COPPER AND LEAD RECOVERY FROM DISCARDED PRINTED CIRCUIT BOARDS BY ELECTROLYSING LEACHED SOLUTION

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ABSTRACT

Results of copper and lead recovery from discarded printing circuit boards (PCB) by acidic dissolution and electrodeposition are presented. A preliminary procedure of the recovery process is proposed with the following steps: disposal of the mounted electrical elements, cleaning, grinding, iron separation for grains screening, metal dissolution, and electrolysis. The composition analysis is performed to define suitable electrochemical parameters for recovery. XRF and AAS techniques are used for preliminary estimation of metal content in leached solution. LSV method is implemented to establish parameters for copper electrodeposition. The product quality is evaluated through XRD analysis. The high recovery efficiencies, 97.61% and 96.59 % for copper (in metallic form) and lead (in dioxide form), respectively, were reached.

Keywords: printing circuit board, copper and lead recovery, dissolution, electrodeposition.

1. INTRODUCTION

Due to the growing consumption of electronic devices and tendency of their shorter end–of–life, the modern world is facing a rapid accumulation of electronic wastes (e–waste). With global discarded amount estimated at 41.8 million tons in 2014 [1, 2] and 4–5 % increase annually [3], e–waste has become an emerging problem for the environment nowadays. However, alongside the negative impact on environmental issues, which are to be solved by appropriate treatment measures, e–waste is considered as a potential reusable resource for different materials, especially metals and their compounds. Yan Xu et al. data for 2014 provide a considerable quantity of iron (16.5 million tons), copper (1.9 million tons), gold (300 tons), and a significant amount of other precious metals such as silver, palladium, etc. with an estimated

value of about US $52 billion [2]. Discarded printing circuit boards (PCB), which has been recovered for years, comprise a substantial amount of valuable metals. Copper and lead are the main metals recovered due to their higher contents in discarded PCB and in e–wastes. Various processes have been applied to extract these metals and have normaly been divided on thermal and non–thermal methods including chemical and/or electrochemical steps [3]. Based on the different deposition potentials, the electrochemical approach has widely been applied to remove various metals from leachates.

According to Vijayaram R. et al. [3], copper could be obtained from PCB waste by non–thermal method through chemical treatment with 8.5 – 92.7 % efficiency, depending on used acid compositions. Nitric acid and its mixture with hydrochloric acid are proven to be the most suitable solvents for copper extraction. Similarly, Andrea M. and Keith S. [4] used nitric acid to dissolve copper and lead. Metallic copper and lead in the lead dioxide form were recovered in the followed step by electrolysis. Kumar M. et al. [5] reported 98.3 % efficiency of copper recovery from leachate under optimum conditions of 800 rpm agitation and 60 ^{o}C using 3 mM/L nitric acid.

Sulfuric acid was also used as leaching agent to extract copper and other metals from e–wastes [6–9]. Due to the unavailability of direct copper transformation into its sulfate salt, oxidizing agents such as hydrogen peroxide are required. With 1 M $H_2SO_4+H_2O_2$ mixture, 82.1 % dissolution efficiency was reached by Nguyen T. T. H. et al. [9]; meanwhile, 88.07 % extraction efficiency was shown for copper by Zhang Z. J. [2]. To improve the copper extraction, aqua regia was added to sulfuric acid and 98 % efficiency was reported by Weit H. M. et al. [6].

Nowadays, selective and efficient recovery of metals from e–waste is considered a challenging issue. In this paper, the results of copper and lead recovery from discarded PCB are provided based on a non–thermal technique using nitric acidic as leaching agent followed by electrodeposition.

2. MATERIALS AND METHODS

2.1. Procedure of PCB recycling process

Discarded PCBs were collected from e–waste slump and all active and passive components were dismantled before transferring to the recycling process.

The scraps were thoroughly rinsed, dried, weighed and fed to ball milling process until powder with maximal grain sizes of 1 mm was achieved. Then, a magnetic device was used to separate iron fillings from the powder. The following steps were conducted as described according to the block diagram in Figure 1. This diagram was designed based on a generally accepted procedure [3, 10] with some modifications: by adding the second electrolysis step for copper deposition and the anodic lead removal. The modifications were introduced assuming that both metals occurred at high content in PCB scraps and copper recovery was preferential as more valuable material.

The grinded powder was dissolved in 6 M nitric acid (1 :1 ratio) at room temperature, followed by filtration to separate leachate from residues containing H_2SnO_3 and other solid substances. The leached solution was then analyzed to reveal elemental contents and underwent first step electrolysis afterwards.

PbO$_2$ and copper were deposited on the anode and cathode respectively as a result of the electrodeposition process. The formed anodic product was then separated, rinsed with distilled water, dried and weighed. Simultaneously, the cathodic copper was purified by repeated electrodeposition after dissolution in 6 M nitric acid. The obtained PbO$_2$ can be transferred into solution using nitric acid to receive Pb2+ solution, from which the second step electrolysis was conducted for metallic lead deposition. However, in this work the final product for lead compound in form of PbO$_2$ was recovered and the last step was not conducted.
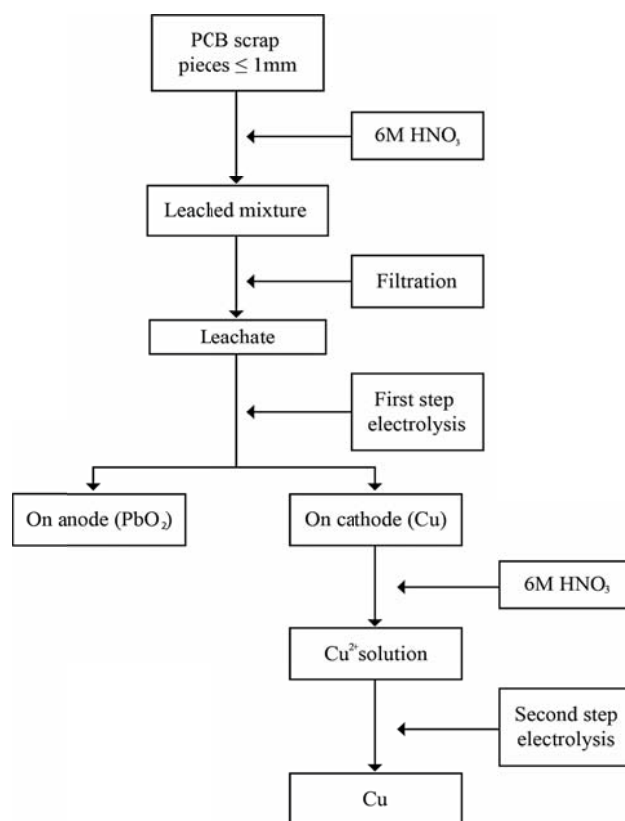

Figure 1. Block diagram of PCB treatment process.

2.2. Electrochemical investigation

A preliminary electrochemical investigation of mixed copper and lead solution was conducted on *Metrohm Autolab PGSTAT 30* potentiostat (The Netherlands), using cyclic voltammetry (CV) technique in the conventional three electrode cell with glassy working electrode, platinium counter electrode, and Ag/AgCl reference electrode. The scanning was performed in a potential window ranging from –0.8 to 0.5 V at 50 mV/s scan rate.

The linear sweep voltammetry (LSV) was also applied to identify reduction and oxidation peaks during electrolysis, followed by further determination of optimal current density for electrolysis. Potential swept at 2 mV/s scan rate and in the range of –0.9 to –0.1 V was conducted for similar cell with Ag/AgCl reference electrode and platinized titanium counter electrode. Surface area of copper working electrode was defined as 0.071 cm^2. The measurements were conducted on the *Biologic MPG2* (France).

Electrodeposition was processed in an electrolyzer with *GW Instek GPR–3510HD* DC power supply at various current densities and solution stirring of 600 rpm. As in LSV case, copper and platinized titanium were selected as cathode and anode respectively. The efficiency of the electrolysis process was determined as a percentage ratio between the experimental data obtained by mass gain method (difference of the electrode mass weighed before and after electrolysis) and the data calculated by Faraday law ($m_{Far.} = \frac{M}{zF} \cdot I\tau$, where $m_{Far.}$ is the calculated mass gain, M is the molar mass, z is the valency number, F is the Faraday constant, I is the current, and τ is the total electrolysis time).

2.3. Elemental analysis and characterization

The leachate collected after PCB powder dissolution in HNO_3 was filtrated for separation from H_2SnO_3 and other residues, followed by elemental analysis using X–ray fluorescence (XRF) and Atomic absorption spectroscopy (AAS) techniques.

The XRF analysis was conducted on *SPECTRO XEPOS XRF* Spectrometer in the Center of Analytical Services and Exprimentation of Hochiminh City (CASE). The AAS determination of Cu and Pb content was performed on AAS spectrophotometer from the Laboratory for Analytical Chemistry (Hochiminh City University of Science). Another volume of leachate was analyzed for iron content using AAS technique to determine the efficiency of the magnetic iron separation.

Phase compositions of the electrodeposited metals were identified by X–ray diffraction method on *Bruker XRD–D8 Advance* in the Center for Innovative Materials and Architectures (INOMAR) of Ho Chi Minh City.

3. RESULTS AND DISCUSSION

3.1. Metal composition of the PCB scrap

Considering the material composition, e–waste can be defined as a mixture of numerous metals and alloys, particularly copper, lead, aluminum, steel, etc. alongside the various types of ceramics and plastics [10]. To clarify the metallic composition, the PCB scrap was dissolved in 6M nitric acid as described in 2.1 and its leachate was analyzed by XRF technique. The analyzed results were calculated as percentage to initial PCB scrap mass and presented in Table 1.

Table 1. Metallic composition of PCB leachate (%).

Element	Si	P	K	Ca	Ti	V	Cr
m (%)	0.0020	0.00023	0.0244	0.0132	< 0.0006	0.00025	0.00021
Element	Mn	Fe	Co	Ni	**Cu**	Zn	As
m (%)	< 0.0011	0.0086	0.00082	< 0.00071	**5.552**	0.05287	< 0.00065
Element	Zr	Mo	Ag	Cd	In	Sn	Sb
m (%)	0.020	0.0110	< 0.0016	< 0.0017	0.0022	0.01349	< 0.0034
Element	Te	Ba	Hg	Tl	Pb	Bi	Sr
m (%)	< 0.0047	0.0260	< 0.00079	< 0.0025	2.596	0.01048	0.00248

Data listed in Table 1 show high content of copper and lead in wasted PCB, where copper occurred in conductive traites and lead is used in tin–lead solder. Tin as a common welding material is previously removed from leachate after filtration in the form of H_2SnO_3 precipitation. Other elements in Table 1 are quantified in minute contents. These data are comparable with data reported by others authors, namely 3.4 to 10% for copper and 0.2 to 1.0 % for lead [10].

Simultaneously, AAS analysis was also applied to determine the exact concentrations of iron, copper and lead in leachate. These values were necessary for calculation of efficiency of electrolysis step. Results presented in Table 2 reflect a preferably higher content of copper and lead compared to iron, which proved an effective method for separation of iron filling. Other elements occurred at unsignificantly low content and were not investigated furthert in this work.

Table 2. Results of leachate's analysis by AAS technique.

Element	Fe	Pb	Cu
Concentration (mg/L)	3.25	5,901.88	12,796.60

The analytical results show a significantly high content of copper and lead in leachate extracted from discarded PCB scraps, the recovery of which is worth considering from a technical and economical point of view.

3.2. Investigation of electrodeposition process

To define the electrodeposition parameters, CV and LSV were applied to PCB leachate as well as to the simulated solutions prepared with copper and lead concentrations in leachate (Table 2).
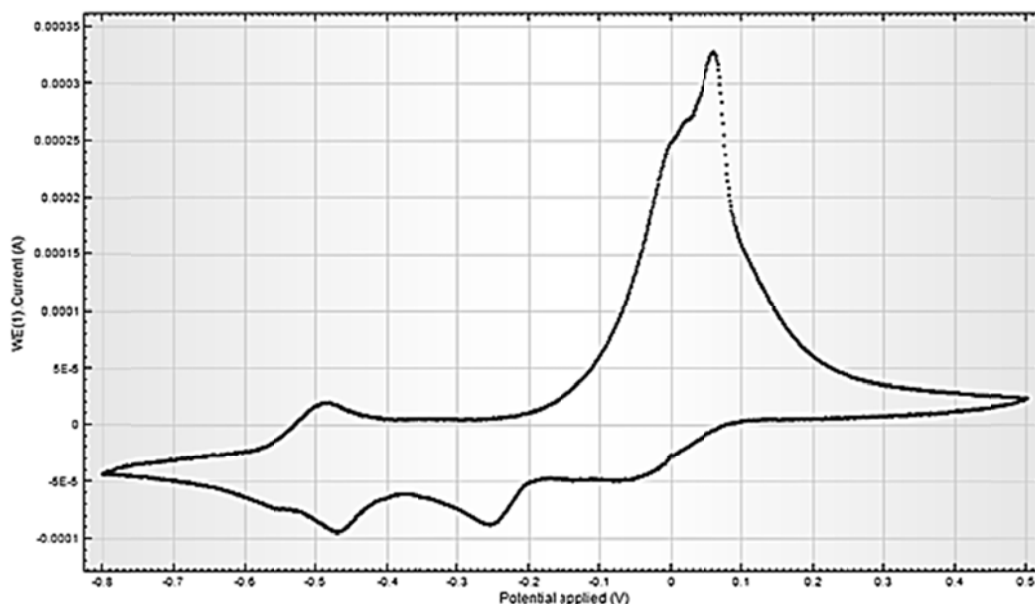

Figure 2. Cyclic voltammogram recorded for mixed copper and lead solution (Ag/AgCl).

The cyclic voltammogram in Figure 2, recorded for the mixed copper and lead solution, clearly shows two distinct peaks at –0.25 V and –0.47 V at cathodic branch, characterizing two

specific reactions of lead and copper cations reduction ($Cu^{2+} + 2e \rightarrow Cu$ and $Pb^{2+} + 2e \rightarrow Pb$). The reversible reactions are revealed for the anodic branch with oxidation processes [11]. These results also show high selectivity of copper reduction if cathodic reaction is conducted in a range around -0.25 V SCE deposition potential.

Theoretically, the standard potential for lead in aqueous solutions is -0.12 V and under high hydrogen overpotential, this metal can easily electrodeposited from strongly acidic solutions with a cathodic efficiency approaching 100 % as revealed on CV scans. These data are obtained only under fast CV scanning (50 mV/s). In practical conditions, due to slow electrolysis in the aerated mixed solutions, metallic copper is cathodically deposited and lead dioxide is anodically formed. According to Velichenko et al. [12], lead dioxide is formed by the following steps: (i) the electron transfer and generation of oxygen–containing nucleus on the electrode surface; (ii) the nucleus interacts with lead ions, forming an oxygen–containing intermediate product of Pb(III) (e.g. $Pb(OH)^{2+}$ type); (iii) the product is oxidized, with the transfer of the second electron, forming Pb(IV) compounds associated with oxygen (e.g. $Pb(OH)_2^{2+}$ type); and (iv) the latter decomposes to form PbO_2.
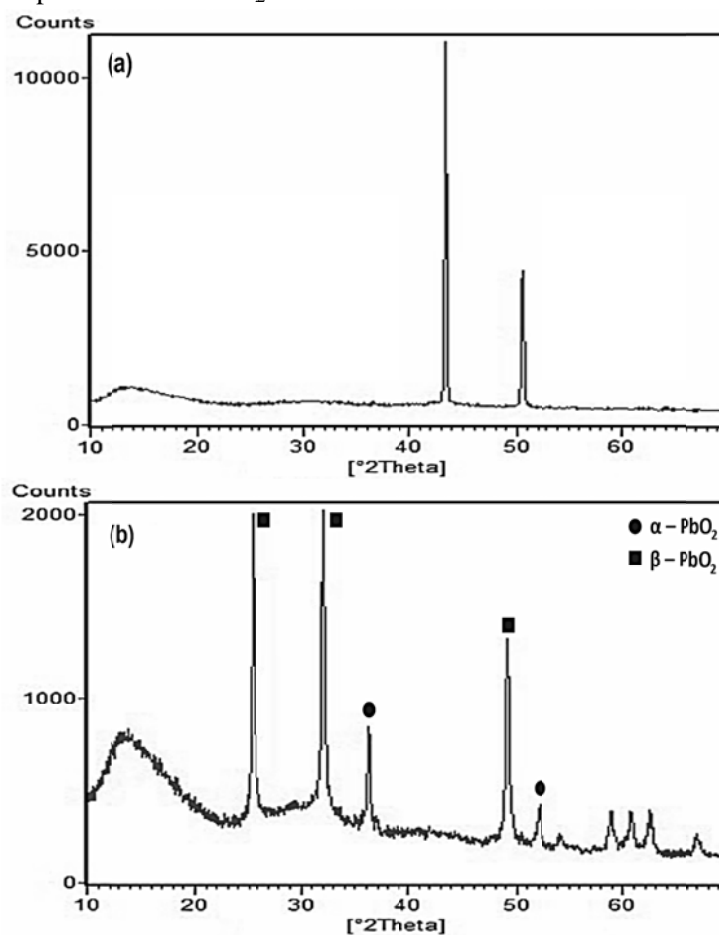

Figure 3. XRD patterns of cathodic (a) and anodic (b) products.

This proposed mechanism was practically confirmed by XRD analysis of products formed on both electrodes after electrolysis. XRD patterns presented in Figure 3 show diffraction peaks at $2\theta = 43.5°$, $50.6°$ for copper (JCPDS card No. 04–0836) in the cathodic product and $25.5°$,

32.0°, and 49.5° for β–PbO$_2$ (JCPDS card No. 14–4192) and 36.5°, 52.0° for α–PbO$_2$ (JCPDS card No. 37–0517) in the anodic product.

To clarify the necessity of the second step of copper cathodic deposition, the products formed after the first step and second step of electrolysis were also examined. The XRD patterns of both products were compared in Figure 4.

Clearly, the XRD patterns for products of two processes were similar at 2θ = 43.5°, 50.6° for copper and the additional second electrolysis step in Figure 1 may not be required for further copper purification.
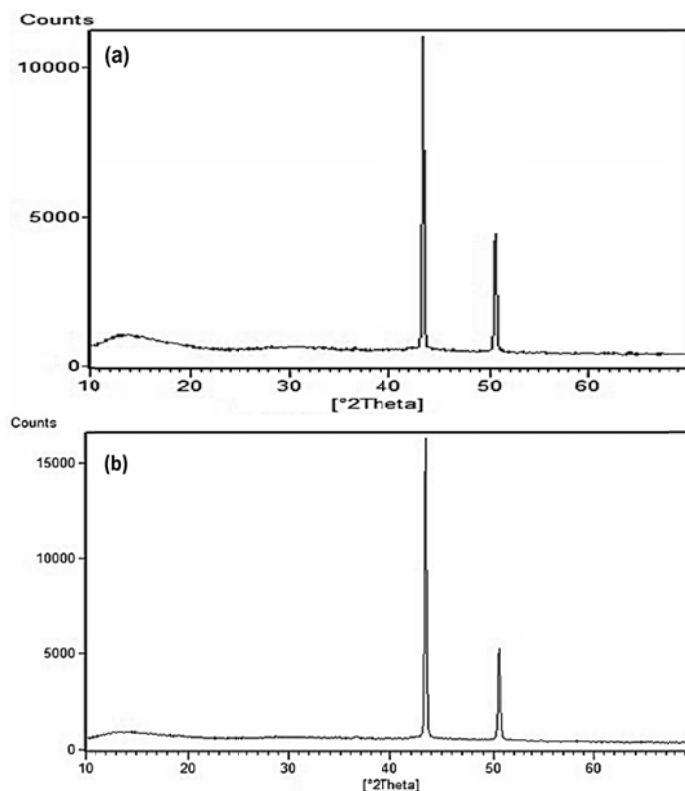

Figure 4. XRD patterns for the products after first (a) and second (b) step of cathodic deposition.

On the basis of these preliminary data, the possibility of electrochemical recovering route of lead and copper was defined: lead can be anodically deposited in the dioxide form and copper is parallely removed by cathodic deposition as pure metal. To identify electrolytic parameters for lead dioxide and metallic copper removal, LSV scanning was conducted for separately prepared lead nitrate, copper nitrate, and for their mixed solutions in a potential window of –0.9 to –0.1 V. The obtained voltammograms are presented in Figure 5.

The turning points of potential sweep scan are consistent at –0.306 V for copper and copper–lead mixed solutions (Figure 5). This potential value is equivalent to 38.34 mA/cm^2 of cathodic current density for both solutions. Similar scans were repeatedly performed and all data of current density were varied in a range of 30 to 40 mA/cm^2 and this range was chosen for further investigation of the electrolytic process.

Selective and effective removal of metals from PCB leachate has been conducted based on the electrolytic parameters defined from above chosen data. The relation between electrolytic efficiencies obtained by conventional weight gain method and the applied current densities are summarized in Table 3 and Table 4. The theoretical copper and lead contents as stated in part 2.2 were calculated by Faraday law.
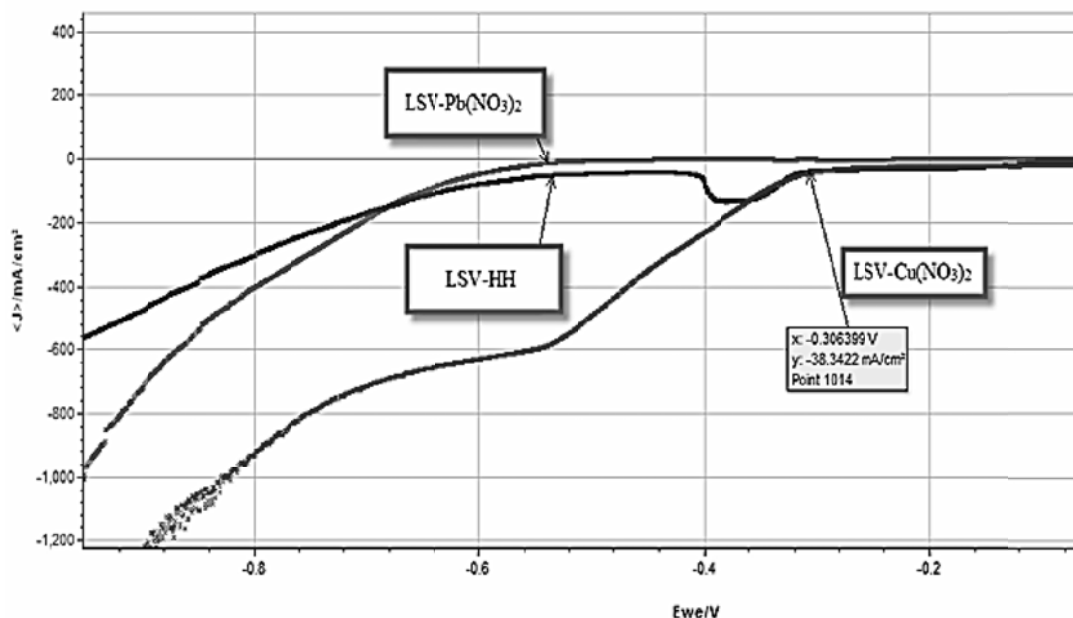

Figure 5. LSV course for the mixed (LSV–HH) and separate copper and lead nitrate solutions.

Table 3. Relation between cathodic current density and copper removal efficiency.

D_c (mA/cm^2)	30	35	40	50
Efficiency (%)	97.61	95.40	91.91	92.43

Table 4. Relation between anodic current density and lead removal efficiency.

D_a (mA/cm^2)	30	35	40	50
Efficiency (%)	82.72	83.80	84.96	96.59

The cathodic deposition efficiencies reported in Table 3, are considerably high above 90 % and tend to decrease with increasing current density in the investigated range from 30 to 50 mA/cm^2. In contrary, lead recovery efficiencies are increased with current densities in same range with a sharp rise is observed at 50 mA/cm^2 current density (Table 4). In practice, the necessary current density can be selected depending on efficiency requirements, considering the values of the product to be recovered on each electrode.

4. CONCLUSIONS

Copper and lead are presented in discarded PCB scraps with substantially higher contents compared to other metal's constituents. Based on these results, copper and lead can be effectively recovered from their acidic leached solutions by electrodeposition.

A preliminary procedure of the recovery process is proposed with the following steps: disposal of the mounted electrical elements, cleaning, grinding, iron separation for grains screening, metal dissolution, and electrolysis.

Copper and lead were recovered using electrochemical technique from discarded PCB scraps. The high recovery efficiencies, 97.61% and 96.59% for copper (in metallic form) and lead (in dioxide form), respectively, were reached.

REFERENCES

1. Baldé C. P., Wang F., Kuehr R., Huisman J. – The global e–waste monitor – 2014, United Nations University, IAS – SCYCLE, Bonn, Germany, 2015.

2. Xu Y., Lia J. H., Liu L. L. – Current status and future perspective of recycling copper by hydrometallurgy from waste printed circuit boards, Procedia Environmental Sciences **31** (2016) 162–170.

3. Vijayaram R., Nesakumar D., Chandramohan K. – Copper extraction from the discarded printed circuit board by leaching, Research Journal of Engineering Sciences **2** (1) (2013) 11–14.

4. Andrea M., Keith S. – Leaching and electrochemical recovery of copper & lead and tin from scrap printed circuit boards, Journal of Chemical Technology and Biotechnology **77** (4) (2002) 449–457.

5. Kumar M., Lee J. C., Kim M. S., Jeong J., Yoo K. – Leaching of metals from waste printed circuit boards (WPCB) using sulfuric acid and nitric acid, Environmental Engineering and Management Journal **13** (10) (2014) 2601–2607.

6. Veit H. M., Bernades A.M., Ferreira J.Z. et al. – Recovery of copper from printed circuit boards scraps by mechanical processing and electrometallurgy, Journal of Hazardous Materials **137** (3) (2006) 1704–1709.

7. Cayumil R., Khanna R., Rajarao R., Mukherjee P. S., Sahajwalla V. – Concentration of precious metals during their recovery from electronic waste, Waste Management **57** (2016) 121–130.

8. Zhang Y. H., Liu S. L., Xie H. H., Zeng X. L., Li. J. H. – Current status on leaching precious metals from waste printed circuit boards, Procedia Environmental Sciences **16** (2012) 560–568.

9. Nguyen T. T. H., Dang T. D., Mai T. T., Hoang T. B. T. – Copper recovery from e–waste via leaching–electrodeposition: the influence of parameters, Journal of Science & Technology **53** (1B) (2015) 355–362.

10. Cui J. R., Zhang L. F. – Metallurgical recovery of metals from electronic waste: A review, Journal of Hazardous Materials **158** (2008) 228 – 256.

11. Tavares E. de F. L., et al. – An alternative method for the simultaneous determination of copper and lead for quality control of sugar cane spirit using a nanotube–based sensor, Journal of Brazilian Chemical Society **23** (9) (2012) 1614–1622.

12. Velichenko A. B., Baranova E. A., Girenko D. V., Amadelli R., Kovalev S. V., Danilov F. I. – Mechanism of electrodeposition of lead dioxide from nitrate solutions, Russian Journal of Electrochemistry **39** (6) (2003) 615–621.