

EXTRACTION OF COPPER FROM LEACH LIQUOR OF METALLIC COMPONENT IN DISCARDED CELL PHONE BY CYANEX[®]272

ALAFARA A. BABA^{1,*}, DOYINSOLA G. SOSANYA¹, FOLAHAN A.
ADEKOLA¹, ABDUL G. F. ALABI², ADENIYI S. AREMU³, SEYI E. ADEBOYE⁴

¹Department of Industrial Chemistry, University of Ilorin, P.M.B. 1515, Ilorin-240003, Nigeria

²Department of Material Science and Engineering, Kwara State University,
P.M.B. 1530, Malete, Nigeria

³Department of Water Resources & Environmental Engineering, University of Ilorin, Nigeria

⁴National Biotechnology Development Agency (NABDA), P.M.B. 5112, Wuse, Abuja- Nigeria

*Corresponding Author: alafara@unilorin.edu.ng

Abstract

Discarded cell phones contribute significantly to the amount of electronic waste generation whilst some of its components are toxic and recoverable. Also, due to the increasing demand for Cu(II) in building/construction, electrical and as chemical tool in freshwater, it is imperative to develop low cost and eco-friendly technique as a substitute for the conventional treatments such as reduction-roasting route at elevated temperatures. In the present study, the hydrometallurgical operations involving leaching, solvent extraction and precipitation for the recovery of Cu(II) by Cyanex[®]272 in kerosene was examined. Various parameters affecting the extraction of Cu(II) such as pH, extractant concentration and phase ratio were optimized. At optimal conditions, about 96.3 % Cu(II) was extracted into the organic phase by 0.2 mol/L Cyanex[®]272 at equilibrium pH 5.0 and aqueous to organic phase ratio 1:1. The stripping of the loaded organic was carried out by 0.1 mol/L HCl solution and stripping efficiency of 98 % was obtained. By McCabe Thiele diagram, four stages are required for complete extraction of Cu(II).

Keywords: Discarded cell phone, Cu(II), Acid leaching, Solvent extraction, Cyanex[®]272.

1. Introduction

Electrical and Electronics Equipment (EEE) such as various audio and video players, computers, and cell phones, have generally made life easy and

convenient because of their effectiveness and efficiency. Rapid economic growth, urbanization and demand for EEE have made the production one of the fastest growing manufacturing activities across the globe [1]. The intensifying “market penetration” in developing countries, increasing “replacement market” in developed countries and “high obsolescence rate” of EEE have made EEE waste prolific worldwide [2]. In developed countries, it accounts for 2% of the total solid waste while in developing countries, it accounts for 0.01% to 1% of the total municipal solid waste generation [3]. An estimated 20 to 50 million tons of e-waste containing lead, cadmium, mercury and other hazardous substances are generated annually worldwide [4] and these wastes have far reaching environmental, economic, and health implications.

Consequently, recycling rates for metals are growing in many developed countries, as cost for safe disposal of hazardous material is quite high due to the amount of waste produced and the limited storage capacity of landfills and/or waste dumpsites [5, 6]. Since developing countries like Nigeria are not economically buoyant of carrying out concurrent waste disposal standard practice, it is pertinent to work around recycling activities using discarded cell phone.

A cell phone consists of different components – a circuit board, a liquid crystal display (LCD), and a rechargeable battery. In general, the components of a cell phone are metals, plastics, ceramics and trace materials. However about 90 % of the materials within a cell phone including metals can be recycled [7]. Metals play an important part in modern societies and have historically been linked with industrial development and improved living standards. Society can draw on metal resources from Earth’s crust as well as from metal discarded after use in the economy [8]. The circuit boards of a mobile phone consist of Cu(II), gold, nickel, zinc, beryllium, tantalum and other metals. Cu(II) and its compounds represent 15% of the weight of a typical circuit board. The world uses more than 15 million tonnes of Cu(II) in building, construction and electrical applications as well as in all aspects of infrastructure and technology [9].

Considering the aforementioned applications of Cu(II), extraction of the metal by recycling of waste mobile phone is required for both environmental protection and resource conservation [10]. To date, both pyrometallurgical and hydrometallurgical techniques are currently employed to recover metal from ores and spent materials. The conventional method involves the roast-leach-electrowining process. The roasting step produces sulphur dioxide, and as the policy on discharge of SO₂ becomes stricter, hydrometallurgical routes involving leaching, solvent extraction, precipitation and cementation purification operations often avoid SO₂ production become more attractive, economical and environmentally suitable [11,12]. Thus, the need for developing an eco-friendly technique for the extraction of Cu(II) from discarded cell phone leach liquor by Cyanex[®]272 in chloride medium is a worthwhile venture in the waste-to-wealth campaigns for economic sustainability and development. It is pertinent to note that metal separations by hydrometallurgical options are characterized by low energy consumption and higher metal selectivity [12-14]. Therefore, the aim of this study is to assess the potential of Cyanex[®]272 in the extraction of Cu(II) from metallic component of discarded cell phone.

2. Methodology

2.1. Material and methods

The discarded cell phone sample was collected from a cell phone repairer shop at Computer Village, Ikeja, Lagos, Nigeria. After dismantling by hammer mill followed by separation of the plastic-like types from the metal containing parts, the metal-like parts were treated hydrometallurgically [5,12]. Prior to treatment, the metal product after dismantling was reduced to powder by grinding using acetone-rinsed mortar and pestle and sieved into three particle sizes (0.03mm, 0.06mm and 0.09mm). Considering the particle surface area, the smallest size (0.03mm) was used for all experiments in this study, viz-a-viz the chemical analysis/and material purity by X-ray fluorescence (XRF) and X-ray diffraction (XRD) respectively. The aqueous metal analysis was also carried out by ALPHA-4 atomic absorption spectrometer (AAS).

The leaching solution consisted of hydrochloric acid (HCl, BDH product) at different concentrations of 0.1 mol/L – 8.0 mol/L. The Cyanex[®]272 extractant (85wt % purity) was supplied by Cytec Inc., France. The kerosene used as diluent obtained from Rajrab Filling Station, Ilorin, Nigeria was re-distilled prior to use. Other chromogenic reagents used including potassium hydroxide (KOH) are of analytical reagent grade.

2.2. Leaching procedure

Leaching experiments were carried out to evaluate the leaching behavior of metals of interest under different acid concentration (0.1 mol/L – 8.0 mol/L) at a fixed temperature of 80°C for 2 hours. 10 g/L of the sieved cell phone sample was put into 100 ml of 0.1 mol/L HCl solution in a reactor placed on 78 HW-1 hot plate equipped with a stirrer. The same procedure was repeated for other concentrations of HCl (0.5, 1.0, 2.0, 4.0 and 8.0 mol/L). At the end of the leaching process, the mixture was allowed to cool and then filtered through a Whatmann filter paper cat no. 1001110 [5, 12, 15]. The filtrate was examined by AAS analysis to determine the metals present at various HCl concentrations.

2.3. Solvent extraction procedure

The leach liquor obtained on leaching 10 g/L cell phone sample by 4 mol/L HCl solution at 80°C for 2 hours was used for solvent extraction experiments. Extraction by Cyanex[®]272 in kerosene and scrubbing batch experiments were carried out by contacting 25 mL each of aqueous and organic phases in a 150 mL cylindrical glass reactor provided with magnetic agitation for 25 minutes. This time was sufficient to reach equilibrium as verified in preliminary investigations [12]. Experiments were performed at 25±2°C and the pH was constantly adjusted to the appropriate pH value through the addition of 1 mol/L KOH or HCl (37%) solutions. After phase separation, the metal content in the aqueous phase was determined by AAS. The influence of extractant concentration, pH and phase ratio was evaluated [6, 16]. Prior to total Cu(II) extraction, metals such as Mn, Fe, Zn, Co and Pb constituting impurities in the leach liquor were appropriately removed using combinations of

cementation and precipitation methods [12,17]. The initial/purified total Cu(II) solution used for solvent extraction studies was 1187 mg/L.

3. Results and Discussion

3.1. Characterization studies

The composition of the metallic component in discarded cell phone by XRF gave Cu (65.64%), Pb (16.54%), Zn (8.65%), Mn (4.99%) and Fe (3.93%). The Co and Cd occur from low to trace levels (< 0.1%). It is of importance to note the high level of toxic metals such as Pb and Cu and hence the proposal to develop an eco-friendly route for extraction and separation of Cu from other impurities. Evidently, XRD with the Joint Committee on Powder Diffraction Standard (JCPDS) file number showed that the concentrate contained Tenorite (CuO : 05-0661) and Massicot (PbO : 38-1477). Other compounds detected include Iron zinc compounds of the form (FeZn₅ : 32-0478; Fe₁₁Zn₄₀ : 34-1314) and Hausmannite (Mn₃O₄ : 24-0734).

3.2. Leaching studies

Effect of HCl concentrations

The result of effect of HCl concentrations on discarded cell phone sample was examined. The concentration was varied from 0.1- 8 mol/L at a constant temperature of 80 °C for a period of 120 minutes. The result of the AAS analysis for the leach liquor obtained at the aforementioned conditions is presented in Table 1.

Table 1. Metal composition of the leach liquor by AAS.

[HCl], mol/L	Mn, mg/L	Fe, mg/L	Cu, mg/L	Zn, mg/L	Co, mg/L	Cd, mg/L	Pb, mg/L
0.1	5.72	16.90	119.00	10.05	29.69	0.0017	17.45
0.5	21.20	66.00	133.80	52.50	2.61	0.0050	99.30
1.0	67.40	84.00	251.40	62.50	3.57	0.031	445.00
2.0	87.80	69.00	405.00	102.50	3.77	0.027	277.50
4.0	90.30	71.00	1187.00	156.50	4.40	0.014	299.00
8.0	83.10	66.00	1022.00	128.30	3.45	0.009	281.00

The result of the analysis of the leachate from Table 1 shows that Copper is the predominant metal present in the discarded cell phone sample followed by lead and zinc, i.e Cu>Pb>Zn. Other metal such as Mn, Fe, Co and Cd were recorded at low to trace levels. The leach liquor of the discarded cell phone sample at 4 mol/L gave the highest metal ion and this was used for further work in the study, since with further increase in acid concentration led to decrease in metal ion concentrations due to possible precipitation phenomena [12, 18].

3.3. Extraction studies on Cu(II)

3.3.1. Effect of extractant concentration

To study the effect of extractant concentration on the extraction of Cu(II), the concentration of Cyanex[®] 272 in kerosene was varied in the range 0.05 to 0.25 mol/L. The experimental results are shown in Fig. 1.

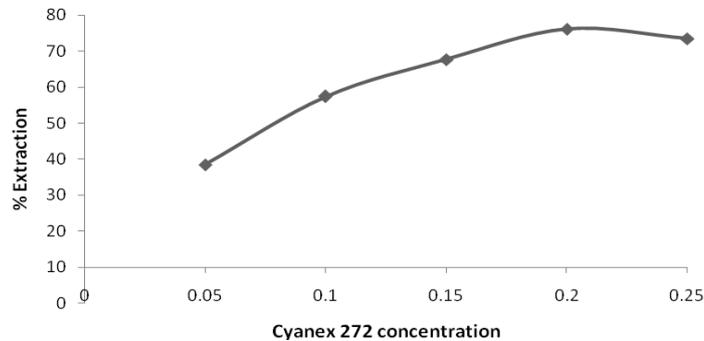


Fig. 1. Effect of Cyanex 272 Concentration on the Extraction of Cu(II)
 $[\text{Cu}^{2+}]_{\text{aq}}=1187 \text{ mg/L}$, phase ratio= 1:1, contact time =25 minutes,
 Temperature = $25\pm 2^\circ\text{C}$, pH = 2.1.

It is evident from Fig. 1 that Cu(II) extraction increases with increasing Cyanex 272 concentration. With increasing extractant concentration, Cu^{2+} extraction increases from 38.44% to 76.14% by 0.05 mol/L to 0.2 mol/L Cyanex in kerosene, but apparently decreases above 0.2 mol/L. Hence, 0.2 mol/L Cyanex 272 in kerosene gave the highest extraction yield and was kept for subsequent use in this study.

In order to establish the number of moles of Cyanex 272 extractant participating in the extraction system, the plots of the distribution ratio, D (the ratio of the metal concentration of organic to the aqueous phase) against the log of Cyanex 272 concentration was made as shown in Fig. 2. It was observed that a slope of 1.1~1(one) was obtained; indicating the association of 1 mole of Cyanex 272 participated in the extraction process to form Cu(II) complex in the organic phase.

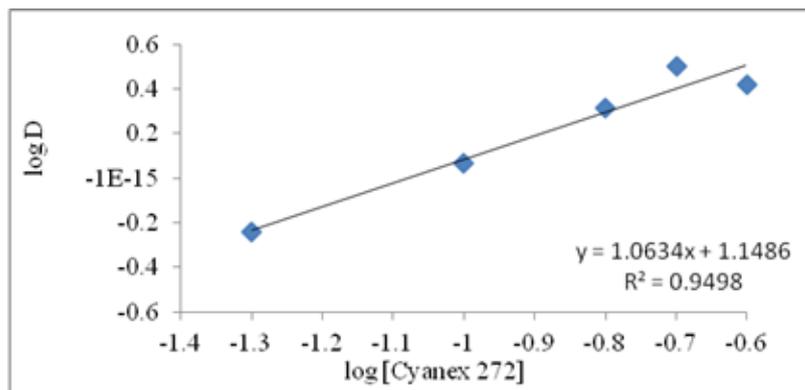


Fig. 2. Effect of Cyanex 272 concentration on Distribution ratio of Cu(II).

3.3.2. Influence of pH

The extraction of Cu(II) was studied over the equilibrium pH ranges from 1 to 6 with equal volumes of aqueous Cu(II) phase and organic phase containing 0.2 mol/L Cyanex 272 in kerosene at $25 \pm 2^\circ\text{C}$. The results are presented in Fig. 3. It was observed that the percentage extraction of Cu(II) increase with increasing equilibrium pH of the aqueous phase. A slight decrease was however noticed at $\text{pH} > 5.0$ resulting from the inability of Cu(II) to be extracted at that pH by Cyanex 272 [5,19].

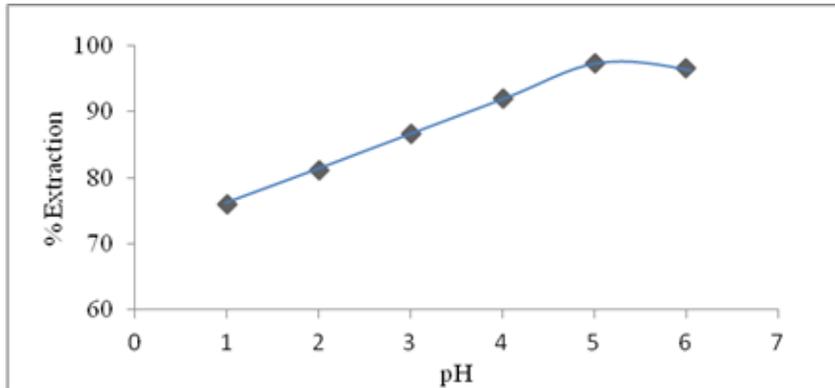


Fig. 3. Effect of pH on Extraction of Cu(II) by 0.2 mol/L Cyanex 272 in kerosene.
 Conditions: $[\text{Cu}^{2+}]_{\text{aq}} = 1187\text{mg/L}$, phase ratio= 1:1, Temperature = $25 \pm 2^\circ\text{C}$.

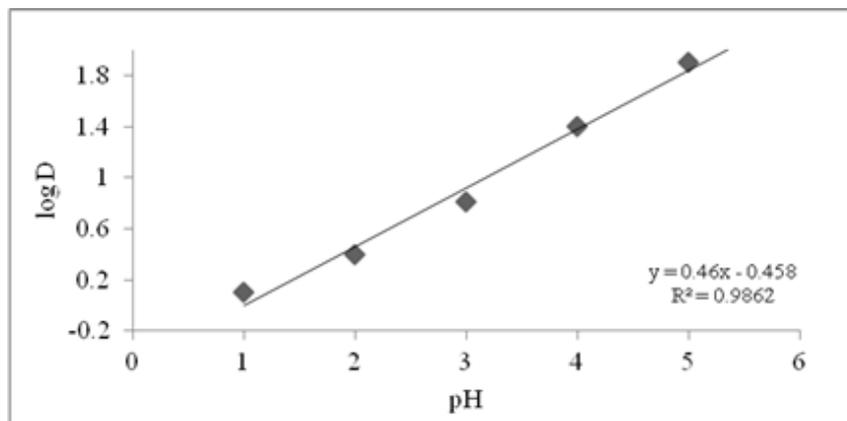
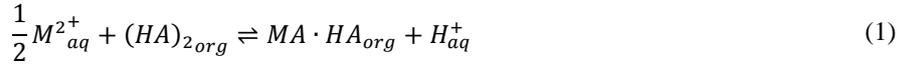


Fig. 4. Effect of pH on Distribution ratio of Cu(II) extraction.

As seen from Fig. 4, the plots of $\log D$ against the equilibrium pH gave a straight line with a slope of 0.46 (~ 0.5) indicating the exchange of $\frac{1}{2}$ mole of H^+ ion with 1 mole of the Cu(II) ion in the extraction process is apparently possible. Considering the results of the effects of extractant concentration and pH of the aqueous media, it is

important to note that acidic extractant such as Cyanex 272 often exists as a dimer [12,20]. Consequently, extraction of metal M^{2+} including Cu^{2+} by Cyanex 272 of the form HA can be expressed by the following stoichiometry:



The equilibrium constant K_{ex} is given by

$$K_{ex} = \frac{[MA \cdot HA][H^+]}{[M^{2+}][(HA)_2]} \quad (2)$$

Rewriting equation (2) and taking \log of both sides

$$\log D = \log K_{ex} + \log[(HA)_2] + pH \quad (3)$$

where

$$K_{ex} = \frac{[MA \cdot HA][H^+]}{[M^{2+}][(HA)_2]} \quad (4)$$

The slope analysis confirms the extraction equilibrium in Eq. (1).

3.3.3. Effect of phase ratio

The effect of organic to aqueous (O/A) ratio on the extraction of Cu(II) was examined at equilibrium pH 5 by 0.2 mol/L Cyanex 272 in kerosene at $25 \pm 2^\circ\text{C}$. The extraction of Cu(II) is apparently equal on varying the volume phase ratio of organic to aqueous phases (O/A = 1:1, 2:1 and 1:2). The results of 1:1, 2:1 and 1:2 phase ratios gave 97.1, 98.3 and 96.6%, respectively. Thus, in this study, the use of 1:1 vol/vol (O/A) mixture was preferable due to ease of separation and economic considerations.

The number of the counter-current stages required for complete metal extraction was calculated by the McCabe-Thiele diagram constructed by standard procedures [20, 22]. In constructing this diagram, the extraction isotherm which represents the relation between Cu(II) concentration in raffinate and its concentration in the organic phase was first drawn. A vertical line is then drawn from the concentration of Cu(II) in the feed solution on the x-axis. The operating line was then inserted, the slope of which is equal to the phase ratio (aqueous : organic = 1:1) [21, 22]. Thus, from Fig. 5, it was observed that the extraction isotherm for Cu(II) indicates that a total of four stages are required for complete extraction.

3.3.4. Stripping investigation

The stripping investigation of Cu(II) from loaded Cyanex 272 extractant was carried out by contacting the organic phase with 0.1 mol/L HCl solution. The result of the stripping studies allows the possible recovery of $\approx 98\%$ total Cu(II) from the Cu-metal complex by 0.1 mol/L HCl solution. The stripped/pure Cu(II)

obtained could be further recovered as salts by evaporation-crystallization or metal cathodes powder through electrowining.

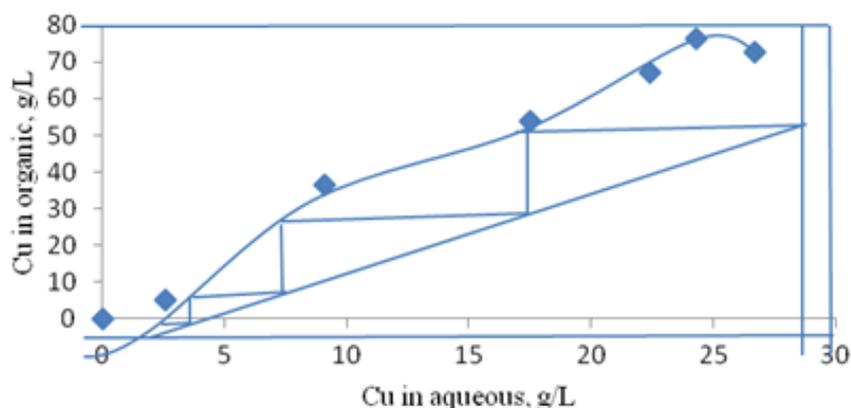


Fig. 5. The McCabe-Thiele Diagram for Extraction of Cu(II) by 0.2 mol/L Cyanex 272 in kerosene, pH 5, O/A Phase ratio =1:1.

3.4. FT-IR analysis of Cu(II) extraction by Cyanex 272

FT-IR analysis of the extracted Cu-metal complex by 0.2 mol/L Cyanex 272 in kerosene was carried out with Shimadzu H400F FT-IR spectrometer using NaCl windows. The FT-IR spectrum of the main extractant obtained was quite similar to those found by Menoyo et al [23] where the characteristic bands for Cyanex 272 i.e. P=O, P-O-H and OH are shown in Fig. 6(a).

These characteristic vibrational bands are identified at 1237, 1034, and 1601 cm^{-1} . The bands at 2929 and 2861 cm^{-1} corresponds to the C-H stretches. The deformation bands at 1459 cm^{-1} and 1374 cm^{-1} , confirms the presence of more than one CH_3 group on a carbon atom [20, 23].

Also, the FT-IR measurements were carried out for Cu(II) loaded Cyanex 272 in kerosene at optimum pH, phase ratio 1:1 and the stripped organic phase and the results of the analysis are shown in Figs. 6(b), 6(c) and 6(d), respectively. Evidently, the interaction of Cu(II) with extractant affects the characteristics vibrational bands at 1237 and 1601 cm^{-1} apparently increases the transmittance of these bands. The band broadening at 420 - 480 cm^{-1} is attributed to the presence of Cu-O [24] and a bending vibration of O-H at 1601 cm^{-1} (Figs. 6(b) and (c)). Thus, the absorption spectra indicate $\text{H}_2\text{O}^{(+)}$ (metal with water) is present in the analysis of the extracted complex as -OH group. Hence, the FT-IR spectra showed that Cu(II) in the form of hydrated Cu-O has been extracted by Cyanex 272. Thus, the FT-IR analysis of the stripped loaded Cyanex 272 shown in Fig. 6(d) is similar to that of the Cyanex 272 in kerosene (main extractant) indicating high level of Cu(II) separation from the loaded Cyanex 272 at optimum condition.

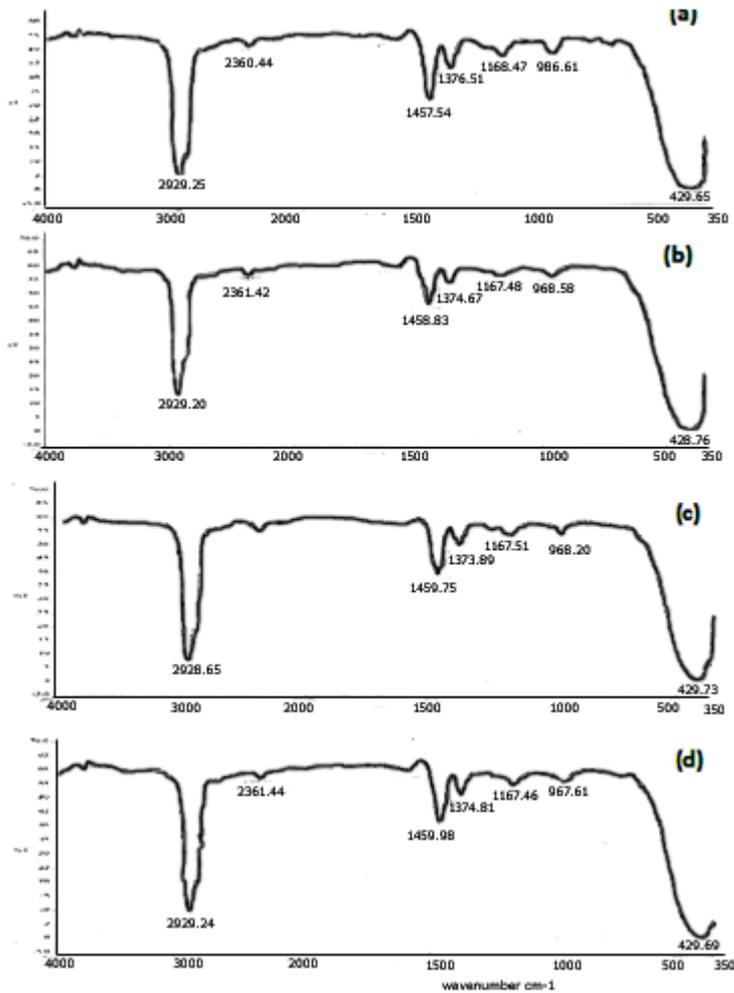


Fig. 6. FT-IR Analysis of (a) 0.2 mol/L Cyanex 272 in Kerosene; (b) Cu(II) Loaded Organic at Optimum pH; (c) Cu(II) Loaded Organic at Optimum O/A=1:1; (d) Stripped Loaded Organic.

4. Conclusion

Solvent extraction of Cu(II) from discarded cell phone was studied using Cyanex 272 in kerosene. The study gave an optimum extraction of Cu(II) by 0.2 mol/L Cyanex 272 at pH 5 within 25 minutes at aqueous: organic ratio of 1: 1. At these conditions, about 95% of total Cu(II) was extracted from which ~ 97% of the Cu-loaded organic phase was quantitatively stripped into aqueous phase by 0.1 mol/L HCl solution. Thus, the purified, stripped Cu(II) could further be recovered as salts by evaporation-cum-crystallization or metal cathode powder through electrowining. Finally, the present investigation opens up a technique to recover and recycle Cu(II) from the metallic components of discarded cell phone.

Acknowledgement

The authors sincerely thank Dr. Oliver Rouher and Mrs. Christine Salomon of Cytec Industries, Rungis Cedex, France for supplying Cyanex[®]272 extractant used in this work.

References

1. Balakrishnan, R.B.; Anand, K.P.; and Chiya, A.B. (2007). Electrical and electronic waste: a global environmental problem. *Journal of Waste Management and Research*, 25, 307-317.
2. UNEP (2007b). *E-waste Volume I: Inventory Assessment Manual*. United Nations Environment Programme. Division of Technology, Industry and Economics, International Environmental Technology Centre, Osaka/Shiga, Japan.
3. UNEP (2007a). *E-waste Volume II: E-waste Management Manual*. United Nations Environment Programme. Division of Technology, Industry and Economics, International Environmental Technology Centre, Osaka/Shiga, Japan.
4. UNEP (2006). Call for Global Action on E-waste. *United Nations Environment Programme*. Retrieved November 14, 2013, from [http://www.unep.org/DocumentsMultilingual/Default.asp? DocumentID=496 &ArticleID=5447&l=en](http://www.unep.org/DocumentsMultilingual/Default.asp?DocumentID=496&ArticleID=5447&l=en)
5. Martha-de-Souza, C.C.B.; and Tenorio, J.A.S. (2004). Simultaneous recovery of zinc and manganese dioxide from household alkaline batteries through hydrometallurgical processing. *Journal of Power Sources*, 136, 191-196.
6. Salgado, A.L.; Veloso, A.M.O.; Pereira, D.D.; Gontijo, G.S.; Salmon, A.; and Monsur, M.B. (2003). Recovery of zinc and manganese from spent alkaline batteries by liquid-liquid extraction with Cyanex 272. *Journal of Power Sources*, 115, 367-373.
7. Sahu, S.; and Srinivasan, N. (2008). Mobile phone waste, current initiatives in Asia and the Pacific. *Technology Monitoring*, 32-39.
8. Wernick, I.; and Themelis, N.J. (1998). Recycling Metals for the Environment. *Annual Reviews of Energy and Environmental*, 23, 465-497.
9. Mahmoud, M.H.H.; and Barakat, M.A. (2001). Utilization of discarded Cu(II)-pickle liquor for recovery of metal values. *Renewable Energy*, 23, 651-662.
10. Cui, J.; and Roven, H.J. (2001). Electronic Waste, Bulletin, Department of Materials Science and Engineering, Norwegian University of Science and Technology, Norway.
11. Nikam, G.H.; and Mohite, B.S. (2012). Development of analytical method for extraction and separation of Zn(II) using Cyanex 272. *International Journal of Analytical and Bioanalytical Chemistry*, 2 (1), 116-121.
12. Baba, A.A.; Adekola, F.A.; and Bale, R.B. (2009). Development of a combined pyro-and hydro-metallurgical route to treat spent zinc-carbon batteries. *Journal of Hazardous Materials*, 171, 875-881.

13. Laubertova, M.; Novicky, M.; and Vindt, T. (2011). The possibilities of hydrometallurgical treatment of discarded mobile phones, *XVIII International Students' Day of Metallurgy, 2011 – Montanuniversitat Leoben*, 412-418.
14. Begun, N.; Bari, F.; Jamaludin, SB.; and Hussin, K. (2012). Solvent extraction of copper, nickel and zinc by Cyanex 272. *International Journal of Physical Sciences*, 7(22), 2905-2910.
15. Baba, A.A.; Adekola, F.A.; and Faseki, M. (2005). A study of the kinetics of the dissolution of a Nigerian Tantalite ore in hydrochloric acid. *Ife Journal of Science*, 7(2), 221-227.
16. Bartkowska, M.; Regel-Rosocka, M.; and Szymanowski, J. (2002). Extraction of zinc(II), iron(III) and iron(II) with varying mixtures containing Tributyl phosphate and Di-(2-ethylhexyl) phosphoric acid or Cyanex 302. *Physicochemical Problems of Mineral Processing*, 36, 217-224.
17. Baba, A.A.; and Adekola, F.A. (2011). Beneficiation of a Nigerian sphalerite mineral by Cyanex 272. *Hydrometallurgy*, 110, 878-883.
18. Olanipekun, E. (1999). A kinetic study of the leaching of a Nigerian ilmenite ore by hydrochloric acid. *Hydrometallurgy*, 53(1), 1-10.
19. Rotuska, K.; and Chmielewski, T. (2007). Solvent extraction of valuable metals from pregnant leach solutions of cupriferous shale. *Physicochemical Problems of Mineral Processing*, 41, 365-372.
20. Darvishi, D.; Haghshenas, D.F.; Alamdari, E.K.; Sadrnezhada, S.K.; and Halali, M. (2005). Synergistic effect of Cyanex 272 and Cyanex 302 on Separation of Cobalt and Nickel by D2EHPA. *Hydrometallurgy*, 77, 227-238.
21. Martin, D.; Garcia, M.A.; Diaz, G.; and Falgneras, J. (1999). A new zinc solvent extraction application: spent domestic batteries treatment plant. *Proceedings of the International Solvent Extraction Conference (ISEC'99), Vol. 1, Barcelona, Spain, 201-206*.
22. Ali, A.M.I.; Ahmed, I.M.; and Daoud, J.A. (2006). Cyanex 272 for the extraction and recovery of zinc from aqueous waste solution using a mixer-settler unit. *Separation and Purification Technology*, 47, 135-140.
23. Menoyo, B.; Elizalde, M.P.; and Almela, A. (2002). Determination of the degradation compounds formed by the oxidation of Thiophosphinic acids and Phosphine sulfides with Nitric acid. *Analytical Science*, 18 (7), 799-804.
24. Islam, M. B.; Haque, M. Z.; and Islam, M. S. (2007). Studies on Cyanex 272 complexes of Mg(II), Ca(II) and Fe(III). *Bangladesh Journal of Science and Industrial Research*, 23, 651-662.