

Article

# Urban Mining and Electrochemistry: Cyclic Voltammetry Study of Acidic Solutions from Electronic Wastes (Printed Circuit Boards) for Recovery of Cu, Zn, and Ni

Ma. Isabel Reyes-Valderrama, Eleazar Salinas-Rodríguez \*, J. Fabian Montiel-Hernández, Isauro Rivera-Landero †, Eduardo Cerecedo-Sáenz, Juan Hernández-Ávila and Alberto Arenas-Flores

Área Académica de Ciencias de la Tierra y Materiales, Universidad Autónoma del Estado de Hidalgo, Carretera Pachuca—Tulancingo km. 4.5, Mineral de la Reforma, Hidalgo C.P. 42184, México; isareyv@hotmail.com (M.I.R.-V.); jfmomt17@hotmail.com (J.F.M.-H.); isaurorivera@yahoo.es (I.R.-L.); mardenjazz@yahoo.com.mx (E.C.-S.); herjuan@uaeh.edu.mx (J.H.-Á.); arenasa@uaeh.edu.mx (A.A.-F.)

\* Correspondence: salinasr@uaeh.edu.mx; Tel.: +52-771-717-2000 (ext. 2280)

† This author died last September, that is why the sign

Academic Editors: Jae-chun Lee, Bong-Gyoo Cho and Kyoungkeun Yoo

Received: 30 November 2016; Accepted: 6 February 2017; Published: date

**Abstract:** We report potentiodynamic studies to characterize copper, nickel and zinc leaching solutions from electronic waste. The metals were leached using oxygen and sulfuric acid (pH = 1.5). As is known, reduction potentials are determined using thermodynamics laws, and metal recovery strategies from electronic waste are usually considered according these thermodynamic values. Pourbaix-type diagrams are not appropriate to plan strategies in electrochemical processing. Therefore, knowledge of electrode potentials for the metal deposit/dissolution process is the basis for the selective recovery planning. For this reason, potentiodynamic studies, specifically cyclic voltammetry, are revealed as a good way to decide the best conditions for the process of electrochemical recovery of metals from electronic waste, which is also cost-efficient and has no interference from strange ions, such as lead, in this case.

**Keywords:** urban mining; leaching solutions; printed circuit boards; electronic waste; electrochemical recovery; cyclic voltammetry

---

## 1. Introduction

The implementation of urban mining in recent years has been due to a concern for the environment and the scarcity of natural resources. This term has no specific definition, because if some authors refer to resources that can be obtained only from landfills, others also include the recycling of construction debris, plastics, glass and scrap metal (electronic waste, in many cases nowadays). The term denotes the systematic reuse of anthropogenic materials, from urban areas [1] and this represents a potential source of material resources that would be available for reuse at the end of the product lifetime.

As new generations of electronic gadgets are developed, the capabilities of these tend to change, and their useful lifetimes get shorter. The above began in the 1980s when the development and production of electronic equipment were promoted to increase its consumption among the population. For some materials, a recycling system cannot be spontaneously implemented with high effectiveness, so is an issue that concerns technology, planning, and economic and environmental regulation. For this reason, at present, due to the increase in the stringency of recycling policies,

countries such as China, Japan, Taiwan, and South Korea, including the European Union and some states of the US, have established norms for the management and regulation of electronic waste (e-waste) [2,3]. According to this, strategies for the implementation of an appropriated recycling system should be based on three points: (i) technical viability; (ii) economic sustainability of the process; and (iii) a high and real level of social support for the program [4]. An important aspect that has led to the production of “e-waste” is the steady rise of the computing industry, so it is estimated that one billion computers have been disposed [5]. The e-waste is mostly discharged with domestic waste without receiving any special treatment; on the other hand, 80% of the waste collected is sent to several poor countries [6]. These electronic wastes are received in the form of “donations” by some organizations in rich countries; however, it is simply a way to get rid of electronic equipment considered obsolete, without breaking the Basel Convention, which regulates these kinds of exportations. Seventy percent of “e-waste” is shipped to China [7], but other countries that also receive significant amounts are India, Pakistan, Vietnam, the Philippines, Malaysia, Nigeria and Ghana; finally, on the American continent, the greatest amount discarded is received by Brazil and Mexico. However, it is difficult to quantify the amount of “e-waste” that is being exported due to the semi-clandestine nature of these operations [8,9].

The recovery of materials from electronic scrap involves the disassembly and destruction of the equipment. According to the estimate by Robinson [9], 20 million tons of “e-waste” are generated annually, and this was confirmed according to the data collected by Morf et al. [8]. Thus, it is possible to calculate the annual amount of certain recoverable elements in the electronic scrap (Table 1).

**Table 1.** Elements present in the environment from the disposal of e-waste [10]

Element	Typical E-Waste Concentration (mg/kg)	Annual Global Emission in E-Waste (Tons)
Cadmium (Cd)	180	3600
Chromium (Cr)	9900	198,000
Copper (Cu)	41,000	820,000
Lead (Pb)	2900	58,000
Mercury (Hg)	0.68	13.6
Nickel (Ni)	10,300	206,000
Tin (Sn)	2400	48,000
Zinc (Zn)	5100	102,000

As is shown in Table 1, we must highlight that 820,000 tons of copper, 206,000 tons of nickel and 102,000 tons of zinc are involved during the generation of the “e-waste”, which contributes to pollution and damages to health; at the same time, this production is becoming an important economic opportunity for metals recovery. Furthermore, gold and silver are also present in the “e-waste”, increasing its importance from an economic point of view.

Gold, silver, copper, nickel and zinc are examples of elements in the “e-waste” [10]. These are basically present in computer components, printed circuits boards (PCBs), cell phones, etc. Specifically, circuit boards from computers have a design consisting of a gold layer deposited on a substrate of a non-noble metal such as nickel, zinc and/or copper, which is also inserted into a polymer base. Obviously, there is a huge potential source of gold in the mentioned metals, which nowadays are partially recovered or disposed in the “e-waste” [2,11]. There are previous studies on the leaching of the “e-waste” that report the dissolution of copper, nickel and zinc, and the subsequent recovery of metallic gold with a purity close to 99% [12,13]. Because of the highly heterogeneous mixture of organic materials with metals and ceramics, the PCBs are particularly hard to recycle [14]. Viewed from the different perspectives of the recycling of PCBs, scientists have developed many and varied methods involving physical and mechanical technology for separation, bio-technology, supercritical fluid technology, microwave treatment and processes of extractive metallurgy (hydro and pyrometallurgy). Despite the existence of these routes, the processing of

“mechanical crushing + hydrometallurgy” is the more predominant technology and the most commonly used, because of the advantages reached in the recycling of PCBs [10,15,16].

In an optimal process, PCBs should be processed in an environmentally sustainable way with the purpose of taking advantage of the treatment of the “e-waste” [14,17]. On the other hand, these kinds of residues could, if possible, be naturally leached and some metal contents can migrate to the water and contaminate important aquifers, which increases the degree of contamination not only by e-waste, but also by the more dangerous contamination of metallic ions. Although some works have been developed to detect metals ions, particularly Cu (II), and to remove them properly by using mesoporous materials, calorimetric detection, and adsorbent composites, among others, and with excellent results, it is necessary to initially remove the possible source of contamination of these types of ions [18–21]. There are certain reviews about progress in the recycling of PCBs made by some researchers [2,17,22–24]; however, some of these reviews deal with too many issues and the depth of these studies, related to the summary and discussion of the use of hydrometallurgy technology, tends to be poor. Every year, the amount of discarded computer equipment around the world increases [25], which triggers the exponential growth of the “e-waste”, including PCBs, so it is necessary to accelerate the research to develop an optimal process for the recovery of the PCBs, which can be environmentally friendly, compatible with hydrometallurgical processes and more cost-efficient, and which involves the use of sulfuric acid and oxygen, in comparison with those implicating the use of nitric acid, hydrochloric acid, peroxides and even aqua regia, as they are potential sources of pollution and health risks [26]. An optimum mechanism for the recovery of metal products is to submit them to the process of acid leaching using oxygen and sulfuric acid (pH 1.5) to dissolve the copper, nickel and zinc, with later gold retrieval [11,12,27].

Year after year, the interest in the development of effective electrochemical methods for elimination and recovery of metallic ions from residual waters has increased because studies have demonstrated the possibility of recovering the metals in a pure state [28,29].

The concentrations of metal ions allowed in the effluents have been reduced dramatically since the government laws have been directed to protect the environment, so regulations on their discharge are becoming more stringent [29]. On the other hand, the conventional technique of hydroxide precipitation allows higher concentrations than those established. Accordingly, there is an increasing interest in taking into account the importance of developing ion-exchange techniques as an alternative, instead of the precipitation of hydroxides [30,31].

Previous works about the electrolytic recovery of copper and other metals describe the recovery of a few ppm of metallic ions with low energetic consumption, operating at a relative high electric current density [32]. Cathodic metal deposition is the principle method that leads to the removal of metal ions ( $\text{Me}^{z+}$ ) from waste waters [33,34].



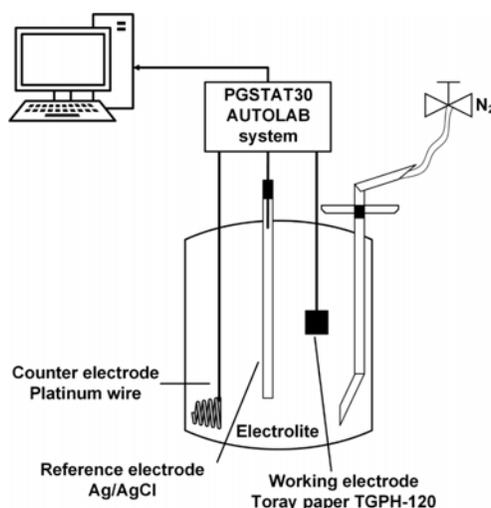
From a thermodynamic point of view, the Nernst equation predicts the individual electro-deposition potential of different metals and their displacement increasing the concentrations, as shown in the Pourbaix diagrams. The strategies to pursue the recovery of the leachate are not perfectly defined with these thermodynamic values. In this regard, it is necessary to perform potentiodynamic studies to characterize the composition of the leachates. The aim of this work is therefore the development of cyclic voltammetry studies with synthetic and real solutions to qualitatively characterize the acid leaching solutions. Through these strategic studies, we try to reach electrochemical recovery for non-noble metals.

## 2. Materials and Methods

The potentiodynamic studies have been carried out using a typical electrochemical cell of three-electrodes: reference, counter and working electrode, as shown in Figure 1. The silver/silver chloride electrode is used as reference, the platinum wire as counter and the Toray paper TGPH–120, (carbonaceous paper from Toray) acquired in Global Proventus, a company located in Monterrey, Mexico, as working electrode, the electrodes configuration was dependent on the way

the experiments were performed. The cyclic voltammetry were performed in 5 mM Cu + 1 mM Ni + 1 mM Zn at a pH 1.5 (sulfuric medium) synthetic solution and leaching solution with sulfuric acid (pH 1.5). In the same way, the cyclic voltammetry were performed in 1 mM Ni + 1 mM Zn at a pH 5 for synthetic solutions and leaching solutions with sulfuric acid (pH 5) without copper. The electrode potential was controlled using a PGSTAT30 AUTOLAB system, from the brand  $\Omega$  Metrohm Autolab B.V., equipment located at the University of Alicante, Spain and used during a research stay at the University Institute of Electrochemistry. All the cyclic voltammetry were carried out at a scan rate  $50 \text{ mV}\cdot\text{s}^{-1}$  and at room temperature. All the solutions were purged with nitrogen for 20 min before the experiments were conducted.

Furthermore, morphological and compositional analysis of the electrodeposited metal on working electrodes, were carried out using Scanning Electron Microscopy (SEM, Hitachi S-3000 N at 20 kV, acquired in the company Hitachi in Spain, Madrid, Spain) and Energy Dispersive Spectrometry of X-rays (EDS, Bruker XFlash 3001, detector acquired joint with SEM Hitachi S-3000 N in the company Hitachi in Spain, Madrid, Spain). The metals were electrodeposited on paper Toray, fixing the working electrode potential at  $-1.6 \text{ V}$  vs. Ag/AgCl during 600 s for each one of the solutions described before, i.e., chronoamperometry at  $-1.6 \text{ V}$  vs. Ag/AgCl during 600 s.



**Figure 1.** Scheme of a three-electrode electrochemical cell.

### 3. Results

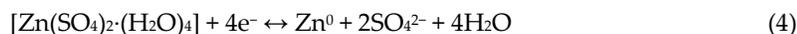
In previous works, the chemical species and the equilibrium potential in the leached solution have been established through thermodynamic studies using Pourbaix-type diagrams [35–37]. For the results concerning Cu, the predominant chemical species is  $\text{CuSO}_4$ , found by carrying out the following reaction:



For Ni, the predominant chemical species is  $\text{NiSO}_4$ , found by carrying out the reaction:



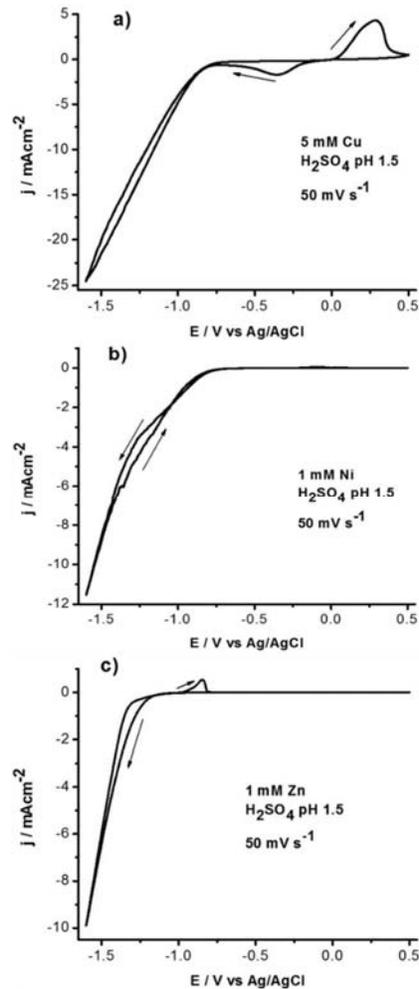
In addition, for Zn, the predominant chemical species is  $[\text{Zn}(\text{SO}_4)_2 \cdot (\text{H}_2\text{O})_4]$ , found by carrying out the reaction:



In the same way, it was possible to observe the influence of the concentration of each metal with respect to the reduction potential. In general, a displacement of the reduction potential for each one was observed. Obviously, thermodynamic studies are fundamental, but the viability of the chemical

processes is obtained by kinetic studies. In this case, cyclic voltammetry in both synthetic and leaching solutions was carried out.

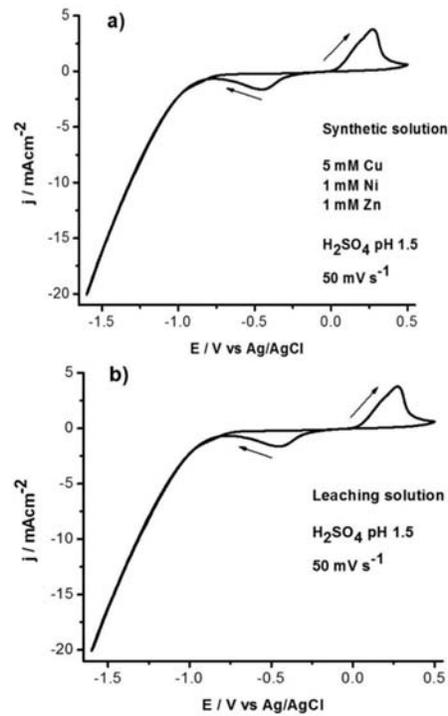
Firstly, cyclic voltammetry was carried out in synthetic solutions of 5 mM Cu, 1 mM Ni and 1 mM Zn, at pH 1.5. In Figure 2a, the cyclic voltammetry for the Cu shows a wave at  $-0.36$  V vs. Ag/AgCl where the deposit of copper starts, and a stripping zone at  $0.25$  V vs. Ag/AgCl where the electrodeposited Cu is dissolved. In Figure 2c, the cyclic voltammetry for Zn shows a little stripping zone at  $-1.0$  V vs. Ag/AgCl. Finally, in Figure 2b, the cyclic voltammetry for Ni does not show a relevant electrochemical process, because the metallic Ni at a pH of 1.5 is not electrodeposited. It is important to notice that all electrodeposited metals are characterized by the existence of stripping zones, and although lead ions were present in the real solutions, they were present in marginal amounts and did not influence the recovery of Cu (II) or Zn (II and Zn (II) in their respective experimental recovery conditions.



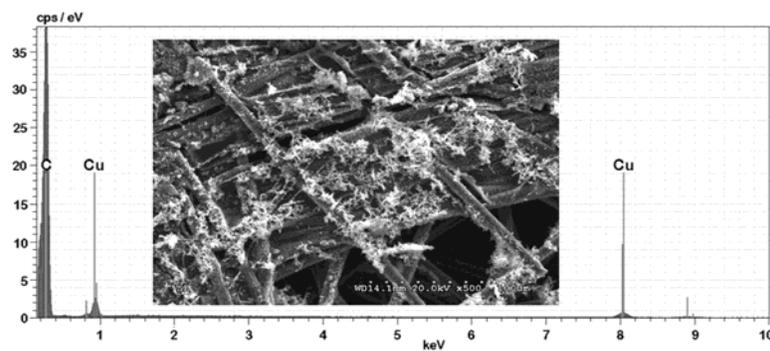
**Figure 2.** Cyclic voltammeteries for: (a) 5 mM of Cu; (b) 1 mM of Ni and; (c) 1 mM of Zn, in  $\text{H}_2\text{SO}_4$ , pH 1.5 solution. Scan rate of  $50 \text{ mV}\cdot\text{s}^{-1}$ .

After studying the behavior of each metal, we carried out cyclic voltammetry in a solution with all the elements together and at the same pH, as shown in Figure 3a. In this case, only the Cu profile is shown. When all the elements are present in the synthetic solution, only the copper electrodeposition appears because the Ni and Zn metals were not electrodeposited in this medium. Similarly, cyclic voltammetry in the leaching solution has the same behavior, as is illustrated in Figure 3b. Both figures are identical, which affirms that we only obtain metallic copper during the electrochemical recovery of solutions of copper, nickel and zinc at pH 1.5, because Zn and Ni are not

electrodeposited under these conditions, without the influence of lead ions. This affirmation is corroborated by SEM and EDS analysis, done on the metal electrodeposited on Toray paper. This electrodeposition was carried out with the fixing of the working electrode potential at  $-1.6$  V vs. Ag/AgCl during 600 s (as shown in Figure 4) on the solution described previously. As is shown, the cyclic voltammetry and the potentiodynamic studies, were a good choice for the qualitative characterization of lixiviate solutions from electronic waste, and the interpretation of the curves obtained is a good way to plan a correct strategy for the electrochemical recovery of the metals involved in these residues.



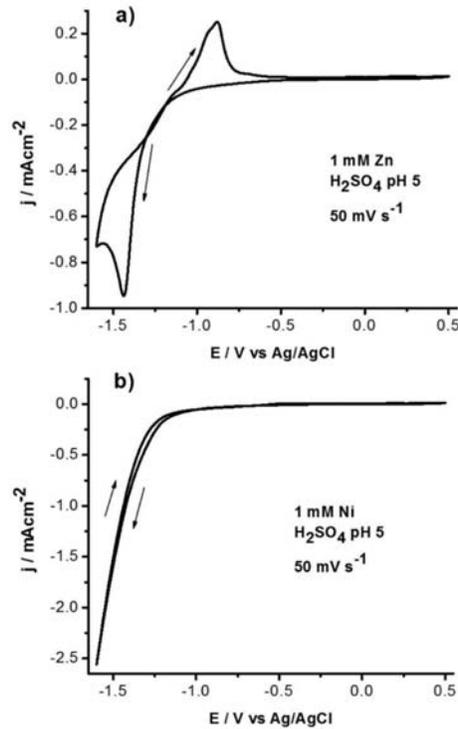
**Figure 3.** Cyclic voltammeteries in: (a)  $\text{H}_2\text{SO}_4$ , pH 1.5 synthetic solution; and (b)  $\text{H}_2\text{SO}_4$ , pH 1.5 leaching solution. Scan rate of  $50 \text{ mV}\cdot\text{s}^{-1}$ .



**Figure 4.** SEM micrograph and EDS analysis of electrodeposition at pH 1.5 on Toray paper carried out with a fixed working electrode potential at  $-1.6$  V vs. Ag/AgCl during 600 s in synthetic and leaching solutions.

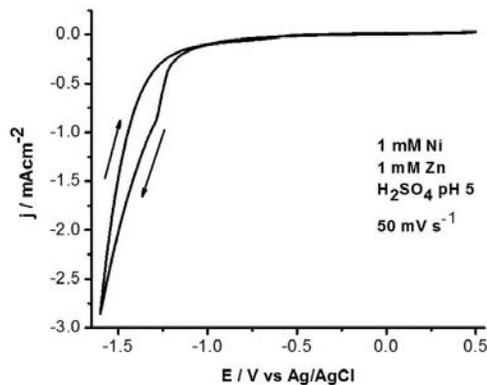
Secondly (with the same idea to characterize solutions involved in the electrochemical recovery of non-precious metals), the pH of the synthetic solutions without copper was raised to pH 1.5 as a possible option to recover Ni and Zn. Likewise, the analysis of the solutions at pH 1.5 in Figure 5a, can reach a Zn deposition at  $-1.4$  V vs. Ag/AgCl, and a stripping zone at  $-1.0$  V vs. Ag/AgCl, which

was carried out by cyclic voltammetry in Zn and Ni solutions at pH 5, respectively. Ag/AgCl can be seen clearly, while the processes of electrodeposited/stripping for Ni are not observed in Figure 5b.

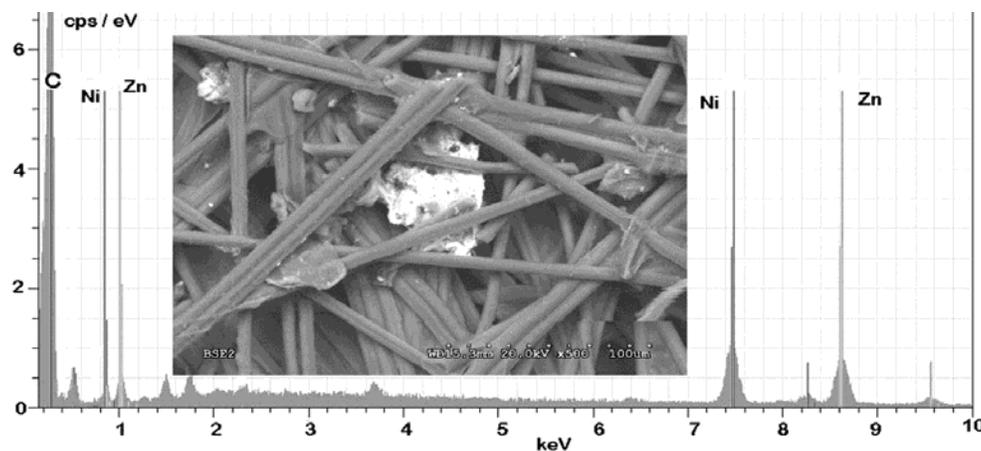


**Figure 5.** Cyclic voltammeteries in: (a) 1 mM Zn and (b) 1 mM Ni, in  $\text{H}_2\text{SO}_4$  solutions. Scan rate  $50 \text{ mV}\cdot\text{s}^{-1}$ .

When the cyclic voltammetry with the two elements together was carried out, stripping processes were not observed due to the corrosion resistance of the Ni-Zn deposit [38], as shown in Figure 6. In this case, SEM micrographs and EDS analysis of the electrodeposition on Toray paper were carried out with fixing the working electrode potential at  $-1.6 \text{ V vs. Ag/AgCl}$  in Zn and Ni solution during 600 s, as is observed in Figure 7. Indeed, the composition of the electrodeposited solids showed only the presence of Ni and Zn, as is shown by the EDS analysis. Clearly, the use of a potentiometer and a simple electrochemical cell could be enough for a qualitative analysis of these metals involved in the leaching process from electronic waste.



**Figure 6.** Cyclic voltammeter of 1 mM Ni and 1 mM Zn in  $\text{H}_2\text{SO}_4$ , pH 5 solution. Scan rate:  $50 \text{ mV}\cdot\text{s}^{-1}$ .



**Figure 7.** SEM micrograph and EDS analysis of electrodeposition at pH 5 on Toray paper carried out with a fixed working electrode potential at  $-1.6$  V vs. Ag/AgCl during 600 s.

#### 4. Conclusions

Generally, thermodynamic studies based on Pourbaix-type diagrams determine the individual electrodeposition potentials of different metals and their displacement, with an increasing concentration in the leaching processes. These values are not appropriate to plan strategies for the electrochemical recovery of metals. In this work, potentiodynamic studies were conducted using cyclic voltammetry studies for synthetic and real leaching solutions from e-waste printed circuit boards. In this sense, the interpretation of the cyclic voltammetry showed the viability of the design of an electrochemical selective recovery of Cu, Zn and Ni for different pHs: the Cu was obtained by electrodeposition at pH 1.5 and the recovery of Ni and Zn was reached when the pH was increased to 5. Furthermore, the previous leaching solution (pH 1.5) can be re-utilized with the adjustment of pH and this, joined with the use of the electrolytic recovery, can make the overall process of leaching and electro-recovery, selective and profitable.

**Acknowledgments:** The authors want to thank the PRODEP-SEP of the Mexico Government for their financial support. Thanks also go to Universidad Autonoma del Estado de Hidalgo, especially to the Materials and Metallurgy Research Center.

**Author Contributions:** I. Rivera and M.I. Reyes conceived and designed the experiments; J.F. Montiel, E. Salinas and J. Hernandez performed and reviewed the experiments; E. Cerecedo and A. Arenas analyzed and helped in characterization of the data. I. Rivera, E. Salinas and J. Hernandez contributed with reagents, materials and tools. Finally, E. Salinas, M.I. Reyes and J. Montiel wrote the paper.

**Conflicts of Interest:** The authors declare no conflict of interest.

#### References

1. Brunner, P.H. Urban mining—A contribution to reindustrializing the city. *J. Ind. Ecol.* **2011**, *15*, 339–341.
2. Cui, J.; Zhang, L. Metallurgical recovery of metals from electronic waste: A review. *J. Hazard. Mater.* **2008**, *158*, 228–256.
3. Rocchetti, L.; Vegliò, F.; Kopacek, B.; Beolchini, F. Environmental impact assessment of hydrometallurgical processes for metal recovery from residues using a portable prototype plant. *Environ. Sci. Technol.* **2013**, *47*, 1581–1588.
4. Kang, H.Y.; Schoenung, J.M. Electronic waste recycling: A review of US infrastructure and technology options. *Resour. Conserv. Recycl.* **2005**, *45*, 368–400.
5. LaDou, J.; Lovegrove, S. Export of electronics waste. *Int. J. Occup. Environ. Health* **2008**, *14*, 1–10.
6. Schmidt, C.W. Unfair trade: E-waste in Africa. *Environ. Health Perspect.* **2006**, *114*, A232–A235.
7. Liu, X.; Tanaka, M.; Matsui, Y. Generation amount prediction and material flow analysis of economic waste: A case study in Beijing, China. *Waste Manag. Res.* **2006**, *24*, 434–445.

8. Morf, L.S.; Tremp, J.; Gloor, R.; Schuppisser, F.; Stengele, M.; Taverna, R. Metals, non-metals and PCB in electrical and electronic waste—Actual levels in Switzerland. *Waste Manag.* **2007**, *27*, 1306–1316.
9. Robinson, B.H. E-waste: An assessment of global production and environmental impacts. *Sci. Total Environ.* **2009**, *408*, 183–191.
10. Xiu, F.R.; Qi, Y.; Zhang, F.S. Co-treatment of waste printed circuit boards and polyvinyl chloride by subcritical water oxidation: Removal of brominated flame retardants and recovery of Cu and Pb. *Chem. Eng. J.* **2014**, *237*, 242–249.
11. Reyes, M.I.; Rivera, I.; Patiño, F.; Flores, M.U.; Reyes, M. Total recovery of gold contained in computer circuit boards. Leaching kinetics of Cu, Zn and Ni. *J. Mex. Chem. Soc.* **2012**, *56*, 144–148.
12. Montiel, J.F.; Reyes, M.I.; Rivera, I.; Patiño, F.; Hernández, J. Caracterización de circuitos impresos vía SEM-EDS y su lixiviación en el sistema O<sub>2</sub>-H<sub>2</sub>SO<sub>4</sub>. *Bol. Soc. Quim. Mex.* **2012**, *6*, 21–23.
13. Montiel, J.F.; Reyes, M.I.; Rivera, I.; Patiño, F.; Hernández, J. Recuperación de Au, Cu, Ni y Zn contenidos en desechos electrónicos. *Bol. Soc. Quim. Mex.* **2013**, *7*, 120.
14. Hall, W.J.; Williams, P.T. Separation and recovery of materials from scrap printed circuit boards. *Resour. Conserv. Recycl.* **2007**, *51*, 691–709.
15. Li, N.; Lu, X.; Zhang, S. A novel reuse method for waste printed circuit boards as catalyst for wastewater bearing pyridine degradation. *Chem. Eng. J.* **2014**, *257*, 253–261.
16. Zhang, Y.; Liu, S.; Xie, H.; Zeng, X.; Li, J. Current status on leaching precious metals from waste printed circuit boards. *Proced. Environ. Sci.* **2012**, *16*, 560–568.
17. Xing, M.; Zhang, F.S. Degradation of brominated epoxy resin and metal recovery from waste printed circuits board through batch sub/supercritical water treatments. *Chem. Eng. J.* **2013**, *219*, 131–136.
18. Awal, M.R. New type mesoporous conjugate material for selective optical copper (II) ions monitoring & removal from polluted waters. *Chem. Eng. J.* **2017**, *307*, 85–94.
19. Awal, M.R.; Hasan, M.M. Colorimetric detection and removal of copper (II) ions from wastewater samples using tailor-made composites adsorbent. *Sens. Actuators B Chem.* **2015**, *2016*, 692–700.
20. Awual, M.R. A novel facial composite adsorbent for enhanced copper (II) detection and removal from wastewater. *Chem. Eng. J.* **2015**, *266*, 368–375.
21. Awal, M.R.; Hasan, M.M.; Khaleque, M.A.; Sheikh, M.C. Treatment of copper (II) containing wastewater by a newly developed ligand based facial conjugate materials. *Chem. Eng. J.* **2016**, *288*, 368–376.
22. Liu, W.Q.; Shang, T.M.; Lei, W.N.; Zhou, Q.F. Progress in the study of recycling and innocuous treatment of waste printed circuit boards. *Huanjing Kexue yu Jishu.* **2011**, *34*, 48–54.
23. Ningtao, Y.; Zhanxu, T.; Fahui, W. The Methods for Recycling of Waste Printed Circuits Boards. *China Resour. Compr. Util.* **2011**, *7*, 024.
24. Yao, Y.Q.; Xu, X.P.; Liu, Y.; Qiu, X.Y. Review on the comprehensive recovery technologies of waste printed circuits boards. *Mater. Res. Appl.* **2011**, *5*, 17–20.
25. Hadi, P.; Ning, C.; Ouyang, W.; Lin, C.S.K.; Hui, C.W.; McKay, G. Conversion of an aluminosilicate-based waste material to high-value efficient adsorbent. *Chem. Eng. J.* **2014**, *256*, 415–420.
26. Habbache, N.; Alane, N.; Djerad, S.; Tifouti, L. Leaching of copper oxide with different acid solutions. *Chem. Eng. J.* **2009**, *152*, 503–508.
27. Kim, E.Y.; Kim, M.S.; Lee, J.C.; Pandey, B.D. Selective recovery of gold from waste mobile phone PCBs by hydrometallurgical process. *J. Hazard. Mater.* **2011**, *198*, 206–215.
28. Kaminari, N.; Schultz, D.; Ponte, M.; Ponte, H.; Marino, C.; Neto, A. Heavy metals recovery from industrial wastewater using Taguchi method. *Chem. Eng. J.* **2007**, *126*, 139–146.
29. Lapique, F.; Storck, A.; Wragg, A.A. *Electrochemical Engineering and Energy*; Plenum Press: New York, NY, USA, 2008; Volume 1.
30. Kammel, R.; Lieber, H.W. Possibilities of treatment electroplating effluents without sludge formation. Pt. 3. metal recovery instead of sludge disposal. *Galvanotechnik* **1977**, *68*, 413–418.
31. Kreysa, G. Festbettelektrolyse-ein Verfahren zur Reinigung metaahaltiger Abwässer. *Chem. Ing. Tech.* **1978**, *50*, 332–337.
32. Scott, K. Metal recovery using a moving-bed electrode. *J. Appl. Electrochem.* **1981**, *11*, 339–346.
33. Gao, J.; Liu, F.; Ling, P.; Lei, J.; Li, L.; Li, C.; Li, A. High efficient removal of Cu(II) by a chelating resin from strong acidic solutions: Complex formation and DFT certification. *Chem. Eng. J.* **2013**, *222*, 240–247.

34. Wong, E.T.; Chan, K.H.; Idris, A. Kinetic and equilibrium investigation of Cu (II) removal by Co(II)-doped iron oxide nanoparticle-immobilized in PVA-alginate recyclable adsorbent under dark and photo condition. *Chem. Eng. J.* **2015**, *268*, 311–324.
35. Espinoza, E.; Escudero, R.; Tavera, F.J. Waste water treatment by precipitating copper, lead and nickel species. *Res. J. Recent Sci.* **2012**, *1*, 1–6.
36. Granados, M.N.; Huizar, L.H.M.; Rios-Reyes, C.H. Electrochemical study about zinc electrodeposition onto GCE and HOPG substrates. *Quím. Nova* **2011**, *34*, 439–443.
37. Montiel, J.H.; Reyes, M.I.; Rivera, I.; Rios-Reyes, C.; Rodríguez, V.; Patiño, F.; Reyes-Cruz, V. Thermodynamic study of leached metals (Cu, Zn and Ni) from waste printed circuits by electrochemical method. *Adv. Mat. Res.* **2014**, *1*, 86–89.
38. Hadi, P.; Barford, J.; McKay, G. Synergistic effect in the simultaneous removal of binary cobalt-nickel heavy metals from effluents by a novel e-waste-derived material. *Chem. Eng. J.* **2013**, *228*, 140–114.



© 2017 by the authors; licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).