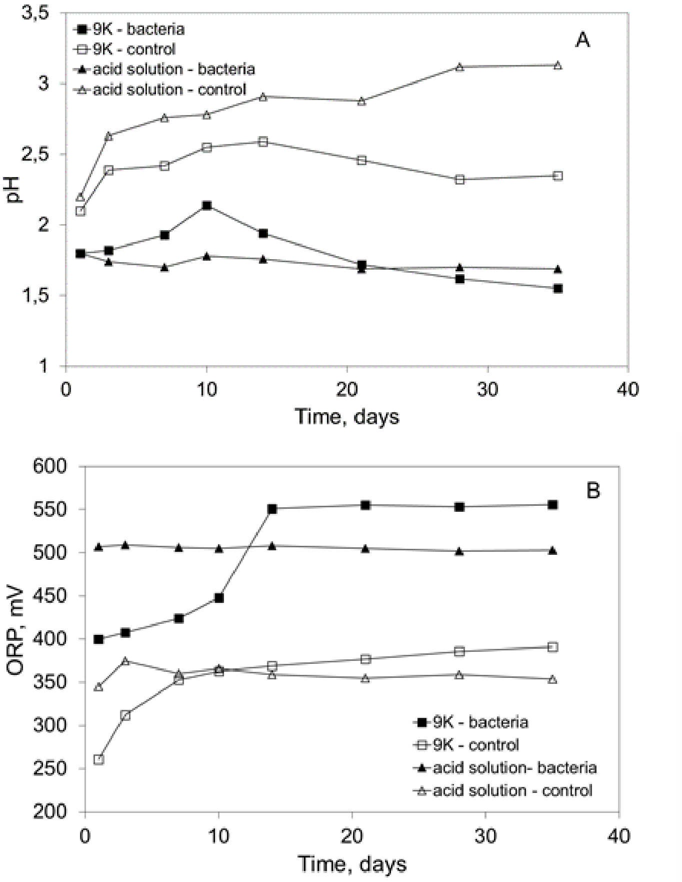

Fig. 2. Changes in pH (A) and ORP (B) in biological and control samples

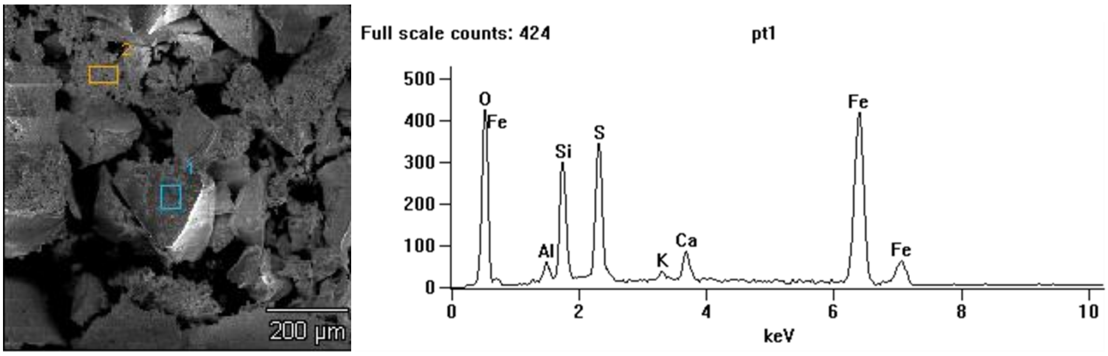

Fig. 3. SEM image and EDS spectra of residue after bioleaching with 9K medium

Table 1. Microanalysis (EDS) of residue after bioleaching with 9K medium (average value from point marked on Fig. 3)

	Weight %							
Analysis, No	O	Al	Si	P	S	K	Ca	Cr	Fe
pt2	50.3	0.6	2.9	0.4	10.6	1.0	0.6	0.1	33.3

Generally, formation of jarosites has a negative effect on the metal leaching process. The degree of release of metals from waste is limited by the precipitation of hardly soluble iron(III) compounds and the small diffusion of reactants and products through the precipitation zone (Jensen and Webb, 1995).

During bioleaching, minor impurities like Cu, Ni, Co, As are dissolved and they form sulfates with mixed bivalent-trivalent metal ions in the leaching solution. Although the article focuses on the bioleaching of indium and tin, the aforementioned issues should be considered in further work on the possibility of metals recycling from LCD. For toxic metals (i.e. As) occurring in LCD, and requiring special treatment, a jarosite may act as an iron-based adsorbent. Apart from the biosorption of arsenic from aqueous solution by *A. ferrooxidans* in the bioleaching process, soluble arsenic might be coprecipitated with Fe(III) and some resorbed by jarosite (Chen et al., 2013). However, for the purpose of determining the role of jarosite present in residues and its effect on the extraction of indium and other minor metals, further investigation is needed.

3.2 Indium and tin extraction efficiency

The efficiency of indium and tin extraction during 35 days of bioleaching in the presence of mixed bacteria of *A. ferrooxidans* and *A. thiooxidans* and in the control test are shown in Fig. 4.

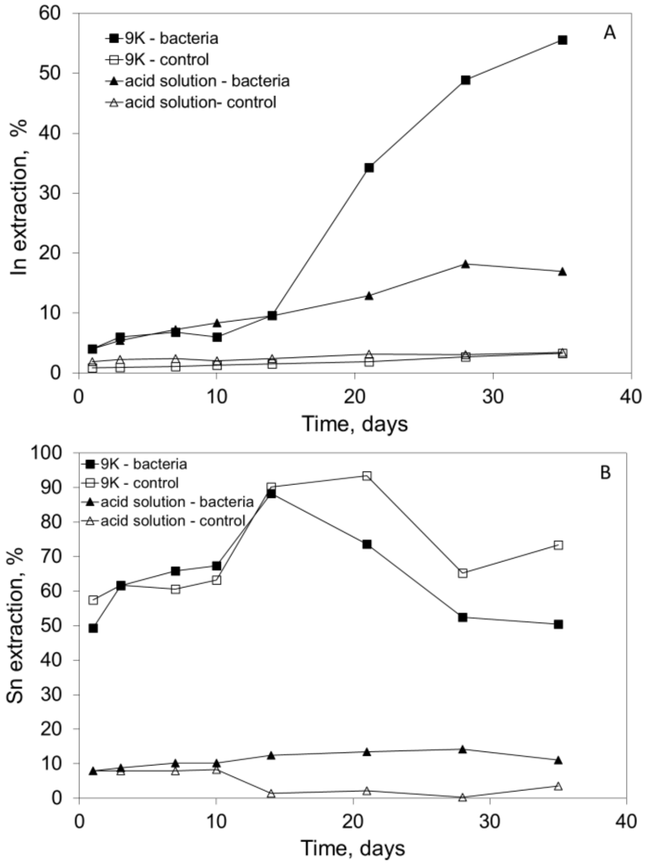

Fig. 4. Leaching of indium (A) and tin (B) by mixed bacteria *A. ferrooxidans* and *A. thiooxidans* in 9K medium, H_2SO_4 solution and in control systems

The leaching experiments conducted in the presence of two media: 9K and H_2SO_4 differed in the extraction of valuable metals. The highest leaching rate of indium was obtained using an inoculated medium of 9K. The degree of indium extraction to the solution initially increased gradually from 4.4% on day 1 to 9.9% on day 14. In the following days there was a noticeable increase in indium concentration in the solution and during 35 days of bioleaching 55.6% of indium could be extracted from LCD panels. Extraction of indium into 9K medium inoculated with bacteria correlates with the course of ORP changes (Fig. 2). The apparent growth of indium content in the solution on day 14 corresponds to a simultaneous increase in ORP value - 551 mV indicating the course of indium oxidation in the biological way with the participation of Fe(III). During the same time 16.9% of indium was recovered for the solution of H_2SO_4 inoculated with bacteria. The chemical leaching experiments resulted in lower recovery of In both for medium 9K and H_2SO_4 (3.4%).

In the case of tin, the leaching curves in the 9K medium solution start at 49.2 and 57.4% extraction of this metal on the first day, for bioleaching and chemical leaching, respectively. The highest degree of tin extraction (90.2%) was recorded on day 14 for the biological system and 93.4% on the 21 day of control leaching. Within days, the concentration of tin in solutions falls to 50.4 and 73.4% of metal extraction rate in the biological and chemical test respectively. Similar observations can be found in previous investigation by Brandl et al. (2001) and Ilyas et al. (2007). They suggest, Sn was not detected in the leachate, rather was speculated to be precipitated as SnO. In the case of ITO compound SnO_2 dissolves in sulfuric acid (produced by bacteria) to give the sulfate $Sn(SO_4)_2$. $Sn(SO_4)_2$ is soluble in water and all aqueous solutions of Sn(IV) tends to hydrolyse to give a precipitate of hydrous tin(IV) oxide (Smith, 1998) or suggested possible tin(II) hydroxide. Therefore, it is a probable mechanism associated with the loss of tin in the solution. Furthermore, since in the solution of H_2SO_4 the level of leaching of Sn reached 14.4% for inoculated systems (in control systems even lower – average 5.4%), it was found that probably the composition of 9K medium, and above all the presence of Fe(II) and Fe(III) ions as a strong oxidant, might intensify the process of tin dissolution in the solutions. Concentration of indium and tin in the leachates are given in Table 2. During 35 days of bioleaching (9K medium) concentration of indium, in the best case, increased from 1 to 13.9 mg/dm^3. While, tin content in the solution raised from 3.08 mg/dm^3 by a maximum value 5.52 mg/dm^3 in the 14 days (Fig. 4), to a final concentration 3.15 mg/dm^3.

Table 2. Composition of leachates after biological and control leaching

Sample	Concentration, mg/dm^3			
	In	In	Sn	Sn
	1st day	35th day	1st day	35th day
9K bacteria	1.00	13.90	3.08	3.15
9K control	0.21	0.82	3.59	4.59
H_2SO_4 bacteria	1.01	4.23	0.50	0.69
H_2SO_4 control	0.47	0.49	0.50	0.22

From the day 14, the increase of indium content in 9K medium with bacteria is accompanied by a decrease in Sn in the solution (Fig. 4). Because the ITO target is a compound of In_2O_3 and SnO_2 with a ratio of 9:1, the key to recover indium from ITO targets is to separate tin from indium (Wang, 2009). From the practical point of view, this dependence should be taken into account when considering the possibility of indium recovery from the 9K medium and indium separation from tin. However, the potentiality of obtaining a higher degree of indium extraction in the extended bioleaching process and verification the correlation between indium and tin in the long run should be investigated.

4. Conclusions

Based on the results of bioleaching studies of used LCD panels by an adapted culture of bacteria, it was found that the extraction of these metals is different in the applied leaching solutions. The highest leaching rate of indium (55.6%) was obtained using a 9K medium inoculated with microorganisms. It suggests that bacteria play a key role, intensifying the dissolution of indium oxide present in ITO. Tin leaching proceeded with efficiency of > 90% both in biological and control systems with 9K medium. It seems that presence of ferrous/ferric ions plays the important role in tin extraction from LCD. The increase in indium recovery rate in the solution is accompanied by a simultaneous decrease in the content of tin. The observed relationship may be useful to separate indium from tin, however, it certainly should be investigated further.

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