



Complex electronic waste treatment – An effective process to selectively recover copper with solutions containing different ammonium salts



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ABSTRACT

Recovery of valuable metals from electronic waste has been highlighted by the EU directives. The difficulties for recycling are induced by the high complexity of such waste. In this research, copper could be selectively recovered using an ammonia-based process, from industrially processed information and communication technology (ICT) waste with high complexity. A detailed understanding on the role of ammonium salt was focused during both stages of leaching copper into a solution and the subsequent step for copper recovery from the solution. By comparing the reactivity of the leaching solution with different ammonium salts, their physiochemical behaviour as well as the leaching efficiency could be identified. The copper recovery rate could reach 95% with ammonium carbonate as the leaching salt. In the stage of copper recovery from the solution, electrodeposition was introduced without an additional solvent extraction step and the electrochemical behaviour of the solution was figured out. With a careful control of the electrodeposition conditions, the current efficiency could be improved to be 80–90% depending on the ammonia salts and high purity copper (99.9 wt.%). This research provides basis for improving the recyclability and efficiency of copper recovery from such electronic waste and the whole process design for copper recycling.

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1. Introduction

Electronic waste or waste electrical and electronic equipment (WEEE) contains significant amount of valuable metals including copper, zinc, gold, silver, etc (Bigum et al., 2012; Cui and Zhang, 2008; Kiddee et al., 2013). It has been considered as one of the most important resources during urban mining. Processing of WEEE or recovering valuable metals from the waste is however energy intensive because of its complex nature. A typical industrial process is based on pyro-metallurgy including high temperature burning of organics, smelting of metal and oxides, refining and further electrochemical treatment after chemical leaching (Bigum et al., 2012). Comparing with high-temperature processes, a low temperature hydrometallurgical process is always preferable especially for WEEE with low calorific values (Akcil et al., 2015b; Havlik et al., 2011; Jha et al., 2013). However, it has been mostly focused

on mono-streams or relatively ‘clean’ WEEE, for instance, printed circuit boards (PCB), batteries and mobile phones after disassembly/dismantling (Koyama et al., 2006). Processing of a more complex type of electronic waste, usually mixtures of all kinds of end-of-life products or waste from different streams is still not well considered.

In previous research, the possibility to selectively extract metals from a highly complex industrial information and communication technology (ICT) waste by using a hydrometallurgical method has been approved to be feasible (Sun et al., 2015c; Xiao et al., 2013). Specifically, copper in the ICT waste could be selectively extracted by using an ammonia-ammonium carbonate solution. In the downstream to recover copper from the leached solution, direct copper electrowinning from the ammonia-based leaching solutions is usually introduced. It was found that the current efficiency is quite low comparing with traditional copper electrowinning from acidic solutions (Rudnik et al., 2014). With this concern, research was carried out trying to obtain Cu^+ in the ammonia-based solution in order to develop an energy saving copper electrowinning process by electrowinning Cu^+ instead of Cu^{2+} into metallic copper (Oishi et al., 2006). Cu^{2+} in the solution is in principle to react with metal-

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lic copper through the $\text{Cu}^{2+}/\text{Cu}^+$ redox reaction to form Cu^+ . However, it is difficult in practice to keep a high concentration of Cu^+ in the solution since Cu^+ is easily oxidised into Cu^{2+} even at low oxygen partial pressure. On the other hand, it is rather sensitive to the impurities contents in the solution and solvent extraction is usually required prior to copper electrowinning (Oishi et al., 2008). As a follow-up of our previous research (Sun et al., 2015b, c; Xiao et al., 2013), this research focuses on the role of different ammonium salts during copper recovery from the complex ICT waste. In both stages i.e. selective extraction of copper from the waste and copper electrowinning from the solution, the effects of ammonia salt are being identified, for the leaching kinetics and electrochemical features, respectively. During copper electrodeposition, instead of trying to maintain a high concentration of Cu^+ , ammonia salt is found to have significant effects on the current efficiency as well as the energy consumption. With this research, it is providing more established understanding on the nature of selective copper recovery from complex electronic waste.

2. Experimental

2.1. Materials

The ICT waste is provided by Van Gansewinkel Groep (VGG). The material has been pretreated and concentrated physically and shredded into size of smaller than or equal to 8 mm. This size is defined to be a limit since further shredding will significantly increase the processing cost. The material is inherent with high inhomogeneity from observation and contains a large fraction of sand, stones, glass, ceramics and plastic particles. Metallic materials are either trapped in non-metallic components or present as metal wires. The general compositions are given elsewhere (Xiao et al., 2013). Copper content in the ICT waste is 40.8 wt.%. Ammonia (25% in water, Alfa Aesar), ammonium carbonate, ammonium sulphate and ammonium chloride (99.0%, Alfa Aesar) are used in the experiments.

2.2. Experimental set-up and procedures

The ICT waste received from VGG was directly used as the feed-stock for metal recovery. In each lab-scale experiment, a sample size of around 50 g was taken which would be a relatively representative sample size of the bulk composition according to our previous investigations (Xiao et al., 2013). The leaching experiments were carried out in a glass reactor and the detailed set-ups have been given in our previous research (Sun et al., 2015c). A round shape of the reactor could help to ensure a better mixing condition. Air was purged into the bottom of the reactor and the gas bubbles could be further broken up by the agitator. The gas flow rate was controlled by a flow meter. During leaching, system temperature was slightly fluctuating because of the exothermic reactions. A heating bath/thermo-stat with water was used to control the temperature and an additional thermometer was used to monitor the temperature fluctuation during leaching. The temperature was found to change within $\pm 2.5^\circ\text{C}$ of the required temperature. The pH values were detected by a pH meter in the whole leaching process (pH meter was calibrated at 18°C). Prior to the leaching, the ammonium salt ($(\text{NH}_4)_2\text{CO}_3$, $(\text{NH}_4)_2\text{SO}_4$ and NH_4Cl) was firstly dissolved into the ammonia solution and demineralised water was added to reach a liquid volume of the required liquid to solid ratio (5 ml/1 g in current research). The starting ammonia concentration is set to be 7.8 wt.%. The solution was kept in the reactor for a period to reach the required temperature ($18\text{--}45^\circ\text{C}$) before the ICT waste was added. Liquid samples were taken at certain time intervals to track the leaching behaviour of different metals in the ICT

waste. The sample size was 1–2 ml which is considered to have insignificant effect on the liquid to solid ratio. Since the waste exhibits high heterogeneity, the residue after leaching was also analysed to diminish any discrepancy in composition. The extracted fraction of different metals is therefore calculated from

$$X_M = W_t / (W_f + W_r) \quad (1)$$

where W_t and W_f are the metal contents in the sampled solution at time t and the final solution, respectively; W_r is in the metal content in the final residue after leaching.

2.3. Copper electrodeposition

From the leached solution, copper is further recovered by electrowinning/electrodeposition process (galvanostatic). In previous research, cylindrical electrodes had been proved significant to improve the current efficiency (Sun et al., 2015b). The copper electrodeposition was conducted in a rectangular cell. A copper cylinder (height 10 mm $\times$ diameter 10 mm), a height 10 mm $\times$ diameter 40 mm graphite cylinder and the Ag/AgCl electrode (3 M KCl) were used as the cathode, anode and reference electrodes, respectively. The reference electrode was connecting to the solution via a salt bridge. The current efficiency was determined as the ratio of the experimental weight difference of the cathode before and after the electrodeposition to the theoretical weight change by assuming that metallic copper is deposited from the bivalent state. At a later stage, cylindrical electrodes were used with the aim to improve the current efficiency. Copper obtained at the cathode was analysed to determine the purity.

2.4. Characterisation

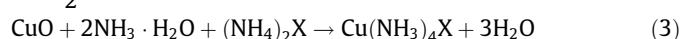
A sequential wavelength dispersive X-ray Fluorescence Spectrometry (XRF, PANalytical Axios) was used for compositional analyses of the bulk composition and the composition of the residue after leaching. The liquid solution was analysed by inductively coupled plasma – optical emission spectrometry (ICP-OES, PerkinElmer Optima 3000DV) and the residue was analysed by XRF. Although XRF has relatively high detection limit, the sample was prepared according to the procedures in Sun et al. (2015a) was pressed into pellets for analyses in order to minimise the inhomogeneity of the sample and ensure the reliability of the analyses. The morphologies of the ICT waste were both characterised with digital camera and scanning electron microscope (SEM, JEOL JSM 6500F) with energy-dispersive spectroscopy (EDS). The sample was polished and carbon coated when necessary. Liquid samples were diluted and prepared for analyses with ICP-OES.

3. Results and discussion

3.1. Copper leaching from ICT waste using different ammonium salts

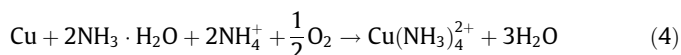
3.1.1. Leaching efficiency

During copper extraction from the ICT waste using an ammonia-based solution, the role of ammonium salt is providing anions (e.g. CO_3^{2-}) to the ammine complex ($\text{Cu}(\text{NH}_3)_4^{2+}$) and proton to compensate with hydroxide anion generated during ammine complex formation. The reactions between copper and the leaching solution include two steps as (Meng and Han, 1996; Sun et al., 2015c)



where X represents an anion from the ammonium salt (carbonate or sulphate for instance).

The total reaction can be expressed by



If only reaction (4) is considered, it seems that the copper leaching is not directly related to the type of the ammonium salt since the anion does not participate the copper leaching reaction. However, the different in copper leaching kinetics is found to be significant with different ammonium salts. In order to identify the reasons and exact role of ammonia salt during copper leaching, different ammonium salts were used during selective copper leaching from the electronic waste. The leaching conditions were kept consistent with different ammonium salts while the amounts of the salts were calculated according to the same NH_4^+ mole amount. In this case, the ammonium carbonate concentration is 120 g/L, ammonium sulphate is 165 g/L and ammonium chloride is 134 g/L. As given in Fig. 1, ammonium chloride shows the lowest copper leaching rate while copper is more favourable to be leached when ammonium carbonate is used than other ammonium salts (Temperature: 18 °C, ammonia content 7.8 wt.%, solid to liquid ratio 1/5, stirring rate 600 rpm and air flow rate 50 L/h). At the early stage of copper leaching at room temperature, low copper leaching rate is noticed for all the ammonium salts which is consistent with the previous research (Sun et al., 2015c). This period is clearly longer for ammonium chloride which is believed to be related to the effect of the anions. Considering the copper leaching reaction, the activity or concentration of NH_4^+ is one of the critical factors that influence both the thermodynamics and kinetics of copper leaching. For a given ammonium salt, the dissociation reaction is given as



The dissociation of NH_4^+ follows



It means that the activity of NH_4^+ is highly related to the pH of the solution. During leaching, the pH changes were recorded as given in Fig. 1. For the starting pH and pH during the whole leaching process, the values follow a sequence of $(\text{NH}_4)_2\text{CO}_3 > (\text{NH}_4)_2\text{SO}_4 > \text{NH}_4\text{Cl}$ and the changing rates indicate similar tendency with a faster change at the early stage of the leaching while it becomes slower at the later stage. Considering the equilibrium state of the NH_4^+ dissociation (with dissociation constant of K_a), its activity can be calculated by

$$a_{\text{NH}_4^+} = \frac{a_{\text{H}^+}}{K_a} \cdot a_{\text{NH}_3} \quad (7)$$

The reactivity of the leaching solution with a certain ammonium salt can therefore be reflected by the pH values (a_{H^+} is the activity of H^+) which determines the activity of the NH_4^+ in reaction (4). In addition, in the last stage where the copper recovery profile is approaching flat for the cases of ammonium carbonate and ammonium sulphate, mass transfer or diffusion becomes important since both ammonia and ammonium salt are reacted to form ammine complexes in the solution and probability of reaching the copper metal surface becomes prohibited. At this stage, the transfer or diffusion of NH_4^+ into the copper metal surface (more of apparent behaviour) can be influenced by the dissociation of ammonium salt according to Eq. (5). Concerning different anion ions, the dissociation constant varies significantly which subsequently influences the leaching behaviour of different salts in accordance with Fig. 1. For instance in the standard state, K_a for NH_4^+ is 9.25, K_b for CO_3^{2-} , SO_4^{2-} , Cl^- are 3.67, 12.1, 17 respectively (Lower, 1996). They are at the same time influencing the dissociation of different ammonium salts corresponding to reaction (5). A high concentration of the salt anion can result in a low dissociation

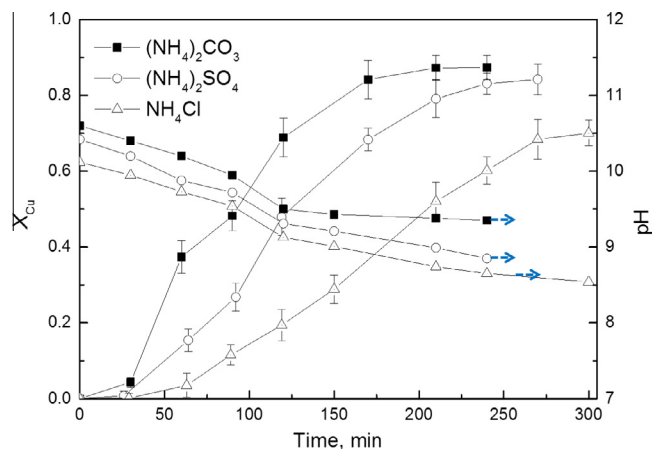


Fig. 1. Effect of different ammonium salts on copper extraction rate from the ICT waste (Temperature: 18 °C, ammonia content 7.8 wt.%, solid to liquid ratio 1/5, stirring rate 600 rpm and air flow rate 50 L/h).

of NH_4^+ into H^+ corresponding to Eqs. (5) and (6) at a fixed temperature (e.g. $K = \frac{a_{\text{NH}_4^+} \cdot a_{\text{Cl}^-}}{a_{\text{NH}_4\text{Cl}}}$). Since the initial NH_4^+ mole amount was kept the same for different ammonium salts, the anion concentrations vary during leaching. It is clear that the mole concentrations of carbonate and sulphate are the same while the mole concentration of chloride is much higher (2 times) than other salts. Additionally, in the thickness of the mass transfer boundary layer (or Stern layer) is also related to the anion concentration and a thick layer may prohibit the mobility of cations. As a result, the leaching rate is much lower at the later stage than other ammonium salts when mass transfer becomes more important for copper leaching in the ammonium chloride solution. On the other hand, other physiochemical properties of the leaching solutions of different ammonium salts may also contribute to the effects including the viscosity and conductivity. With preliminary measurement on the solution viscosity, it has been noticed that the difference is insignificant to induce large difference in the copper leaching rate. Conductivity of the solution is also associated with the pH difference and its effect on copper leaching is still unclear.

However, this effect becomes less pronounced at higher than room temperatures. Fig. 2 shows the copper leaching rate at different temperatures. At the early stage of copper leaching, ammonium carbonate still shows significant potential to react faster with copper from the waste. When the reaction time is significantly long, the copper extraction rate in ammonium chloride and ammonium sulphate solution is also approaching to the same level as that in the ammonium carbonate solution. It means that at high temperature and especially at the later leaching stage with mass transfer controlled, the leaching is less dependent on the anion species (CO_3^{2-} , SO_4^{2-} , Cl^-) than at low temperatures. At the same time, the slow leaching period is not observed or it has been too short to be detected in current sampling intervals. With an increased temperature, copper extraction rate is clearly improved for all types of ammonium salts (Fig. 2). However, for ammonium carbonate, the difference between 35 °C and 45 °C is insignificant which may be in accordance with the decomposition of ammonium carbonate from 35 °C. The effect of temperature is clearly more pronounced for ammonium chloride (Fig. 2c) than other salts that the recovery rate can reach more than 80% in 2 h at 45 °C. On the other hand, the ammonia vapour pressure increases significantly with temperature and for instance, at 35 °C, it is approaching 15 kPa (almost 3 times of the vapour pressure of water) (Sun et al., 2015c). Loss of ammonia during copper leaching or corrosion by the ammonia vapour on the reactor, if metallic materials are used, can be issues for further design of an industrial implementa-

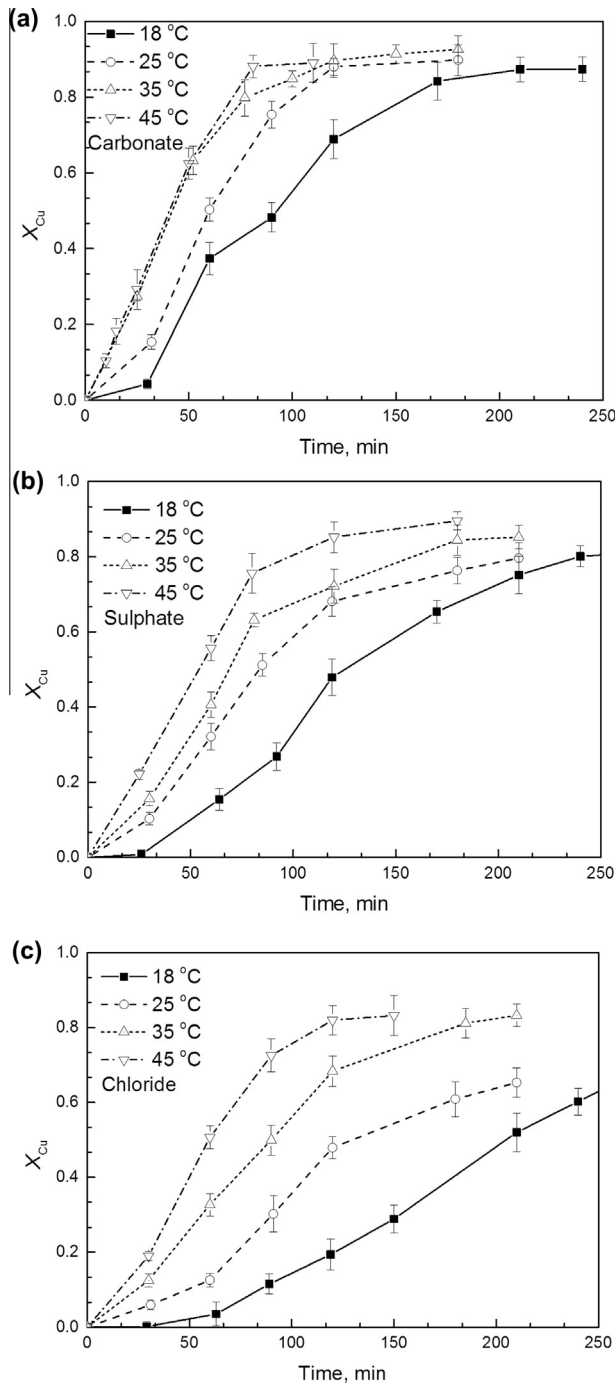


Fig. 2. Effect of temperature on copper extraction rate from the ICT waste with different ammonium salts (a) ammonium carbonate; (b) ammonium sulphate and (c) ammonium chloride (ammonia content 7.8 wt.%, solid to liquid ratio 1/5, stirring rate 600 rpm and air flow rate 50 L/h).

tion (Jones and Wilde, 1977). From both cost and environmental point of views, room temperature is preferred for copper recovery from the ICT waste although this will be highly influenced by the economical evaluation planned in the next step. The selection of ammonium salt is however also depending on the nature of the salt and the following copper electrodeposition behaviour from the leached solution.

3.1.2. Kinetics consideration

Using the method developed previously (Levenspiel, 1999; Sun et al., 2015c), the following assumptions were associated: (1) the

kinetics consideration is focusing on the stage before the leaching rate profile bended to be flat; (2) due to the high heterogeneous nature of the copper particles (the shapes can be sphere, plate, wire etc.) in the waste, for simplification, a spherical model of shrinking core without product layer was used. According to reaction (4), copper leaching mainly consists of two steps: mass transfer of oxygen and ammonia ($[O_2 \sim NH_4OH]$) to the surface of copper metal and copper dissolution via chemical reaction (4). Comparison of the morphologies before and after copper selective leaching is given in Fig. 3. It clearly indicates the process could selectively extract copper without significant size change before and after the leaching. The kinetics equation can be expressed as

$$\frac{X_{Cu}}{3k_M} + \frac{1}{k_{rea}} [1 - (1 - X_{Cu})^{1/3}] = \frac{MC_0}{\rho R_0} t \quad (8)$$

where $\rho = 8.96 \times 10^3 \text{ kg/m}^3$ for copper, the average particle size in current research is $R_0 = 1.82 \text{ mm}$, $M = 63.55 \text{ g/mol}$, $C_0 = 4.44 \text{ mol/L}$ for ammonia concentration is 75.5 g/L .

More detailed deviation and description of the procedures were given in previous research (Sun et al., 2015c). In order to obtain the values for the mass transfer coefficient and the reaction rate constant during copper leaching, Eq. (8) was solved numerically according to the experimental data at various conditions. It was found that the chemical reaction is fast enough to be ignored and copper leaching in all type of ammonium salts is mass transfer controlled (Sun et al., 2015c) where both the solid-to-liquid ratio and agitator stirring rate are significant to influence the copper leaching. The activation energy for a mass transfer controlled leaching of Cu was subsequently calculated using the Arrhenius equation. The results are shown in Fig. 3. For different ammonium salts the relationships between the mass transfer coefficient and temperature are given as

$$\begin{aligned} \ln k_M &= -1.1 - \frac{19217.7}{R} \times \frac{1}{T} \text{ for ammonium carbonate (18–45 °C)} \\ \ln k_M &= -0.53 - \frac{21398.7}{R} \times \frac{1}{T} \text{ for ammonium sulphate (18–45 °C)} \\ \ln k_M &= 5.2 - \frac{36954.2}{R} \times \frac{1}{T} \text{ for ammonium chloride (18–45 °C)} \end{aligned} \quad (9)$$

The activation energy follows a sequence of $(NH_4)_2CO_3 < (NH_4)_2SO_4 < NH_4Cl$ at current experimental conditions, 19.2 kJ/mol, 21.4 kJ/mol and 36.9 kJ/mol respectively. The values are in the same levels as copper leaching with other methods in literature (Huang et al., 2014; Lambert et al., 2015). Based on the results, it indicates that ammonium chloride is more sensitive to the temperature than other salts and this behaviour will be important to be considered in further design of the whole copper recovery process.

3.2. Copper electrodeposition from different salts

Copper electrodeposition is a conventional process to recover copper from a solution. It is widely used under acidic conditions which is also the current industrial practice. For ammonia-based solutions, research on copper electrodeposition is relatively limited. On one hand, it usually has low current efficiency as mentioned above. On the other hand, copper leaching by using ammonia-based solutions is not common in practice. The main reason is that copper-bearing ore is mostly in sulphide state with which it is difficult to be leached directly by ammonia-based solutions and sulphur is one of the main impurities during current copper production. In this research and related, the application of ammonia-based solutions bears significant advantages because of the copper states (mainly as entrapped copper metal or copper oxides) in the electronic waste. It has been proved that copper can be

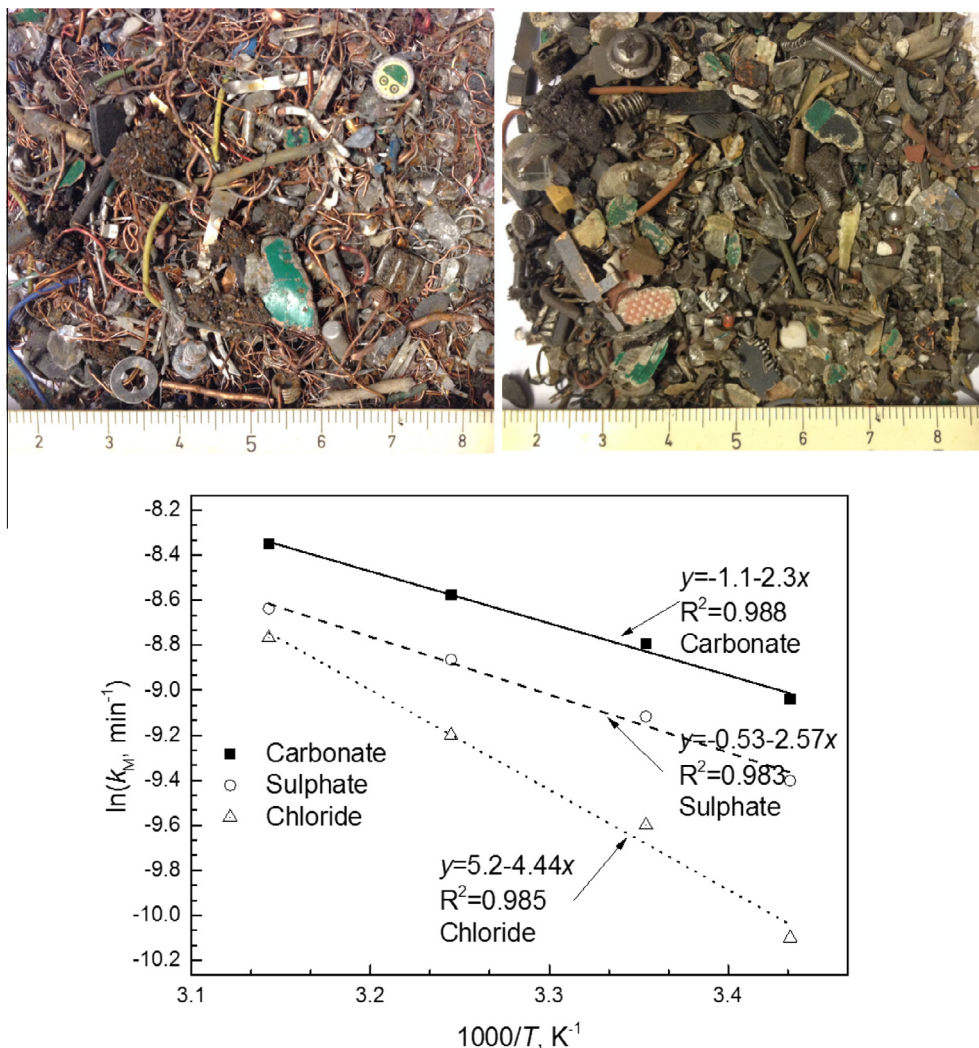


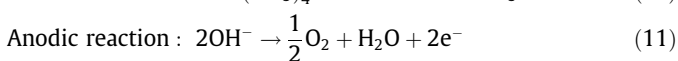
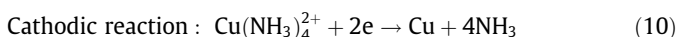
Fig. 3. Comparison of the original ICT waste (a) and the end residue after selective leaching (b) (copper could be selectively leached into ammonia containing solutions) and (c) effect of ammonium salt on the apparent mass transfer coefficient during copper recovery.

Table 1
Metal contents of a typical ammonia-ammonium carbonate leached solution.

Elements	Al	Cu	Fe	Ni	Pb	Zn	Sn
Concentration, g/L	0.01	57.01	0.02	0.10	0.13	1.75	0.06
wt. %	0.001	5.70	0.002	0.010	0.013	0.17	0.006

selectively recovered into the ammonia-based solutions with minimised impurity content. Table 1 gives the metal contents of a typical ammonia leached solution. It can be found that the selectivity of copper is more than 96% which is the ratio of copper to all metallic elements in the solution.

Because of the very low impurity contents, it becomes possible for direct copper recovery from the solution without a solvent extraction step. The copper electrodeposition reactions are as follows



3.2.1. Reduction potentials

A cyclic voltammogram (CV) is usually used to identify the possible electrochemical reactions during copper electrodeposition. In

this research, the measuring solution is with ammonium carbonate and the composition is given in Table 1. A Ag/AgCl reference electrode (together with a salt bridge) and graphite anode were used during the measurement. The distance between the anode and cathode was kept at 1 cm while the anode area is 4 times of the cathode area. According to the Nernst equation given below, the actual potential of different ions in the solution can be calculated by roughly assuming the ion activity coefficient is unit.

$$E = E^0 + \frac{RT}{nF} \ln \frac{a_{\text{ox}}^m}{a_{\text{red}}^n} \quad (12)$$

The calculated potentials for different metal ions are given in Table 2. It can be found that copper has the least negative potential which will be firstly reduced at the cathode. However, other side reactions as the hydrogen evolution can happen especially with depleted $\text{Cu}(\text{NH}_3)_4^{2+}$ ions. At the same time, electrodeposited copper can also be dissolved by the $\text{Cu}(\text{NH}_3)_4^{2+}$ ions through



It may significantly influence the copper electrodeposition process and the current efficiency can be highly decreased. However, this reaction is relatively slow at room temperature according to Oishi et al. (2007) especially in the case of low $\text{Cu}(\text{NH}_3)_4^{2+}$

Table 2

The electrochemical potential of different metal ions in a typical ammonia-ammonium carbonate leached solution with pH = 9.5.

Half reactions	E^0 (SHE) (Lide, 2005)	E^0 (Ag/AgCl)	E (Ag/AgCl)
$\text{Cu}(\text{NH}_3)_4^{2+} + 2e \rightarrow \text{Cu} + 4\text{NH}_3$	−0.04	−0.27	−0.31
$2\text{H}_2\text{O} + 2e \rightarrow \text{H}_2 + 2\text{OH}^-$	−0.43	−0.66	−0.79
$\text{Ni}(\text{NH}_3)_6^{2+} + 2e \rightarrow \text{Ni} + 6\text{NH}_3$	−0.52	−0.75	−0.86
$\text{Pb}^{2+} + 2e \rightarrow \text{Pb}$	−0.83	−1.06	−0.92
$\text{Zn}(\text{NH}_3)_4^{2+} + 2e \rightarrow \text{Zn} + 4\text{NH}_3$	−1.04	−1.27	−1.37

*SHE: Standard hydrogen electrode.

concentration. By using a colorimetric method (Cu^{2+} is directly measured by a UV–visible spectrometer (Secomam Uvikon XL) at 630 nm), Cu^+ in the solution was determined and it was found that the concentration is only 0.66 ppm when the electrodeposition is at 1 h even under Ar atmosphere. Cu^+ in the ammonia-based solution could be used during copper electrowinning process (Oishi et al., 2007). However, it is not practically feasible to maintain a high concentration of Cu^+ since it is very easily oxidised. Other side reactions as reduction of Ni and lead may also be possible which will be present as impurities in the electrodeposited copper. Fig. S1 shows the cyclic voltammogram at different scanning rates, both the reduction and oxidation peaks of copper ammonia complex can be identified from the CV profile. Redox peaks of other metals are not observed which is most probably due to their low concentrations. During copper electrodeposition, the reduction peak covers a wide range of potentials that impurities are possibly deposited from the solution associated with side reactions such as hydrogen evolution, nickel and lead reduction appears to be simultaneously occurring. Clear hydrogen evolution (bubbling) has been more easily observed at the cathode when the copper content is <5 g/L and the solution becomes light blue. It was also found that Pb is the main impurity of the electrodeposited copper when a lead anode was used (Xiao et al., 2013). During copper electrodeposition, it is always important to dictate the deposition potential as well as the current density trying to avoid the effects of side reactions in order to improve the current and power efficiencies.

3.2.2. Effect of copper content and ammonium salt on current efficiency

Current efficiency is an important factor that determines the effectiveness of the electrodeposition process. It describes the efficiency with which electrons or charge are transferred in the cell facilitating the copper electrodeposition. Usually, the current efficiency for copper electrodeposition is calculated by

$$\eta = \frac{m_{\text{Cu}}}{M_{\text{Cu}}} \cdot \frac{nF}{It} \quad (14)$$

where m_{Cu} is the weight the electrodeposited copper, M_{Cu} is the molar weight, n is the transferred electron number, F is the Faraday constant, I is the supplied current in the cell and t is the time (the electrodeposition is galvanostatic).

Fig. 4 shows the effect of the concentration of copper ammonia complex in the solution on the current efficiency during copper electrodeposition with ammonium carbonate. The concentration is the starting copper content in the solution. Since the deposition time is relatively short and a large volume of solution was used to ensure the change in copper concentration be insignificant. Synthesized ammonia carbonate containing solutions were used in this case. Improvement on current efficiency is observed until the copper concentration is 50 g/L while further increasing in the copper concentration, the improvement becomes negligible (Fig. 4).

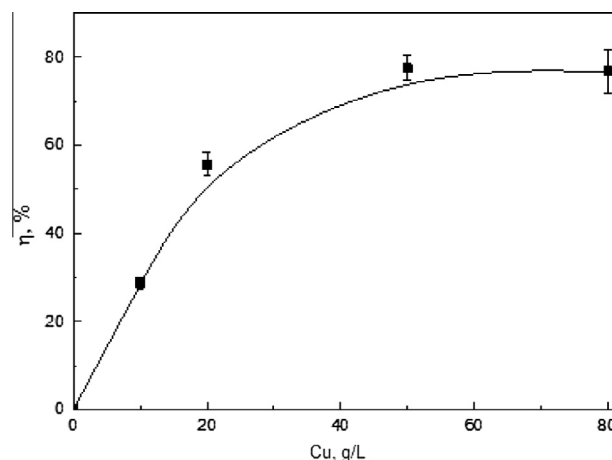


Fig. 4. Effect of copper content on the current efficiency during electrodeposition with ammonium carbonate (at the same electrodeposition time of 2 h, the copper concentration is for Cu^{2+} and the current density was set at 450 A/m²).

With the above considerations, the effect of different ammonia salt on the copper electrodeposition was investigated. The leached solutions from Fig. 1 using different ammonium salts were directly applied as the electrolytes for copper electrodeposition. Although the copper content is lower in the ammonium chloride solution, it ends with the highest current efficiency (Fig. 5) indicating more pronounced effect of the ammonium salt on the current efficiency than the copper concentration (comparing with Fig. 4). It shows a different sequence of $\text{NH}_4\text{Cl} > (\text{NH}_4)_2\text{SO}_4 > (\text{NH}_4)_2\text{CO}_3$ from the leaching effectiveness. As the current efficiency is an indication of the electron transfer, the physiochemical properties of the solutions will play an important role in the electrochemical behaviour. On one hand, the mobility of $\text{Cu}(\text{NH}_3)_4^{2+}$ cations is the ability of the ions to migrate in response to the applied electrical field which may be influenced by the conductivity of the ammonia-based solution. Although it is difficult to conclude that the current efficiency is directly determined by the solution conductivity, it may still be, to some extent, affecting the hydrogen evolution which is believed to be the main reason for lowering the current efficiency. The ionic conductivities of different ammonia-based solutions are shown in Table 3 and the ammonium chloride solution has the highest value. A more detailed investigation on the electrochemistry will follow-up to identify the role of different factors that determines the electron transfer.

Based on the leaching effectiveness and the electrochemical behaviour during the electrodeposition with different ammonium salts, it is found that ammonium carbonate has the most effective leaching rate for the ICT waste while the current efficiency is relatively low while ammonium sulphate appears to have both better efficiencies in both stages. In a later phase for scaling-up or further process design in processing the ICT waste, these behaviours will be critical in decision making for selecting the right leaching reagent and ammonium sulphate is considered the best option within the conditions for copper recovery from this type of electronic waste.

3.3. Characterisation of the electrodeposited copper

Copper surface/morphology needs to be well controlled during electrodeposition. Usually, oriented growth of copper should be prevented in order to avoid possible short cut from cathode to anode during electrodeposition. It has been found that (111) direction is the preferred growth orientation when copper film is prepared (see Fig. 5(b) the XRD patterns) (Ibanez and Fatas,

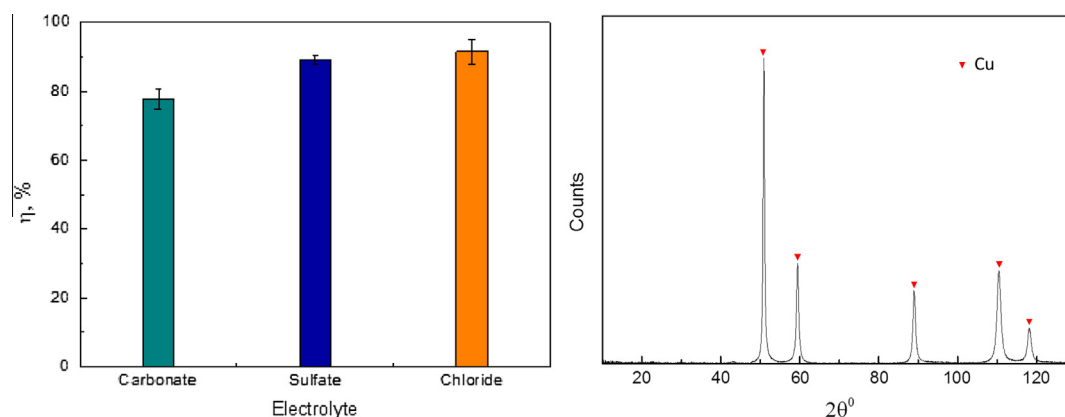


Fig. 5. (a) Current efficiency during copper electrodeposition from different electrolytes (the current density was set at 450 A/m²) and (b) XRD patterns of the electrodeposited copper.

Table 3
Ionic conductivity of the ammonia-based solutions.

Solutions	Ammonium carbonate	Ammonium sulphate	Ammonium chloride
Cu concentration, g/L	57.01	52.36	35.28
Conductivity, mS/cm	71.9	118.9	207.7

2005). Concerning this issue, it is well known that one way to control the cathode morphology is to adjust the current density during copper electrodeposition or to apply a periodically changing current signal. Intensive investigations have been done in acidic solutions by considering different electrochemical factors as well as additives into the solution (Ibanez and Fatas, 2005) while in an ammonia-based solution, the morphology dependent on the electrolyte is still not well understood. In order to develop a non-additive electrodeposition process coupling with effective copper extraction, the difference in electrochemistry of the leaching solution from the ICT waste needs to be well identified. In this research, it has been focused on the surface waving of the electrodeposited copper and preliminarily understanding the cathode morphology difference with different ammonium salts. Solutions from Table 3 had been used to perform the electrodeposition by keeping the same electrical conditions. Fig. 6 gives the representative 3D microscope images (Keyence, VHX series) of the cathode in different solutions. Significant difference in the copper morphology indicates different electrochemical behaviour of the ammonium salts during electrodeposition. With the ammonium chloride solution, large grains of copper is observed and the uneven grain size shows a potential for oriented growth. Both the ammonium carbonate and ammonium sulphate have relatively smooth surface while the morphology varies. However, a large amount of defects or pores are still visible at the cathode for both solutions. As given in Fig. 6(d), the surface waving can be related to the salt type that is the lowest for ammonium carbonate solution. The purities of the electrodeposited copper were analysed and are shown in Table 4. It can be found that the 99.9% purity of copper can be obtained directly from the leach solutions without solvent extraction. The main impurities are lead and nickel that possibly due to the side reactions.

According to both the leaching and electrochemical behaviour of different ammonium salts, it can be found that with ammonium sulphate the copper extraction rate and current efficiency during copper electrodeposition are both significant. Although in ammonium chloride, the current efficiency as well as the copper purity is rather high, the leaching rate of copper from the ICT waste is too low.

3.4. Improvement on the management of complex electronic waste

The management indicates the whole process of waste treatment including collection, disassembly/dismantling, mechanical and metallurgical recycling or landfilling (Cui and Zhang, 2008). Proper management of electronic waste is of great importance for the pollution control. In the case of electronic waste disposal, it may bring significant environmental and societal impacts including (1) food chain – contamination by toxic substances from disposal and primitive recycling processes that result in secondary waste entering the food chain; (2) direct impact on workers who labour in primitive recycling areas from their occupational exposure to toxic substances. Along with this, numerous researchers have demonstrated a direct impact of backyard recycling on workers. The danger of electronic waste toxicity to human health, both in terms of chronic and acute conditions, has become a serious societal problem (Kiddee et al., 2013). In the EU, landfilling or disposal is not the favourable solution with its cost increasing instantly and public awareness is also significantly promoted. According to the most recent directive (directive 2012/19/EU), clear targets have been settled in order to promote metal recycling from electronic waste which is so far still lower than 30%. On the other aspect, electronic waste is considered as a significant secondary resource which is believed to play an important role on securing supply of metal resources for the EU.

This research deals with a complex electronic waste stream with high complexity nature. Recycling of metals using traditional processes, e.g. acidic leaching (Erust et al., 2016; Tuncuk et al., 2012), had been proved inefficient for this type of waste since large amount of impurity metals could be leached together with the targeting metals. This brought difficulties in the separation and purification steps in order to effectively recover the valuable metals from the leached solutions. With this consideration and in order to ensure its proper management, an effective recycling process to selectively recover valuable metals, i.e. copper and precious metals, were developed. Taking copper as the targeting metal, this paper proves the possibility that it recovers pure copper (99.9 wt. %) directly from the leached solution without intermediate separation and purification steps. Precious metals concentrated in the residue could be further recovered using non-cyanide leachant (Akcil et al., 2015a). Along with this research, a large scale processing line (i.e. 500 kg waste) is under construction and preliminary results have been promising. With this research it provides a method that may improve the efficiency of electronic waste management by implementing selective metal recovery. Following this research, it is still required to understand the detailed behaviour of other elements, for instance, Fe, Al and Pb which are currently not included.

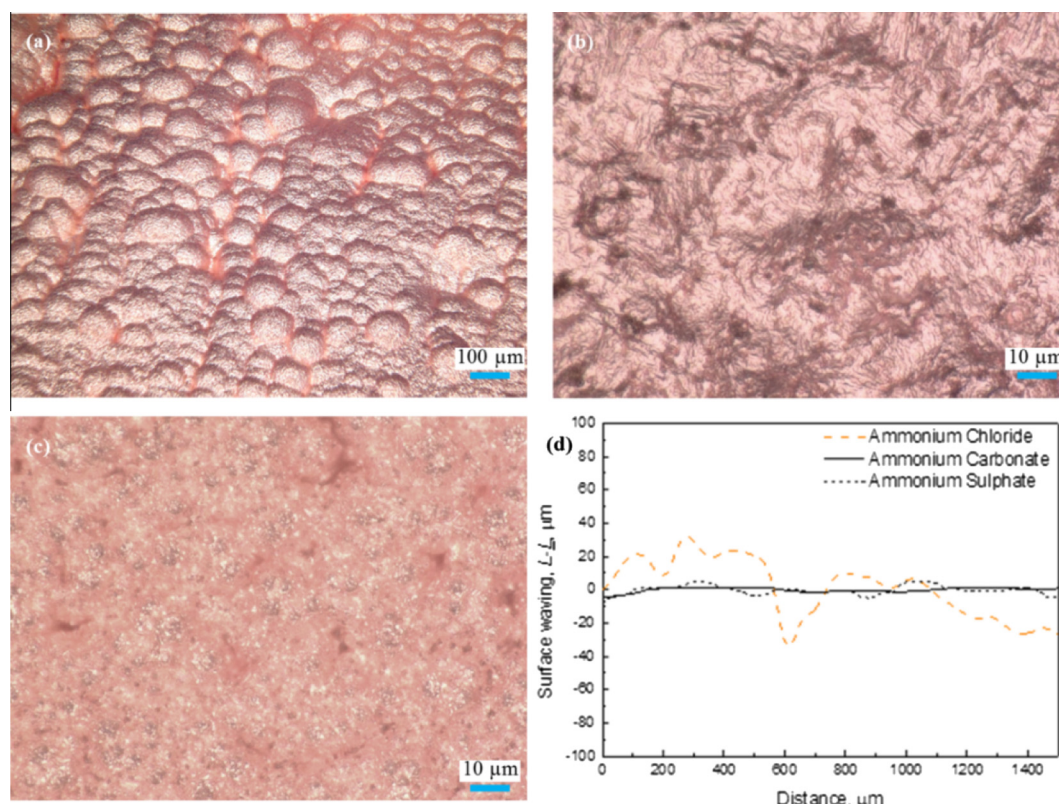


Fig. 6. Electrodeposited copper morphology from different ammonium salt solutions. (a) Ammonium chloride solution; (b) ammonium carbonate solution; (c) ammonium sulphate solution and (d) the surface waviness of the cathode.

Table 4
Comparison of the cathode purities from different ammonia-based solutions (wt.%).

Elements	Cu	Al	Si	Ni	Pb
Ammonium carbonate	99.88	0.018	0.006	0.013	0.079
Ammonium sulphate	99.79	0.011	–	0.065	0.075
Ammonium chloride	99.91	0.015	–	0.034	0.026

4. Conclusions

The effect of ammonium salts on copper recovery from an industrially provided ICT waste was investigated by using an ammonia-based leaching solution. The solutions were further treated to electrodeposit copper. With a systematic understanding of the copper leaching and electrochemical behaviour of different leached solutions, the features of different ammonium salts for copper recovery can be identified which will be the basis for optimising the copper recovery process. The conclusions can be drawn as follows:

- (1) The pH values of the leaching solutions follow a sequence of $(\text{NH}_4)_2\text{CO}_3 > (\text{NH}_4)_2\text{SO}_4 > \text{NH}_4\text{Cl}$ and the changing rates of pH have similar tendencies with a faster change at the early stage of leaching while it becomes slower at the later stage. The reactivity of the leaching solution with a certain ammonium salt is reflected by the pH values. Ammonium chloride solution shows the lowest copper leaching rate while it is the highest for ammonium carbonate solution. It was found that copper leaching from the ICT waste in all type of ammonium salts is mass transfer controlled. The activation energy

of the mass transfer coefficient follows a sequence of $(\text{NH}_4)_2\text{CO}_3 < (\text{NH}_4)_2\text{SO}_4 < \text{NH}_4\text{Cl}$ at current experimental conditions, 19.2 kJ/mol, 21.4 kJ/mol and 36.9 kJ/mol respectively.

- (2) Ammonia carbonate containing solutions were used to investigate the effect of copper content on the current efficiency during electrodeposition. Significant improvement on current efficiency is observed until the copper concentration is 50 g/L while further increasing in the copper concentration, the improvement becomes negligible. Current efficiencies for leach solutions with different ammonium salts show a sequence of $\text{NH}_4\text{Cl} > (\text{NH}_4)_2\text{SO}_4 > (\text{NH}_4)_2\text{CO}_3$ which is different from the leaching efficiency.
- (3) From all three types of ammonia-based solutions, copper metal can be obtained with the highest purity of 3 N for the ammonium chloride solution. Based on the leaching effectiveness and the electrochemical behaviour during deposition with different ammonium salts, leaching solution with ammonium sulphate shows more superior features for copper recovery. In the next stage for further optimisation of the copper recovery process to fulfil industrial application, more detailed investigations on the characteristics of the ammonium salts including the corrosion behaviour, decomposition and recyclability in the whole process loop are being carried out.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.wasman.2016.03.015>.

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Concentration of precious metals during their recovery from electronic waste



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ABSTRACT

The rapid growth of electronic devices, their subsequent obsolescence and disposal has resulted in electronic waste (e-waste) being one of the fastest increasing waste streams worldwide. The main component of e-waste is printed circuit boards (PCBs), which contain substantial quantities of precious metals in concentrations significantly higher than those typically found in corresponding ores. The high value and limited reserves of minerals containing these metals makes urban mining of precious metals very attractive. This article is focused on the concentration and recovery of precious metals during pyro-metallurgical recycling of waste PCBs. High temperature pyrolysis was carried out for ten minutes in a horizontal tube furnace in the temperature range 800–1350 °C under Argon gas flowing at 1 L/min. These temperatures were chosen to lie below and above the melting point (1084.87 °C) of copper, the main metal in PCBs, to study the influence of its physical state on the recovery of precious metals. The heat treatment of waste PCBs resulted in two different types of solid products, namely a carbonaceous non-metallic fraction (NMFs) and metallic products, composed of copper rich foils and/or droplets and tin-lead rich droplets and some wires. Significant proportions of Ag, Au, Pd and Pt were found concentrated within two types of metallic phases, with very limited quantities retained by the NMFs. This process was successful in concentrating several precious metals such as Ag, Au, Pd and Pt in a small volume fraction, and reduced volumes for further processing/refinement by up to 75%. The amounts of secondary wastes produced were also minimised to a great extent. The generation of precious metals rich metallic phases demonstrates high temperature pyrolysis as a viable approach towards the recovery of precious metals from e-waste.

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1. Introduction

The manufacturing of electronic and electrical equipment (EEE) and the associated generation of electronic waste (e-waste) is experiencing a rapid growth due to the high consumption of electronic devices and their early obsolescence throughout the world. The lifespan of most of EEE is considerably shorter now than a decade ago. The emergence of electronics industry has impacted the environment in two different ways: large volumes of e-waste being disposed/or landfilled (this waste stream is increasing by 4–5% every year (Baldé et al., 2015)), and the increasing demand for rare and precious metals from primary resources (Veit and Bernardes, 2015). The disposal of e-waste has several health issues, such as the release of toxic and hazardous compounds, contamination of water, soil and air, and impacts on regions surrounding recycling

facilities. As a number of countries lack regulations regarding e-waste management, especially developing regions of the third world and Africa, operations in informal sectors extract materials from e-waste in an inappropriate manner using methods such as open burning, dumping and digestion in acids. The use of these inappropriate techniques generates significant amounts of secondary wastes and releases pollutants, dioxins and furans which have deleterious impact on the health of people near the recycling areas. There is an urgent need to develop environmentally sustainable approaches towards recycling e-waste and to reduce the amounts of wastes being trashed or landfilled. It is also desirable to prolong the life spans of precious materials in a range of applications and to minimise their loss and to reduce the amount of natural resources being used to manufacture EEE (Veit and Bernardes, 2015).

E-waste is a heterogeneous mixture of materials; its composition is evolving continuously due to rapid upgrades in functions and design of electronic products (Chancerel et al., 2009). Printed

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circuit boards (PCBs), the key central components of electronic equipment, are generally very complex in nature. Several precious metals are present in PCBs in much higher concentrations than typically found in corresponding ores. With appropriate recycling, e-waste could prove to be an important secondary resource of precious metals (Hagelüken, 2006; Teller, 2006). The electronics industry uses significant amounts of precious metals mainly due to their high chemical stability, corrosion resistance and electrical conductivity. These metals are frequently used as contact materials, for electroplating and/or as connectors. Specifically, silver is used in contacts, switches and solders; gold as a bonding wire, contacts and in integrated circuits; palladium in multilayer capacitors and connectors; and platinum in hard disks, for proton exchange membrane fuel cells and in thermocouples. These are also found as plated gold, palladium on copper laminates and plated silver/gold on nickel or iron (Cui and Roven, 2011; Kogan, 2006; Schluep et al., 2009).

Precious and other metal resources for the manufacture of EEE are mainly obtained from their respective primary production routes. The extraction of these metals through mining is associated with several negative features such as extensive land, energy and water usage, gaseous emissions such as SO₂ and CO₂ and the generation of large amounts of secondary solid and liquid wastes. The environmental footprint of the primary production of these metals is high, especially when the concentration of valuable components is quite low and requires the removal of large volumes of material involving several steps of treatment. Primary production is also associated with high levels of greenhouse gas emissions. For example, 1 tonne of gold produced through mining emits ~17,000 tonnes of CO₂, while palladium and platinum respectively produce ~10,000 and ~14,000 tonnes of CO₂ (Chancerel et al., 2009; Schluep et al., 2009). The demand for precious metals for use in electrical and electronic equipment has increased rapidly due to a significant increase in the number of electronic products being manufactured (Schluep et al., 2009). The annual consumption of silver in the electronics industry is currently estimated to be ~7554 tonne (34% of total primary production); the corresponding estimates for Au, Pd and Pt are 327, 44 and 7 tonnes/year are ~13%, 19% and 4% of the total primary production. The cost of these precious metals was estimated to be ~18.9 billion dollars (Reuter et al., 2013; USGS, 2010).

Environmentally sustainable recovery of precious metals from e-waste is also expected to have a significant economic impact. In waste TV boards and DVD players, the typical value of copper and precious metals amounts to ~40% of the total value of the entire device. In spite of the small amounts used, the estimated value of these metals in waste mobile phones and printed circuit boards can be up to 80% of the total worth (Hagelüken and Corti, 2010; Park and Fray, 2009). While the usage of precious metals in EEE has reduced to some extent in the manufacture of new devices, recent hikes in the price of these metals makes their recycling still very appealing. A rough estimate of precious metals present in mobile phones was determined as follows: One tonne of mobile phones without batteries contains 130 kg Cu, 3.5 kg Ag, 340 g Au and 140 g Pd (Schluep et al., 2009). If all mobile phones discarded in 2008 were recycled, a material flow of 1250 tonne Cu, 13 tonne Ag, 3 tonne Au and 2 tonne Pd would be recovered, representing a market value of USD 105 million (Yu et al., 2010).

In addition to economic incentives, several other benefits are associated with the recovery of precious metals from electronic waste. These include a reduction in the wastes being landfilled, resource utilisation, minimisation of gaseous emissions and toxic compounds generated. There are also potentially high savings in energy consumption. Recycling of gold can reduce energy usage by up to 65% as compared with primary production; corresponding energy savings for Pd were estimated to be 14% (Wang and

Gaustad, 2012). The relative concentration of precious metals in printed circuit boards (PCBs) is also much higher than the corresponding concentration in their ores, e.g., the concentration of silver, gold and palladium in minerals is less than 10 g/tonne, whereas in computer printed circuit boards, the typical average is 1000, 250 and 110 g/tonne PCB respectively (Hagelüken, 2006).

In this article, we report a novel approach to significantly concentrate precious metals present in PCB waste, an approach that is cost-effective and will produce minimal secondary waste. An in-depth investigation was carried out on the recovery of Ag, Au, Pd and Pt during the recycling of waste PCBs through high temperature pyrolysis under Ar atmosphere. The influence of copper, the main metal in PCBs, on the concentration of precious metals was investigated in the temperature range of 800–1350 °C. The physical state of copper, whether solid state or molten state, was one of the key experimental parameters. Precious metals recovered from this process can be refined further or be used as a feedstock in other metallurgical recovery approaches. The main focus of this research was on maximising the recovery of precious and other metals from e-waste while causing minimal environmental damage. The expected outcomes will result in to a significant reduction in the amount of wastes being landfilled or processed inappropriately and will also help develop safe practices for managing electronic waste.

2. Previous studies

Several metallurgical and chemical approaches have been used to recover precious metals from e-waste. Some well-known industrial pyro-metallurgical processes that recover these metals are Noranda, Rönnskar and Umicore. In the Noranda process, copper concentrates and e-waste (up to 14 wt.%) are melted at 1250 °C under an oxidising atmosphere. The resulting metallic fraction, composed of Cu and precious metals, is transferred to the conversion process, producing Cu blister with 99.1% purity. The remaining constituents include several precious metals, which can be recovered in subsequent electro-refining (Veldhuizen and Sippel, 1994). The input for Umicore process includes several types of wastes including up to 10 wt.% e-waste. The process is quite similar to Noranda in other aspects with leaching and electrowinning being carried out after conversion. From the resulting sludge, Ag, Au, Pt, Pd, Rh, Ir and Ru can be recovered with up to 99.9% purity. In the Rönnskar process, metal rich e-waste is recycled along with Cu concentrates, whereas the poor quality e-waste is recycled along with Pb concentrates. Black Cu (slag produced in the Pb process line) is later transferred to copper conversion. The product is then electrolytically refined; the generated slime contained Ag, Au and Pt-group metals in a granulated form (Bigum et al., 2012; Cui and Zhang, 2008; Schluep et al., 2009).

A few studies have been reported on the extraction of precious metals from PCBs through pyro-metallurgy. Zhou et al. (2007) heated a mixture of PCBs and 12 wt.% NaOH at 1200 °C. Complexes containing up to 99% Cu, Au and Ag were recovered in the metallic fraction; some slag was also generated as a secondary by-product. Flandinet et al. (2012) mixed molten KOH and NaOH with crushed PCBs and heated at 300 °C under 2 L/h of Ar. The generated metallic fraction (25 wt.%) contained up to 287, 0.959, 0.725 and 0.238 g/kg of Cu, Ni, Au and Ag, respectively. A brown powder containing fluorides, chlorides and bromides was produced (75 wt.%) as a bi-product; some volatile compounds were also released in ppm range.

A number of investigations have been reported on the use of hydrometallurgical techniques to recover precious metals from waste PCBs. Li et al. (2010) dissolved mixed waste PCBs in HNO₃; the leachate was then mixed with a lime-sulphur-synthetic solution (CaS_x/CaS₂O₃, CuSO₄, aqueous ammonia and sodium

sulphite with a pH of 10). The residue contained concentrates of Au (92%) and Ag (90%). A significant amount of spent acids and aqueous solutions were generated during the process. Joda and Rashchi (2012) leached waste PCB pieces into HNO_3 , dissolving Ag, Cu and other base metals and precipitating Au and Pd. The solution was mixed with NaCl to precipitate silver chloride, followed by leaching in KOH and in H_2O_2 , to recover 82.65% of Ag. A residue consisting of plastics and other metals, mercury, lead chloride, an organic phase and spent solutions were generated as secondary bi-products.

Quinet et al. (2005) treated waste mobile phones PCBs by leaching in H_2SO_4 to remove Cu. The residue was leached in a chloride solution to recover Pd, followed by leaching tests with thiourea and cyanide to recover Au and Ag. Best recoveries were achieved with cyanide and activated carbon. An overall recovery of 93% Ag, 95% Au and 99% Pd was achieved. However, a significant amount of spent acids and waste carbons were produced as well as NO gas from the chloride leaching step when HNO_3 was used as an oxidising agent. Sheng and Etsell (2007) leached waste computer PCB samples in HNO_3 , and the generated solids were treated with aqua regia to dissolve Au, which could then be precipitated with ferrous sulphate. Nitric oxide vapours, spent acids and a solid bi-product containing plastics and ceramics were produced as well.

Jing-Ying et al. (2012) leached waste mobile phone PCBs into a thiourea leaching solution to recover gold and silver. Up to 90% of gold and 50% of silver were extracted after 2 h from the solution containing 24 g/L thiourea and 0.6% Fe^{3+} at room temperatures. Behnamfard et al. (2013) leached waste PCBs to recover copper, silver, gold and palladium. The recovery of copper was carried out by dissolving the samples into a solution of sulphuric acid and hydrogen peroxide. The residue was then leached in a thiourea solution in the presence of Fe^{3+} , recovering up to 85.76% Au and 71.36% Ag. The resulting solid fraction was then leached in a $\text{NaClO}-\text{HCl}-\text{H}_2\text{O}_2$ solution to recover Pd and remaining gold. Best results were obtained with 5 M HCl, 1 V% H_2O_2 , 10 V% NaClO at 336 K for 3 h with a solid/liquid ratio of 1:10, recovering 100% of Pd and Au by precipitating them with sodium borohydride.

Two leaching solutions were used by Birloaga et al. (2014). Waste PCBs were first leached into a 2 M sulphuric acid solution 98% w/v, in the presence of 5% H_2O_2 at 25 °C, 1:10 S:L ratio and 200 rpm to recover 100% copper. The remaining solid was then leached into a thiourea solution of 20 g/L of $\text{CS}(\text{NH}_2)_2$, 6 g/L of Fe^{3+} , 0.5 M H_2SO_4 . A cross-leaching method was carried out, where the spent thiourea solution and 5 g/L of the reagent were used to leach the samples. Concentration of Au was found to have doubled with this treatment, while the recovery of silver had tripled. Some patents have also developed a process to recover precious metals, however, these generally generate aqueous residues during the recycling process (Kogan, 2006; Olper et al., 2004). In addition to the recovery of precious metals, the leaching of copper has also been extensively studied (Chen et al., 2015; Huang et al., 2014).

Few studies have also investigated the use of biometallurgical processes, such as bioleaching (bacteria) and biosorption (algae, bacteria, yeasts and/or fungi) for the recovery of precious metals from e-waste (Cui and Zhang, 2008). Côrtes et al. (2015) investigated the biosorption of gold from waste PCBs by using chitin as a biosorbent. The leaching solution was composed of 50 g/L thiourea and 15 g/L aqueous ferric sulphate. Gold had precipitated out while other constituents had been dissolved in the solution. Biosorption was carried out by using 20 g/L chitin at 25 °C for 4 h; up to 80% gold was recovered in this case. Other studies have used bioleaching to recover copper and precious metals from waste PCBs (Adhapure et al., 2014; Arshadi and Mousavi, 2015; Rodrigues et al., 2015).

While the recovery of precious metals from PCBs has been the focus of several investigations, most of these processes require further improvement and optimisation. There are also several limita-

tions associated with these techniques. Hydrometallurgical and bio-metallurgical processes produce large quantities of secondary by-products during recycling, such as spent acids, sludges, and volatile compounds that may cause significant environmental and health damage. These methods could involve several process steps and a long time may be required to achieve the overall recovery. If e-waste is processed inappropriately during pyrometallurgical treatments, toxic gases, heavy metals and several pollutants would be emitted along with the generation of secondary waste products (Khanna et al., 2014).

This investigation has focussed on the influence of metals in e-waste such as 'copper' on the recovery of precious metals such as Ag, Au, Pd and Pt. from waste PCBs during high temperature pyrolysis. It was expected that the extraction of several metals would be influenced to a great extent by their interaction with major metals present in e-waste. The temperatures were chosen to lie below (800 °C, 900 °C, and 1000 °C) or above (1150 °C, 1250 °C, and 1350 °C) the melting point of copper. This range of temperatures was chosen as these were high enough to achieve the separation of the metallic phase from the carbonaceous/slag residue (Cayumil et al., 2014), thereby reducing the presence of impurities and other materials in copper based products as well as to avoid the formation of harmful dioxins and furans. Inert atmosphere was used to prevent the re-oxidation of metals and the burning of carbons (Cayumil et al., 2014). The influence of polymers and ceramics on the recovery of precious metals has also been investigated.

3. Experimental

A schematic representation of the experimental arrangement is given in Fig. 1. High temperature pyrolysis was carried out in a horizontal tube furnace of 1 m length, 5 cm internal diameter and 5 mm wall thickness, which was maintained at the specific operating temperature (800–1350 °C). The lowest temperature chosen was 800 °C as it was high enough to prevent dioxin and furan formation as indicated by several studies in the literature (Ishida et al., 1998; McKay, 2002; Stieglitz and Vogg, 1987). The outermost end of the furnace, labelled as 'cold zone', was maintained at a temperature of ~200 °C. Specimens used were mixed computer waste PCBs manually crushed to sizes of ~1 cm² and mixed thoroughly. These were composed of several PCB pieces with a total weight of ~2 g. Waste PCB chips were placed on an alumina crucible, positioned into the sample tray on the graphite rod, pushed into the cold zone of the furnace and held there for 10 min to avoid thermal shock. The rod was then pushed to the hot zone of the furnace maintained at the desired experimental temperature and kept there for 10 min. The heat treated samples were then pulled back to the cold zone and kept there for another 10 min to prevent the re-oxidation of products and thermal cracking. The working region was continuously purged with high purity Argon with a flow rate of 1 L/min. Two filters (5 µm and 0.625 µm) were placed in the gas outlet to capture fine particulates in the gaseous fraction. Experiments were repeated at least five times at each temperature with chips from different PCBs to enhance the reproducibility of results as the composition of specimens could have a high variability depending on the initial composition of waste PCBs.

Samples before the heat treatment are shown in Fig. 2A. Reaction products had phase separated during the heat treatment into a carbonaceous fraction (Fig. 2B) and metallic products in the form of droplets/wires/foils (Fig. 2C–E). The chemical composition of these solid products was determined using Inductively Coupled Plasma Optical Emission Spectrometers model Perkin Elmer Optima 7300DV ICP-OES. Other standard analytical techniques

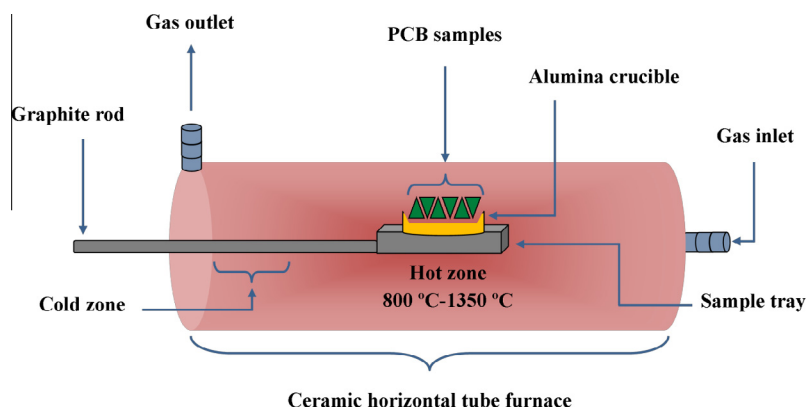


Fig. 1. A schematic representation of the experimental arrangement.

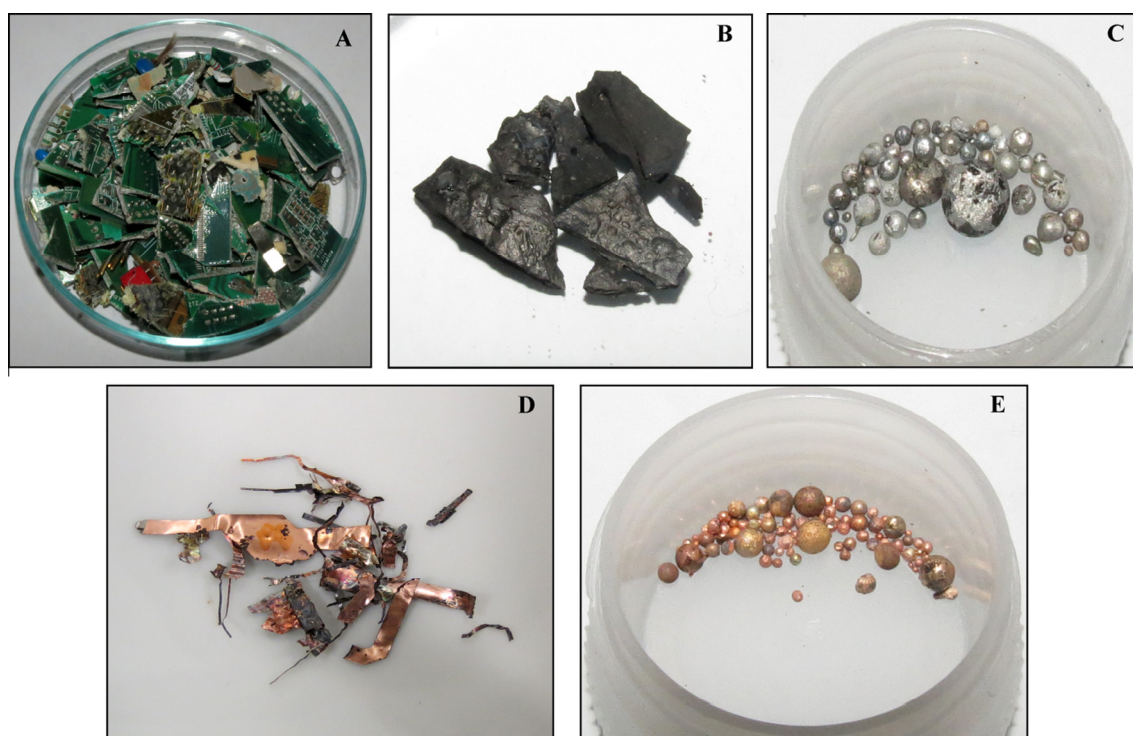


Fig. 2. (A) Crushed PCB samples before heat treatment, (B) carbonaceous/slag phase obtained after various heat treatments, (C) typical representation of tin–lead rich metallic phase obtained after heat treatments at 1150 °C, (D) typical representation of copper rich metallic phase obtained after heat treatments at 800 °C, and (E) typical representation of copper rich metallic phase obtained after heat treatments at 1150 °C.

such as SEM/EDS and XRD could not be used in this investigation due to very small concentration levels of precious metals.

4. Results

This investigation was focused on the extraction of precious metals during high temperature pyrolysis of waste PCBs and to determine their distribution into various reaction products of the heat treatment. Copper being the main metal present in waste PCBs, the extraction of other metals/materials was influenced to a great extent by their interaction with copper. Depending on their affinity, copper was seen to absorb certain metals while expelling others. Operating temperatures were chosen to lie below and above the melting point of copper (1084.87 °C) to study the influence of the physical state (solid or molten) of copper on the capture

of precious metals such as silver, gold, palladium and platinum. The use of inert atmosphere was also a key feature of these investigations as it prevented the re-oxidation of metals and the combustion of carbons while significantly reducing the associated generation of greenhouse gas emissions. These process conditions led to the generation of three types of products over the range of temperatures investigated: a carbonaceous/slag residue (shown in Fig. 2B) and 'red' and 'white' metallic phases (Fig. 2C–E). At temperatures ≤ 1000 °C, the 'red' fraction was predominantly found in the form of foils (Fig. 2D); however, a few droplets were also observed at 1000 °C thereby indicating a partially molten state. While the 'white' fraction was composed mainly of metal droplets, a few wires were also obtained (Fig. 2C). At temperatures ≥ 1150 °C, both 'red' and 'white' phases were found in the form of metal droplets (Fig. 2C and E).

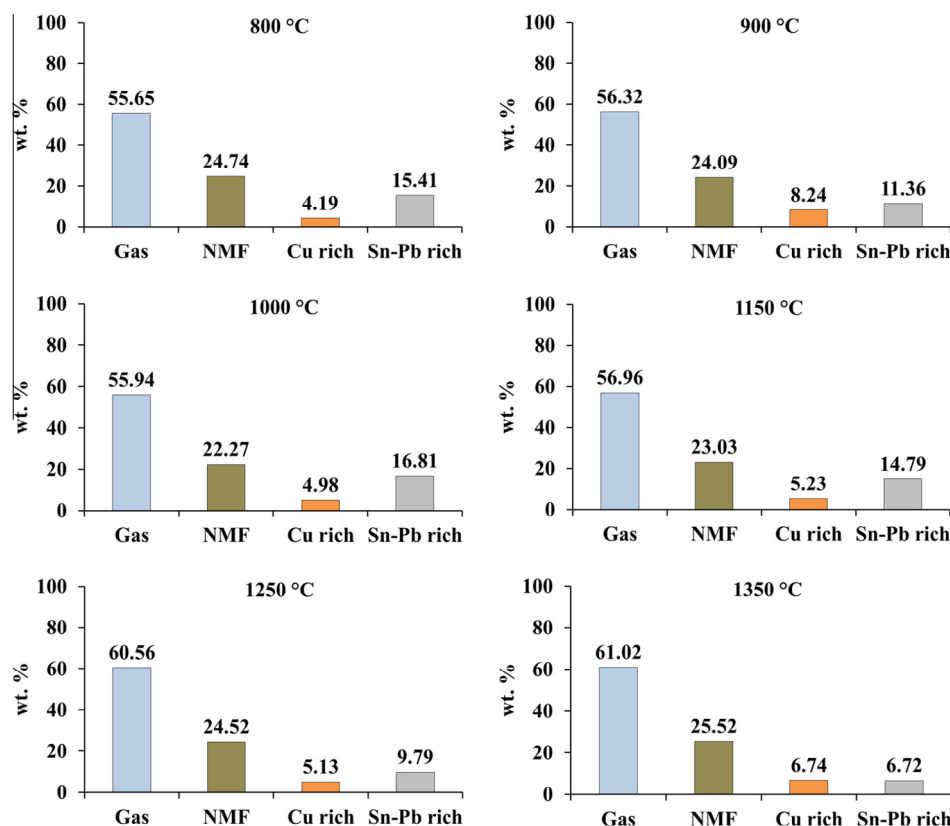


Fig. 3. Weight proportion of gaseous, copper rich, tin-lead rich and non-metallic fractions generated over a range of temperatures.

Fig. 3 shows the relative weight proportion of various fractions produced after the heat treatments. While the gaseous fraction typically corresponded to ~56–61% of the initial weight of the sample, around 22–25% of the waste PCBs had phase separated as a carbonaceous slag residue. The 'red' metallic phase was found to weigh between 4% and 8%, and the 'white' metallic fraction was ~7–17%. Detailed ICP-OES analysis was carried out to determine the chemical concentrations of various products after heat treatments. These results are presented in Fig. 4. Results show that the main metallic constituents were copper, tin and lead. Red fractions were found to be copper rich with very small concentrations of Sn and Pb. While white phases generally had high concentrations of both tin and lead, a significant amount of copper was also present in this phase. Precious metals were found distributed within all three phases, but tended to concentrate predominantly in the two metallic fractions. A very small proportion of precious metals was observed in the carbonaceous/slag residue (NMFs). This data is presented in a tabular form in Figs. 5–8. It is important to note that these values represent a typical case scenario: exact amounts recovered will depend strongly on the corresponding initial concentration in the waste product. These values also do not represent average values as a mix of motherboards were used in this investigation. The distribution may also not be uniform across various waste PCBs. The reported values therefore show the probable distribution of various precious metals among the three phases and provide general tendencies regarding their segregation in ceramics/polymers and other metals present in waste PCBs.

PCBs are a heterogeneous mixture of ceramics, polymers and metals. The process conditions chosen in this investigation led not only to the separation of various phases, but also to the concentration of most metals in the two metallic fractions. A significant amount of precious metals were observed to concentrate into the

copper rich and tin-lead rich fractions, thereby making it much easier to extract valuable metals from waste PCBs. This also resulted in significantly reducing the volume of material for further processing/refining and final recovery. As seen in Fig. 3, the weight of the metallic fraction, where most of the metallic constituents were concentrated, was around 20% of the initial sample. Assuming a minimal loss of precious metals into the gaseous fraction, the relative weight proportion of silver, gold, palladium and platinum into the three solid fractions was computed. Detailed results on their distribution behaviour are presented in the following sections.

4.1. Distribution behaviour of silver

Silver was found distributed among the three solid phases generated after heat treatments at a range of temperatures (Fig. 5B). Observed relative proportions of silver (Fig. 5A) showed that its presence in the non-metallic fraction was significantly lower than the amounts observed in both copper rich and tin-lead rich metallic phases across all temperatures. Quantitative results on silver showed that at 800 °C, 900 °C, 1000 °C – when copper was still in the solid state – a much larger proportion of Ag was found within the Sn-Pb metallic fraction. These results indicate that Pb might have acted as a collector metal for Ag.

At 800 °C, nearly 90.4% of the total silver present in the sample was in the tin-lead fraction, thereby indicating silver preferred to concentrate in this metallic phase. At 900 °C and 1000 °C, while the relative proportions of silver were still higher in the Sn-Pb fraction as compared to the copper rich phase, i.e. 66.5% and 80.5%, respectively, its corresponding concentration in the Cu rich phase showed a moderate increase (Fig. 5A). There is a limited solubility of silver in copper in this range of temperatures

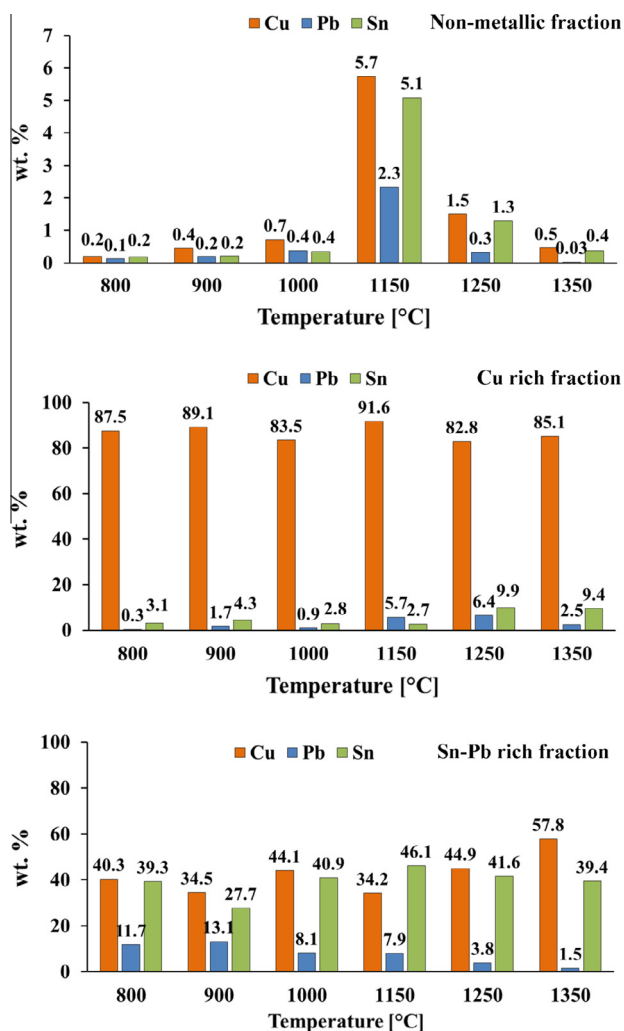


Fig. 4. Main metals (Cu, Sn and Pb) present in the non-metallic fraction, copper rich and tin-lead rich metallic fractions as a function of temperature.

(Subramanian and Perepezko, 1993). However, it can be seen from the Sn–Ag–Pb phase diagram, the system is in a molten state in this temperature range. Therefore Ag is likely to dissolve in the molten Sn–Pb phase rather than in the solid copper phase (Effenberg and Ilenko, 2006). Observed results on silver segregation therefore agree well with the expected phase behaviour. At higher temperatures (≥ 1150 °C) copper is also in the molten state, and the relative concentrations of silver were found to increase in this fraction. Silver concentrations in the copper rich phase showed an increase to 79.2%, 89.8% and 60.3% of the total silver content in the temperature range 1150–1350 °C. When both phases are in a molten state, Ag appears to have a preference for the copper rich phase over the lead rich phase.

A very small amount of silver was observed in the NMFs, which indicates a low affinity of silver with carbon or ceramics. These results also show that lower temperatures (800 °C) could be used for the recovery of precious metals from e-waste. This important aspect can help lower energy consumption during recycling as most of Ag could be recovered at these temperatures and higher temperatures may not be necessary. With most of the silver concentrated within the metallic fraction (~20% of the total pyrolysis residue), this result indicates a significant reduction in the waste volumes being processed for further refining.

4.2. Distribution behaviour of gold

Fig. 6 shows the distribution of gold in the three solid fractions generated after heat treatments. The gold concentration was found to be very low after heat treatment at high temperatures (1150 °C, 1250 °C, and 1350 °C) and its presence could not be detected accurately by ICP analysis. Therefore no comments can be made regarding distribution tendencies for gold at these temperatures. At temperatures ≤ 1000 °C, the relative proportions of gold in the non-metallic fraction were once again much smaller than in both metallic products. At 800 °C, 99.9% of the total gold was concentrated within the copper rich fraction and negligible levels of metal were present in the tin-lead phase. The Cu–Au binary phase diagram shows that these two metals are completely miscible in each other, with gold dissolving in copper when the concentration of copper is high (Okamoto et al., 1987). However due to small concentrations of gold present, it is unlikely that these two metals would form intermetallic compounds. Due to their high affinity, most of the gold present in the sample was found in the copper rich fraction at 800 °C. However, at 900 °C, gold was found almost equally distributed in the two metallic fractions, while at 1000 °C gold showed a higher tendency of getting concentrated in the tin-lead phase, with a 67.1% of the total amount of gold found in this phase. This aspect could also have been influenced by the higher copper concentration in this fraction.

Both silver and gold have a high affinity with copper as indicated in their corresponding phase diagrams. In pure systems, both gold and silver are completely miscible, and will form solid solutions over a wide range of temperatures and composition (Okamoto and Massalski, 1983). Initial diffusion and subsequent concentration of gold and silver in both metallic fractions appears to be unaffected by the presence of impurities, such as polymers and ceramics present in waste PCBs.

4.3. Distribution behaviour of palladium and platinum

Similar to the behaviour observed for both silver and gold, palladium was found mainly in the metallic products (Fig. 7). It was distributed preferentially in the copper rich fraction than in the tin lead rich fraction at all temperatures of heat treatment by a factor of 3:2. Very small amounts of Pd were observed in the NMFs (Fig. 7A). In pure systems, Pd and Cu are completely miscible with each other. In the presence of high concentrations of copper, palladium is likely to dissolve in copper forming solid solutions (Subramanian and Laughlin, 1991).

While most of the platinum was found in both copper rich and tin-lead rich metallic fractions, slightly larger proportions of platinum were observed in the NMFs as compared with other three metals (Ag, Au, Pd). There was no preferred tendency for platinum to choose either of the two metallic fractions. At 800 °C, Pt content (78.5%) in the copper rich fraction was much higher than in the NMF and the Sn–Pb phase. However at 900 °C, the concentration of platinum was considerably higher in the Sn–Pb fraction (56.8%). At 1000 °C, the relative proportion of the metal was once again higher in the copper rich product (56.6%). Upon increasing the temperature to 1150 °C, the proportions of Pt were almost equally distributed in both metallic phases. While a similar result was obtained at 1350 °C, the Pt content was found to be higher in the copper rich fraction at 1250 °C, with 69% of Pt found concentrated into this product.

According to the Cu–Pt phase diagram, there is complete solubility of Pt in Cu in both molten and solid states for Pt concentrations up to ~10% (Predel, 1994). With typical Pt concentration in ppm levels, the formation of intermetallic compounds with copper is once again quite unlikely. When the system has high concentrations of Sn and Pb, Pt can also dissolve in these metals due to their

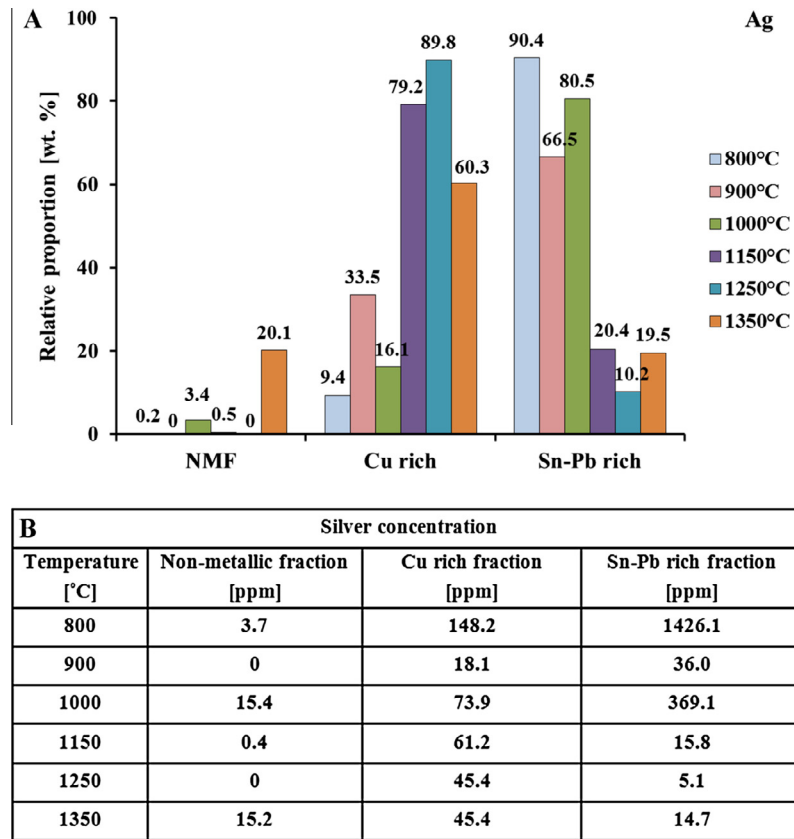


Fig. 5. (A) The proportion of silver distributed among the non-metallic fraction (NMF), copper rich and tin–lead rich metallic fractions as a function of temperature, and (B) concentrations of silver in the non-metallic fraction, copper rich and tin–lead rich metallic fractions obtained after various heat treatments.

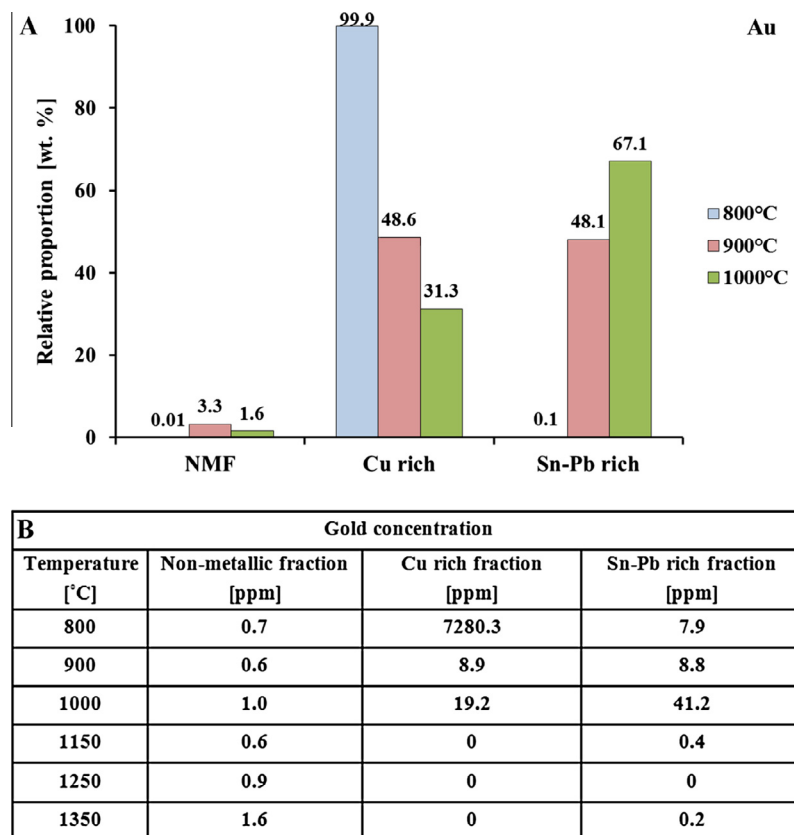


Fig. 6. (A) The proportion of gold distributed among the non-metallic fraction (NMF), copper rich and tin–lead rich metallic fractions as a function of temperature, and (B) concentrations of gold in the non-metallic fraction, copper rich and tin–lead rich metallic fractions obtained after various heat treatments.

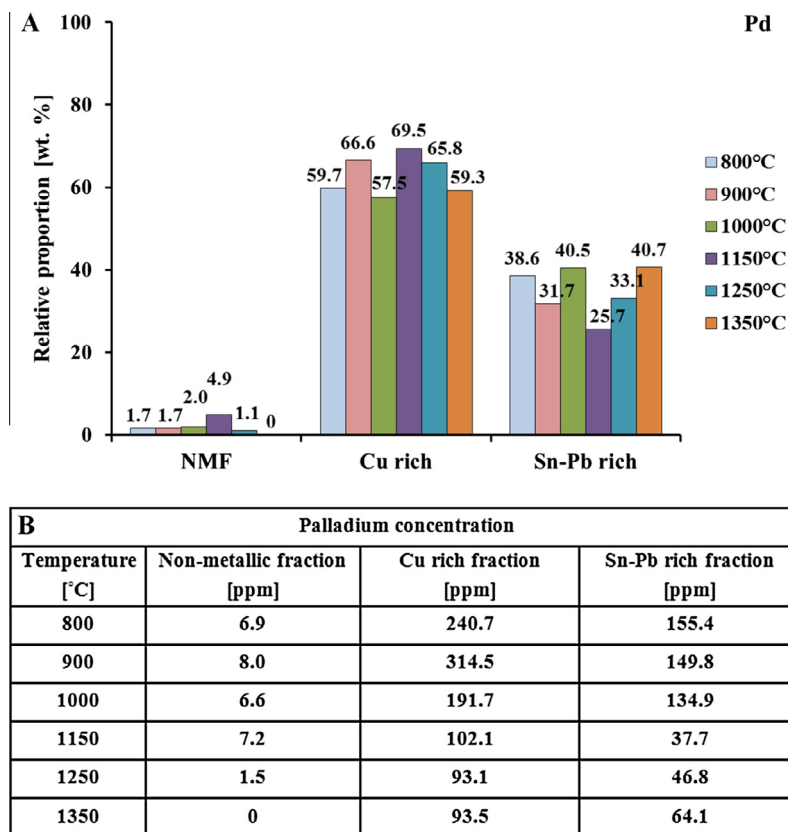


Fig. 7. (A) The proportion of palladium distributed among the non-metallic fraction (NMF), copper rich and tin-lead rich metallic fractions as a function of temperature, and (B) concentrations of palladium in the non-metallic fraction, copper rich and tin-lead rich metallic fractions obtained after various heat treatments.

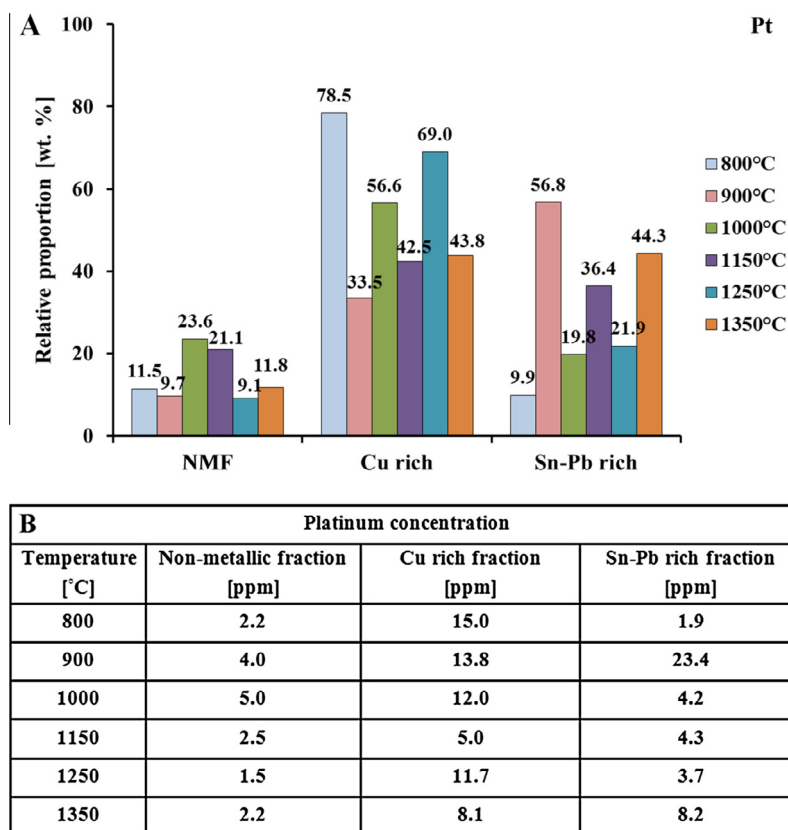


Fig. 8. (A) The proportion of platinum distributed among the non-metallic fraction (NMF), copper rich and tin-lead rich metallic fractions as a function of temperature, and (B) concentrations of platinum into the non-metallic fraction, copper rich and tin-lead rich metallic fractions obtained after various heat treatments.

molten state in the range of temperatures studied. Some amounts of Cu present in this fraction would help absorb platinum as well. Platinum, therefore, showed no preference for either of the two metallic fractions.

In a behaviour similar to that observed for Au and Ag, both Pt and Pd appear to act as a couple. As seen from the Pt–Pd phase diagram, these are completely miscible in the molten as well as solid states (Okamoto, 1991). As both of these belong to the platinum-group of metals, they also have similar features. In pure systems, the affinity between copper and precious metals is well-known. This behaviour may not be replicated in a complex system such as in waste PCBs, as heterogeneous components, including ceramics and polymers were present and mixed along with metals. However, carefully chosen process conditions led copper and precious metals to behave in a fashion similar to that observed in pure systems or ores. When the phase separation occurred, precious metals tended to form either solid and/or liquid solutions with the metallic phase. Limited amounts of these metals retained in NMFs could also be attributed to the small amounts of metals present in this fraction. Ceramics and polymers were not observed to have much influence on the extent of metal extraction or on the relative concentration of precious metals in the metallic fraction.

5. Discussion

During high temperature pyrolysis under inert conditions, the waste PCBs had transformed into copper and lead rich metallic fractions, carbonaceous ceramic residue and a gaseous fraction. This also resulted in an effective concentration of precious metals present in waste PCBs in a much reduced volume of metallic fractions. Our results show that precious metals were mainly accumulated in the metallic phase and very small concentrations were retained by oxides/carbons present into the non-metallic fractions of e-waste. The concentration of precious metals into the metallic fraction makes these metals easily extractable and suitable for further refining. A good example for refining these metals will be copper production processes, as precious metals remain together with copper up to the end stages of the process due to their strong affinity and limited or null affinity with oxides present in slags. The advantages of this approach include significant volume reductions, with no additional generation of secondary by-products such as spent acids and sludges.

When exposed to oxidising atmospheres, such as air or enriched in oxygen, platinum-group metals tend to form volatile compounds at temperatures much higher than the range used in this investigation (Alcock and Hooper, 1960; Jehn, 1984). The formation of these compounds is significantly reduced under vacuum or inert atmospheres, thereby preventing the loss of Pd and Pt (Fromm, 1978; Jehn, 1981, 1984). These metals have low vapour pressures in the temperature range 800–1350 °C (Alcock et al., 1984), with minimal losses in the gaseous fraction. These metals are highly stable and are used in high temperatures applications such as heating elements and thermocouples in the metallic form or as complexes (Habashi, 1997).

Both silver and gold have low melting points (962 °C and 1065 °C, respectively) (Cotton, 1997); these were in the solid as well as in molten states in the temperature range investigated. These metals have a high affinity for lead which can act as a collector metal for their absorption and extraction from e-waste. If the experimental temperature were too high, the volatilisation of lead can lead to a loss of silver (Habashi, 1997). Silver itself has a tendency to volatilise at high temperatures, and has one of the highest vapour pressures in the group of metals studied. However its vapour pressure is quite low at 800 °C. Therefore to

prevent the loss of silver into the gaseous fraction and to maximise its recovery it is desirable to maintain low working temperatures. Gold itself has a relatively lower vapour pressure with low risk of volatilisation (Alcock et al., 1984). Nanda et al. did not detect any particles of gold in the gaseous fraction at 1300 °C (Nanda et al., 2007).

It was observed that Au, Ag, Pd and Pt had a high affinity with the main metals present in waste PCBs. These metals acted as collectors/solvents, capturing precious metals into their molten/solid states. The vapour pressure of copper being quite low, the risk of volatilisation was low when these metals were absorbed by copper (Alcock et al., 1984). However, when the metals were absorbed by lead, which is highly volatile, a fraction of these can get lost in the gaseous phase. To reduce/prevent the volatilisation of lead and the associated loss of precious metals, it is recommended that the recovery be carried out at low temperatures, where lead has a much lower vapour pressure. As these operating temperatures were high enough to prevent the formation of dioxins/furans, the environmental impact of e-waste recycling will also be much reduced. It is to be noted that the overall energy consumption of recovering these precious metals from waste PCBs is expected to be much lower than the corresponding energy consumed during their primary production from ores.

6. Conclusions

A number of novel findings were obtained in this investigation. A range of precious metals present in waste PCBs, i.e. silver, gold, palladium and platinum, showed a clear tendency to form solutions with the main metallic constituents of waste PCBs, namely copper, tin and lead. High affinity between copper and these precious metals led to their effective concentration. A much smaller proportion (up to 5–20%) of precious metals was found in the non-metallic fraction after a range of heat treatments in the temperature range (800–1350 °C). Their limited affinity with ceramics/carbons prevented their concentration and loss in NMFs; and low operating temperatures further reduced the loss of precious metals into the gaseous fraction. The presence of a number of impurities in waste PCBs also did not appear to have much influence on the concentration of precious metals into the metallic fraction. These metals were generally found to behave in a manner quite similar to that observed in pure systems. This study has demonstrated the successful use of high temperature pyrolysis for the recovery of valuable materials from the recycling of printed circuit boards. This process has effectively concentrated several precious metals and significantly reduced the volume of material for further refining and recovery. This study provides further evidence for the use of inert conditions and controlled temperatures for the generation of valuable products from the recycling of waste PCBs, with significantly reduced amounts of secondary wastes (Cayumil et al., 2014; Sahajwalla et al., 2015).

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Copper leaching from electronic waste for the improvement of gold recycling



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ABSTRACT

Gold recovery from electronic waste material with high copper content was investigated at ambient conditions. A chemical preliminary treatment was found necessary to remove the large quantities of copper before the precious metal can be extracted. For this purpose inorganic acids (HCl, HNO₃ and H₂SO₄) and two organic substances EDTA and citrate, were tested. The effect of auxiliary oxidants such as air, ozone and peroxide hydroxide was studied. In pretreatments with peroxide and HCl or citrate, copper extractions greater than 90% were achieved. In the second leaching stage for gold recovery, the solid residue of the copper extraction was contacted with thiourea solutions, resulting in greater than 90% gold removal after only one hour of reaction.

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1. Introduction

In recent years, two simultaneous and contradictory tendencies have occurred world-wide: the first is a renewed interest in environmental protection seeking environmental sustainability, while the second is an exponential increase in the acquisition of electronic devices. Generally, these devices are manufactured using a variety of new materials, rare earths elements, alloys and/or precious metals. Some components, if not disposed of or recycled properly, can generate toxic substances, such as BFR's, Sb, Ni, and Pb, causing environmental problems (Kiddee et al., 2013).

The solution to this paradox, at least partially, involves recovering these metallic values from electronic residues, in this study called EW-PCB (acronym for Electronic Waste from Printed Circuit Boards). A variety of methodologies have been employed to recover especially the precious metals, included in the waste material generated by the constant renovation of electronic devices. The electronic waste usually consists of extremely irregular mixtures of several types of materials, which include polymers, metals and fiberglass.

The electronic components or printed circuits consist of in a polymeric substrate upon which copper is deposited. The majority include a very thin precious metal coating, in order to increase the

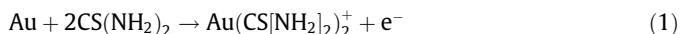
service life (from corrosion and wear) of the elements, such as connectors. In general, the preferred metal for this purpose is gold. Some studies have demonstrated that, in addition to copper and gold, a common electronic card can contain up to 15 additional metals, either in elemental form or as alloys (Cui and Zhang, 2008; Tuncuk et al., 2012; Yang et al., 2011). It is important to note that most of the residues generated by this type of components contain polymers, which can generate an enormous environmental impact, if they are processed by smelting (Guo et al., 2015).

Different process routes for the gold recovery from electronic waste have been reported (Behnamfard et al., 2013; Birloaga et al., 2014a,b). These treatments include total fusion stage, followed by leaching and recovery of metal values (Cui and Zhang, 2008; Guo et al., 2015; Tuncuk et al., 2012). Other authors employ ionic liquids, mixed with acids, to leach base metals (Chen et al., 2015). Precious metals aqueous processing includes the leaching stage with solutions of thiosulfate, thiocyanate, thiourea, cyanidation or total digestion by aqua regia (Akcil et al., 2015; Syed, 2012). Of these, thiourea has several advantages over the others, the most important of which are the high processing rate and the capacity to recycle the solution once the metal values are stripped or precipitated (Poisot-Díaz et al., 2008). In order to design a eco-friendly procedure for recycling the metallic content of electronic waste, specifically for gold, the traditional methods (with aqua regia or cyanidation) should not be considered (Akcil et al., 2015).

The anodic reaction (Eq. (1)) between metallic gold and thiourea can be expressed as follows:

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However, this methodology presents the disadvantage that copper is a metal that consumes and degrades thiourea (Behnamfar et al., 2013; Birloaga et al., 2014a,b; Syed, 2012). For this reason, a preliminary treatment is required to remove the majority of copper present in the EW-PCB, before leaching with thiourea (or other agents). In this manner, the metallurgical extraction of noble metals can be effectively accomplished.

For copper extraction from EW-PCB, leaching procedures based on the use of inorganic acids have shown acceptable results. However, in most cases, elevated acid concentrations (up to 2.5 M), considerable quantities of oxidants (up to 15% by volume) and process temperatures above 70 °C were necessary (Calgaro et al., 2015; Ghosh et al., 2015; Silvas et al., 2015). In general, these procedures do not take into account the large amount of liquid and solid waste generated and its management. The present study proposes to demonstrate that less contaminating aqueous processes at more moderate operating conditions, with recovery efficiencies similar to the more traditional methods, can be developed. The principal advantages sought after are the following: low toxicity, possibility of solution re-utilization and ease of management. The principal objective of the study consists on the selective extraction of the majority of copper from the EW-PCB residues, through the use of both conventional inorganic acids as well as carboxylates such as EDTA (diaminoethanetetraacetic acid) and citrate (trisodium 2-hydroxypropane-1,2,3-tricarboxylate), focusing on the improvement of the subsequent precious metals extraction in a thiourea leach of the pretreated materials. The influence of the inorganic acid concentration, in combination, with different oxidizing agents (air, hydrogen peroxide and ozone), on the copper leach will be presented. For the carboxylate systems, the effect of solution pH and reagent concentration will be analyzed. Finally, results of the gold extraction with the thiourea solution will be compared for the most successful pretreatment residues.

2. Material and methods

The study was performed using electronic waste with high copper contents. The electronic components were manually separated from each of the printed cards (EW-PCB), leaving only the substrate with traces of welding (Fig. 1). Once selected, a preliminary milling was performed and the EW-PCB was classified by particle size. Finally, a total digestion with aqua regia was carried out for each particle size and the elemental analysis determined by atomic absorption spectrometry (Varian SpectraAA 220fs).

The chemical pre-treatment for copper removal was accomplished using solutions formulated with analytical grade (J.T. Baker) inorganic acids and organic sodium salts (EDTA and citrate) at

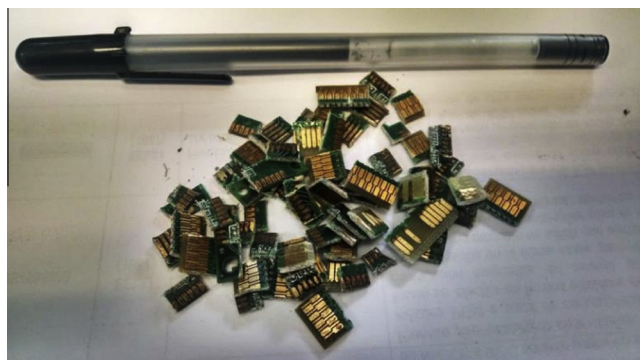


Fig. 1. Example of the unground EW-PCB material used in the experiment.

specific molar concentrations for each experiment and diluted with deionized water (millipore Milli-Q). Atmospheric air (without treatment) was supplied by an adjustable pump at a gas flow rate of 1 L/min. In those experiment requiring hydrogen peroxide, the dosification was practiced using the standard reagent grade (30% w/v, J.T. Baker). The ozone injected into the system was generated in-situ and sparged into the pretreatment solution/EW-PCB mixture. Medicinal grade oxygen (99%, Praxair) was passed through a UV lamp (185 nm) at a flowrate of 1 L/min to produce a constant oxygen-ozone supply, equivalent to 175 mg_{ozone}/L_{dissolution} min.

To determine the conventional behavior in each of the acids during leaching, treatments were performed with constant stirring for 24 h at a concentration of 1 M for each acid. Since the objective of this study consists of analyzing the behavior of inorganic acids in the presence of additional agents, many of leaching parameters, such as temperature and stirring velocity, were held constant.

All leaching experiments were performed in triplicate at 25 °C and ambient pressure, using a mechanical agitation of 125 rpm, with a constant solid-liquid ratio of 20 g EW-PCB per liter of leaching solution. In those tests where gas was sparged (either air or air/ozone mixtures), a Graham condenser, cooled with commercial ethylene glycol (30% by weight) at a temperature of 0 °C, was employed to avoid evaporation of the solution during the leaching process.

The leaching solutions were prepared with the required acid or reagent concentration. For the organic acid tests, the solution pH in each case was adjusted with H₂SO₄. Subsequently, the specific amount of solid (EW-PCB) was added corresponding to the volume of solution employed. In each case, the experiment was initiated upon the commencement of the gas sparge and/or the dosification of peroxide, after which time liquid samples were withdrawn at predetermined intervals. Upon termination of the experiment, the liquid-solid suspension was filtered and air dried. The quantification of metals (copper or gold) in the filtered leach liquor and in the aliquots taken during the process was performed using atomic absorption spectrometry (Varian SpectraAA 220fs). The experimental values reported, both in numerical and graphical form, correspond to the arithmetic averages of the results obtained in triplicate at the specific operating conditions; the error was also incorporated into the table and figures.

All thermodynamic data used in the document were obtained from the NIST database (Database 46–Vers. 8.0). The corresponding diagrams were designed using the MEDUSA© software (Making Equilibrium Diagrams Using Simple Algorithms) (Eriksson, 1979; NIST, 2004; Puigdomenech, 2004).

3. Results and discussion

3.1. Distribution of metal content

The EW-PCB solid samples were digested and analyzed to establish the total amount of metals for several size fractions, which in most cases exceeds 84% of the total weight of the material (Table 1). The preliminary selection by size indicated that gold, as

Table 1
Average chemical content for the principal metals in the EW-PCB with respect to particle size.

Particle size (μm)	≥500	500–400	400–177	<177
Cu (kg/t)	960.0 ± 0.2	898.9 ± 0.2	848.1 ± 0.1	851.1 ± 0.1
Au (g/t)	83 ± 2	48 ± 2	200 ± 1	108 ± 2
Ni (g/t)	169 ± 2	169 ± 2	183 ± 2	13 ± 2
Zn (kg/t)	1.13 ± 0.21	0.97 ± 0.16	1.63 ± 0.11	1.71 ± 0.16
Fe (kg/t)	2.05 ± 0.53	1.97 ± 0.76	10.87 ± 0.33	4.68 ± 0.47
Pb (kg/t)	2.23 ± 0.88	4.76 ± 0.95	1.48 ± 1.13	2.76 ± 1.07

well as zinc, iron and lead have no uniform or homogeneous distribution with respect to particle size.

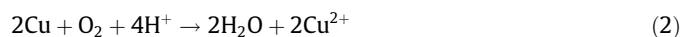
This may occur for three reasons: first the manufacturing process of the same EW-PCB components is heterogeneous in content; secondly, the mechanical behavior of metals in their elemental form or as alloys is different and therefore when milling (and classification) is performed, each metallic substance behaves differently, in some cases with fracturing (reduction in size) and with other plastic deformation (shape change). Several authors have studied these mechanical effects and have proposed methods for grinding and classification (Bachér et al., 2015; Chao et al., 2011). Finally, it should be kept in mind that all EW-PCB are mixtures of different equipment and components, which generally have a random chemical composition, depending on their source (PC, mobile phone, music players, etc.) (Hagelüken and Corti, 2010).

The largest particle size range ($\geq 500 \mu\text{m}$) was selected for leaching copper with various reagents, due to its high metal content. The two-stage tests, (a pretreatment for copper followed by gold leaching) were performed exclusively with the 177–400 μm particle size interval, given its elevated gold content.

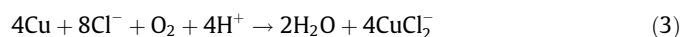
3.2. Copper leaching with inorganic acids (HCl, HNO₃ and H₂SO₄)

3.2.1. Inorganic acid leaching in the presence of air (without the use of additional oxidants)

It is well known that the three inorganic acids can chemically attack metallic copper in the presence of dissolved oxygen (Eqs. (2) and (3)). High acid concentrations provide an adequate amount of hydronium ions and continuous stirring of the solid-liquid mixture can improve the incorporation and dissolution of oxygen gas in the liquid.



For HCl, the following reaction can also take place:



The $\text{Cu}^{2+}/\text{Cu}^+$ redox couple is stable in chloride media and is, in itself, capable of oxidizing metallic copper. Furthermore, the cupric ion is constantly regenerated by the presence of dissolved oxygen. Therefore, it can be considered an auxiliary oxidant in this solution. On the other hand, the chemical system with sulfuric acid has a lower copper leaching capacity from EW-PCB because it does not possess the same oxidizing power.

However, the similar linear tendencies observed for both nitric and hydrochloric acids during the processing (Fig. 2) suggest that the reaction rate is controlled by the mass transfer of oxygen; if this were the case, a higher leaching velocity can be achieved if oxygen is supplied to the system, ensuring an increased amount of dissolved oxygen. Similarly, the oxygen may be replaced by another oxidizing substance to enable effective dissolution of metallic copper. These auxiliary agents selected were air sparging, hydrogen peroxide dosage and sparging of an ozone-oxygen mixture.

3.2.2. Inorganic acid leaching with air sparging

Preliminary tests indicated that air sparging does not significantly improve ability of the sulfuric acid to leach copper. For that reason leaching experiments with auxiliary agents in sulfuric acid were not included in this document. Several studies have demonstrated by using at higher acid concentrations, increased temperatures (up to 75 °C) and additional oxidants (240 mL H₂O₂ per liter of leaching solution), it is possible to completely leach metals from EW-PCB (Birloga et al., 2014a,b; Kamberovic et al., 2010). However, it is not clear whether these operating parameters permit

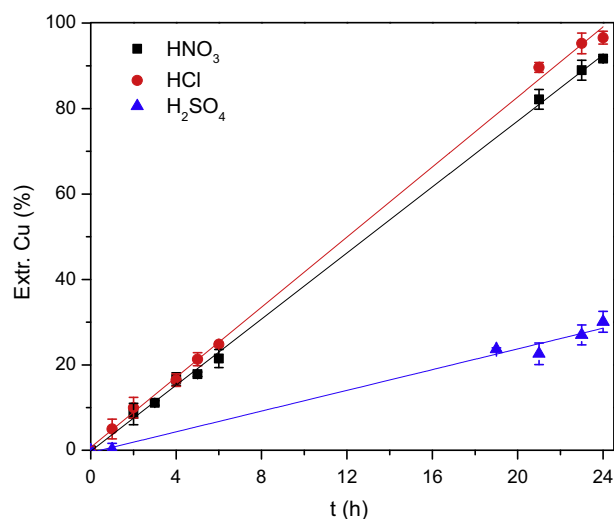


Fig. 2. Copper leaching from the EW-PCB with inorganic acids dissolutions (concentration 1 M for each corresponding acid). All tests were performed at 25 °C and 125 rpm stirring rate, with a constant solid-liquid ratio of 20 g EW-PCB per liter of leaching solution and particle size $\geq 500 \mu\text{m}$.

the selectivity needed for subsequent copper recovery. In any event, the conditions used in those studies are not comparable to those presented here.

Since the objective of the study is to minimize the time (energy) and amount of reactants involved in the processing of EW-PCB, for all subsequent experiments a concentration of 0.5 M was employed for each acid. The effect of the concentration of each acid on the copper extraction is shown in Fig. 3.

In Fig. 4 it may be observed that air sparging affects each acid system differently for the copper extraction from EW-PCB. For nitric acid, it has a slightly detrimental effect compared to the same operating conditions without air sparging (Fig. 4). This decline in reaction rate may be caused by the presence of air bubbles decreasing the solid-solution contact area. In any event, the observed behavior indicates that the increase in dissolved oxygen does not produce a synergistic effect in the chemical reaction between nitric acid and metallic copper.

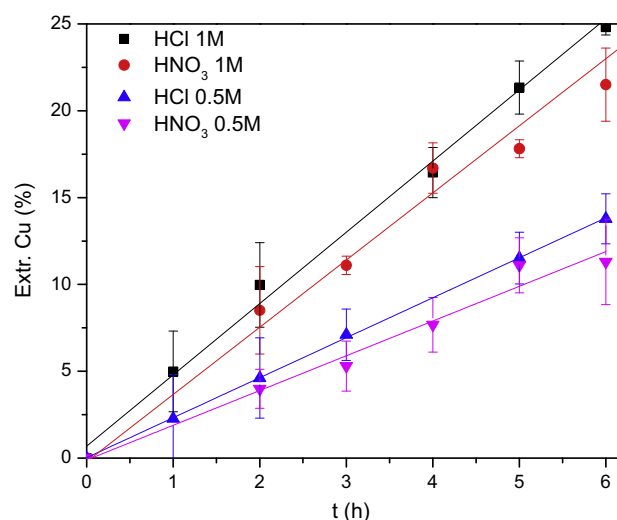


Fig. 3. Copper extraction from EW-PCB using two different acid and solution concentrations (0.5 or 1 M HCl; 0.5 or 1 M HNO₃). All tests were performed at 25 °C and 125 rpm stirring rate, with a constant solid-liquid ratio of 20 g EW-PCB per liter of leaching solution and particle size $\geq 500 \mu\text{m}$.

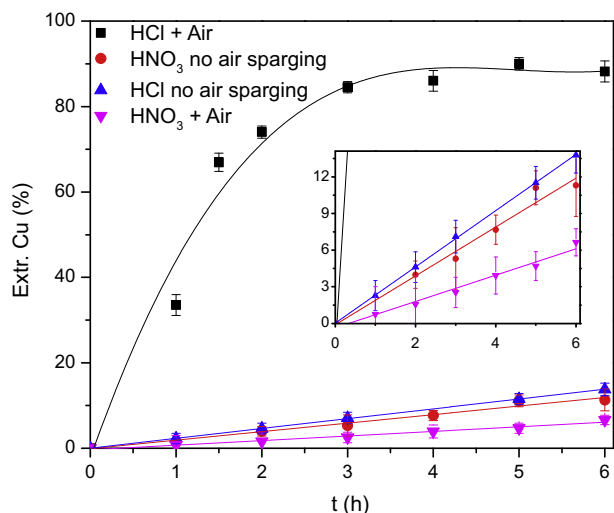


Fig. 4. Effect of air sparging (1 L/min) on copper leaching from EW-PCB for nitric and hydrochloric acids leaching solutions (0.5 M for all experiments). All tests were performed at 25 °C and 125 rpm stirring rate, with a constant solid-liquid ratio of 20 g EW-PCB per liter of leaching solution and particle size $\geq 500 \mu\text{m}$.

Regarding the hydrochloric acid experiments, air sparging considerably increases the copper dissolution (Fig. 4). A continuous supply of oxygen to the system promotes gas-saturation in the leaching solution and consequently, improves the metallic copper leaching (Yazici and Deveci, 2015), achieving a copper extraction greater than 80% in three hours of treatment. After reaching this value, the copper dissolution levels off, probably due to hydrochloric acid depletion. For the coarse material (greater than 500 μm), the required acid concentration corresponds to approximately 0.6 M HCl, not including its consumption by the other metals present, even though they are in smaller proportions.

3.2.3. Hydrochloric acid leaching with ozone sparging

Since the nitric acid medium did not favorably respond to air sparging, the following experiments only correspond to leaching in hydrochloric acid media. In this case, as indicated in the experimental section, ozone was continuously injected as a mixture of oxygen-ozone, generated via a UV lamp, at conditions which it produce a mass flow 175 $\text{mgO}_3/\text{L}_{\text{dissolution min}}$, together with the remaining oxygen (1253 $\text{mgO}_2/\text{L}_{\text{dissolution min}}$).

Under these conditions, ozone does not have a significant effect on the copper extraction, since it shows behavior similar to that observed when air is bubbled (Fig. 5), since both gas mixtures contain principally oxygen. Ozone only has a limited solubility in aqueous solution (Eriksson, 2005) and its injection into the slurry may cause a decrease in the solution-solid contact area.

3.2.4. Inorganic acid leaching with hydrogen peroxide

Hydrogen peroxide is a common oxidant in hydrometallurgical processes (Huang et al., 2014; Quinet et al., 2005; Yang et al., 2011); in this case it acts by oxidizing the metallic copper (and other elements) present in the EW-PCB. This reagent was added to the acidic media in doses of 0.1 M every hour during the entire processing.

The addition of hydrogen peroxide increases the copper removal rate for both the nitric and hydrochloric acid media (Fig. 6), being more effective for the latter. However, the maximum of copper extracted reached in the presence of hydrogen peroxide is similar ($\sim 80\%$) to that achieved for the same conditions where air sparging or ozone is employed. Adding peroxide to the system has the advantage of having a much higher concentration of

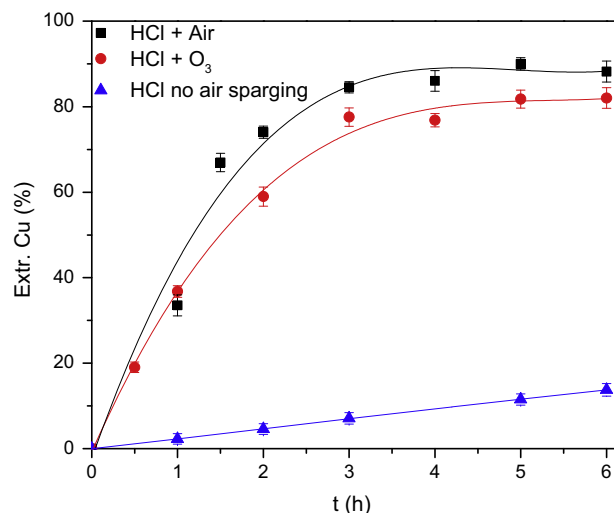


Fig. 5. Effect of ozone injection (175 $\text{mgO}_3/\text{L}_{\text{dissolution min}}$) on the copper extraction for hydrochloric acid (0.5 M HCl in all experiments). All tests were performed at 25 °C and 125 rpm stirring rate, with a constant solid-liquid ratio of 20 g EW-PCB per liter of leaching solution and particle size $\geq 500 \mu\text{m}$.

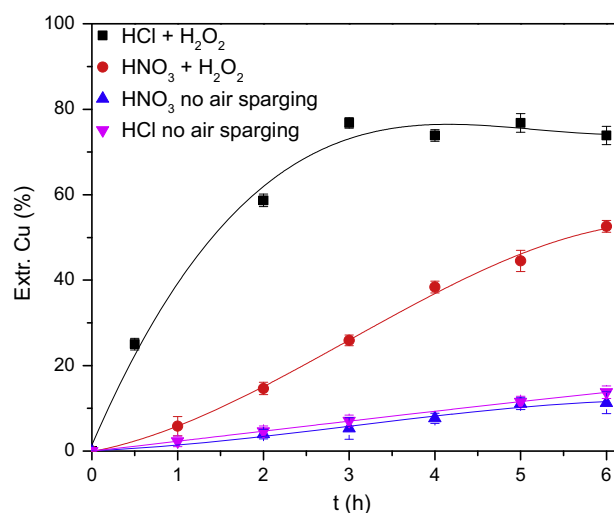


Fig. 6. Effect of peroxide dosification (0.1 M H₂O₂ per hour) on the copper extraction for each acid (0.5 M for all acid solutions). All tests were performed at 25 °C and 125 rpm stirring rate, with a constant solid-liquid ratio of 20 g EW-PCB per liter of leaching solution and particle size $\geq 500 \mu\text{m}$.

oxidant that achieved with ozone, again due to the low solubility of the gas in aqueous solutions (Eriksson, 2005; IUPAC, 1981).

3.3. Part II: Leaching with organic carboxylates: EDTA and citrate

As an alternative to the commonly used inorganic acids, two organic reagents were investigated: EDTA (diaminoethanetetraacetic acid) and sodium citrate. The leaching tests were performed on EW-PCB with the same physico-chemical characteristics using solutions of the sodium salt of EDTA and sodium citrate at the same reagent concentration and temperature.

3.3.1. Thermodynamic aspects of carboxylate solutions

At the inorganic acid concentration used for copper leaching, the solution pH is below a value of 1. In contrast, EDTA and citrate both require pH values that guarantee the formation of soluble complexes. This situation also permits a better hydrometallurgical

management for leached liquors; which can decrease the environmental impact and the possible associate-costs caused by the mandatory use of corrosion resistant materials. Copper can also be leached with citric acid at pH values between 1 and 2 (Saidan et al., 2012), however, the acid concentration used by those authors is relatively high, which probably entails similar inconveniences as those presented by the inorganic acids and for that reason, were not considered in the present study. On the other hand, also exist reports of successfully leaching copper from EW-PCB using EDTA solutions at 100 °C (Jadhao et al., 2016). However, the use of elevated temperatures presents processing and economic inconveniences that limit their applicability.

Predominance (or Pourbaix) diagrams for the organic reagents employed allow the localization of the thermodynamically favorable conditions for copper leaching: maximum pH values of 8 and 7, respectively, for EDTA and citrate (see Fig. 7). Additionally, the system requires an oxidizing agent to obtain a solution potential greater than 200 mV for EDTA and 300 mV for citrate (unless otherwise indicated, all potentials are referred to the standard hydrogen electrode, SHE).

In this regard, the copper leaching from EW-PCB using injected air or an oxygen-ozone mixture are not viable. In the first case, air does not have the enough oxidizing power to achieve the potential for leaching with EDTA or citrate. In the second, because, although ozone is a strong oxidant, its solubility in the solution is

insufficient to leach a large amount of metal. (Eriksson, 2005; IUPAC, 1981) However, with hydrogen peroxide, high concentrations of oxidant are possible. For all of the leaching experiments using the organic reagents, 0.1 M hydrogen peroxide was added each hour over the entire processing time. The potential achieved with this dosage was 182 mV and 253 mV for EDTA and citrate, respectively.

Under these conditions, species distribution diagrams allow the selection of the most suitable pH value at which the soluble species are most stable (Fig. 8). For EDTA solutions in the 3–11 pH range, there are no apparent solubility limitations. Therefore, when leaching is performed, the extraction and formation of copper complexes are thermodynamically favored. In contrast, when citrate is used in the same pH range, two insoluble compounds are formed, metallic copper and cupric oxide, at pH values below 3.4 and above 7.8, respectively. For that reason, leaching tests were performed at pH 3.5, 4.5 and 5.5.

For the sake of comparison with the inorganic acids in the previous section, the citrate concentration was held constant at 0.5 M for the three selected pH values. The pH dependence of copper extraction can be observed in Fig. 9, attaining a maximum at pH 4.5, which is consistent with the species distribution diagram (Fig. 8). At the higher pH values, the generation of solid CuO could be partially passivating the surface. Furthermore, the presence of other metals also in contact with the citrate leaching solution

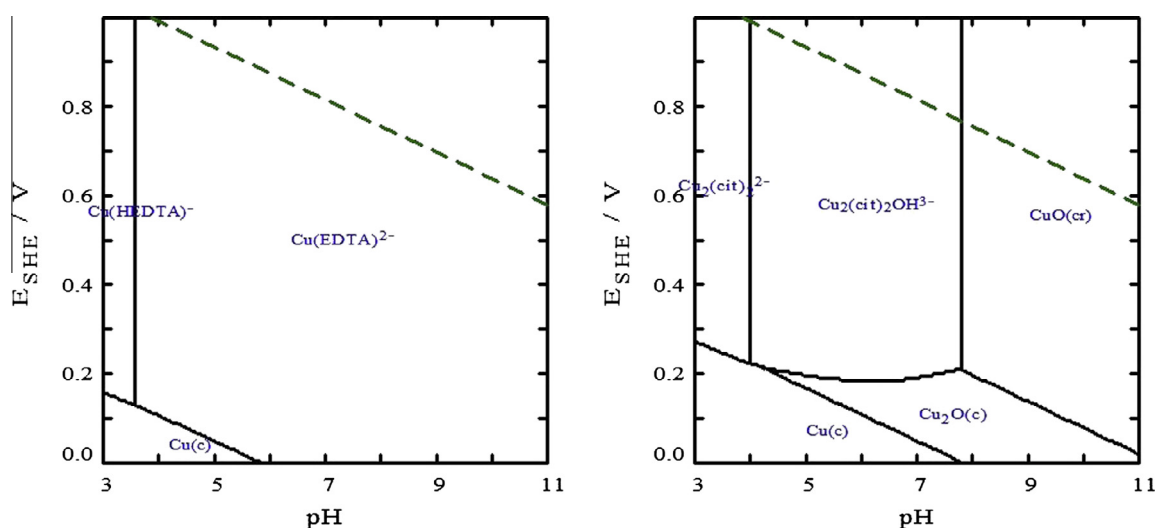


Fig. 7. Predominance diagrams for the organic carboxylates. Conditions: 25 °C, 0.5 M EDTA (left), 0.5 M Citrate (right) with 6.4 g_{Cu}/L. Designed with MEDUSA© software.

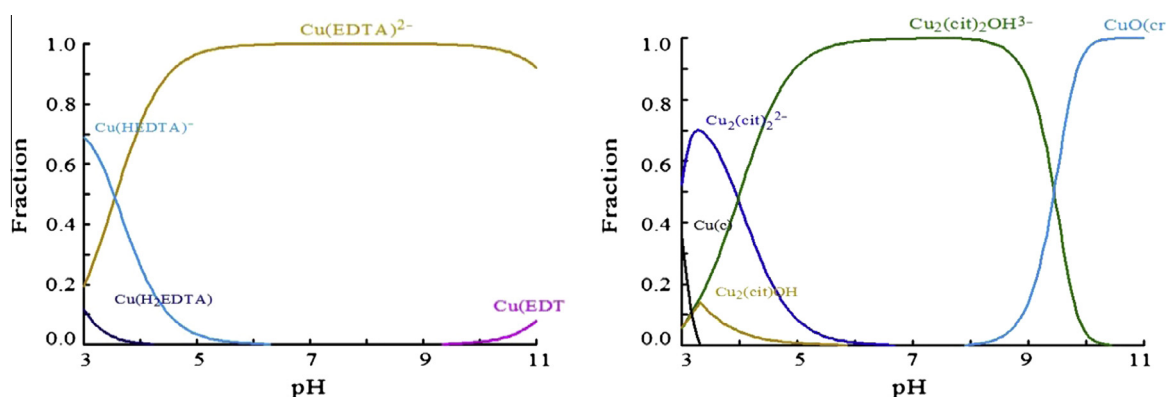


Fig. 8. Copper distribution diagrams for each leaching system: EDTA at 182 mV and citrate at 253 mV. Conditions: 25 °C, 0.5 M EDTA (left), 0.5 M citrate (right) both with 6.4 g_{Cu}/L. Designed with MEDUSA© software.

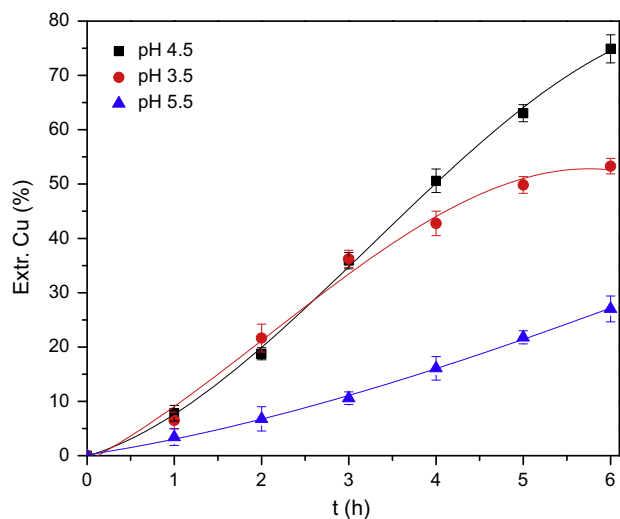


Fig. 9. Effect of pH on copper leaching from EW-PCB in 0.5 M sodium citrate solutions. Oxidant additions: 0.1 M H_2O_2 per hour. All tests were performed at 25 °C and 125 rpm stirring rate, with a constant solid-liquid ratio of 20 g EW-PCB per liter of leaching solution and particle size $\geq 500 \mu\text{m}$.

and under these work conditions act as “consumers” of the leaching reagent, causing a decrease in copper extraction from EW-PCB. This can be demonstrated by observing the distribution diagrams for zinc, iron, nickel and lead (Fig. 10), metals which coexist with copper in this material and are also oxidized by peroxide.

Regarding the EDTA system, as seen previously, there is the advantage of having a much broader workable pH range. However this substance presents the disadvantage of having itself a limited

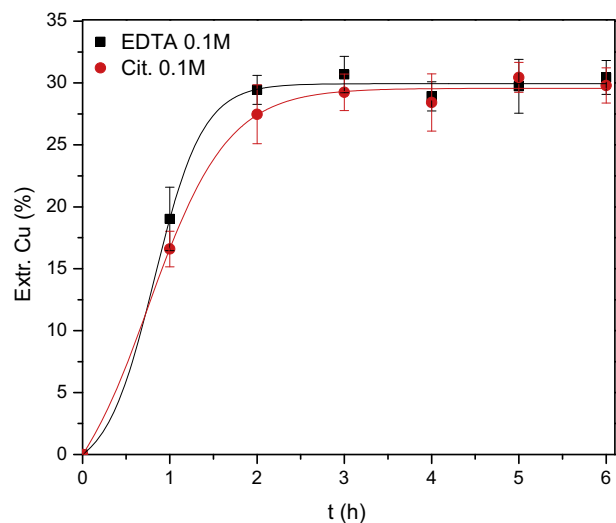


Fig. 11. Copper leaching from EW-PCB using 0.1 M EDTA or 0.1 M citrate solutions. Oxidant additions: 0.1 M H_2O_2 per hour. All tests were performed at 25 °C and 125 rpm stirring rate, with a constant solid-liquid ratio of 20 g EW-PCB per liter of leaching solution and particle size $\geq 500 \mu\text{m}$.

solubility in aqueous media. In this sense, processing of EW-PCB to provide high levels of a particular metal could present problems due to the lack of EDTA in the leaching solution. In order to make a fair comparison between the leaching capacities of EDTA and citrate, leaching tests were performed using solutions with 0.1 M concentration of either reagent (Fig. 11), employing the same peroxide dosing (0.1 M H_2O_2 every hour) at pH 4.5.

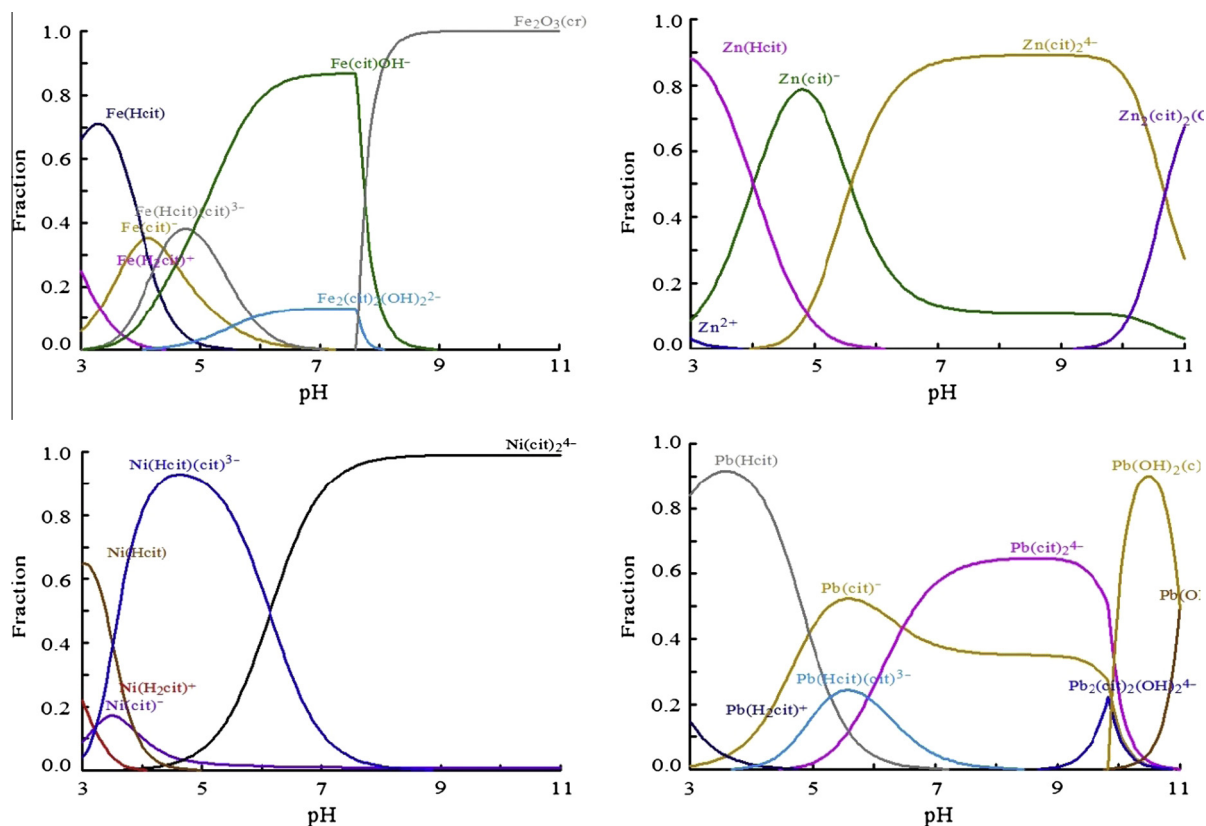


Fig. 10. Species distribution diagrams for iron (III), zinc, nickel and lead in a 0.5 M citrate solution at 253 mV and 25 °C. Designed with MEDUSA® software.

The behavior of copper leaching with EDTA and citrate solutions at the same concentration is very similar, but limited by the amount of reagent available to combine with copper (Fig. 11). The reaction rate is practically the same for both substances, reaching a maximum value (approximately 30%) in two hours. In order to extract more copper, a larger amount of reagent is needed. However, given the limited solubility of EDTA, further testing at higher concentrations was only undertaken with citrate solutions.

3.3.2. Effect of citrate concentration

Additional tests were performed by increasing the citrate concentration (Fig. 12) to determine its effect on the copper extraction using the previously specified conditions (i.e. pH 4.5 and 0.1 M peroxide dosage every hour). As the amount of citrate available in the leaching solution is increased, higher metal extraction is achieved up to a concentration of 0.5 M, after which the increase in the recovery is not significant.

Such behavior may be associated with the amount of oxidizing agent (H_2O_2) available in the leaching solution. In other words, in citrate solutions at concentrations below 0.5 M, the limiting reactant is the citrate available to combine with the copper during the leaching process. When an excess of citrate (greater than 0.5 M) is added, the process becomes limited by the amount of peroxide. For that reason, the copper extraction observed in Fig. 13 is not proportional to the increase of citrate concentration after six hours of processing. To improve the copper extraction at high citrate concentrations, would require also increasing the amount of oxidant, specifically the peroxide dosing.

From the results obtained at the conditions reported here, citrate was deemed adequate to replace the more traditional methods used to extract copper from EW-PCB. Citrate is undoubtedly less toxic than HCl. Furthermore, the authors have undertaken studies to evaluate the degree of reutilization of the citrate leaching solutions, after copper recovery, for EW-PCB pretreatment, which will be reported in a subsequent article.

3.4. Part III: Gold leaching from EW-PCB after copper extraction

The purpose of the pretreatment is to remove the maximum amount of copper from EW-PCB, with the final objective of recovering the noble metals (gold in this study) present therein. Among

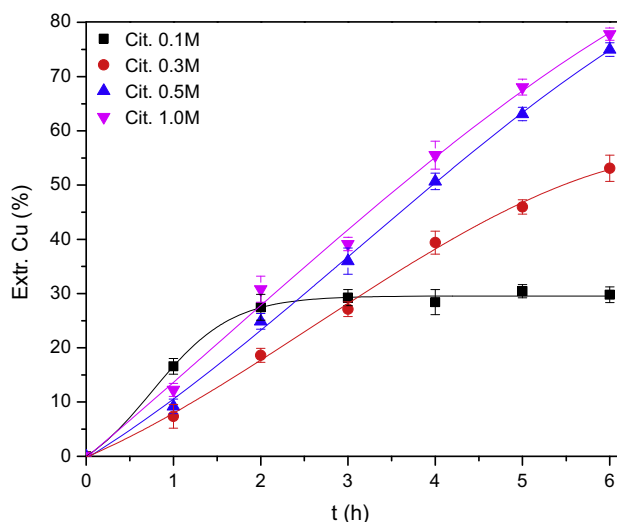


Fig. 12. Citrate concentration effect on the copper extraction from EW-PCB all of them at pH 4.5. All tests were performed at 25 °C and 125 rpm stirring rate, with a constant solid-liquid ratio of 20 g EW-PCB per liter of leaching solution and particle size $\geq 500 \mu m$.

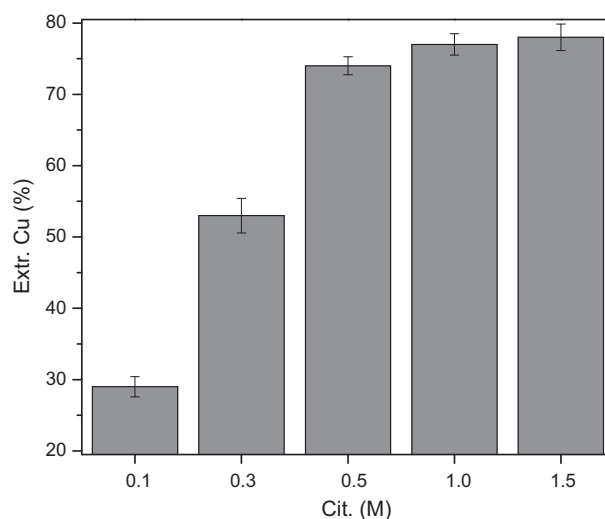


Fig. 13. Copper extraction from EW-PCB after six hours of leaching, varying the citrate concentration (0.1, 0.3, 0.5, 1, and 1.5 M). All tests were performed at pH 4.5 and a 0.1 M peroxide dosing every hour. All tests were performed at 25 °C and 125 rpm stirring rate, with a constant solid-liquid ratio of 20 g EW-PCB per liter of leaching solution and particle size $\geq 500 \mu m$.

the methods included in the state of the art for gold leaching is thiourea (hereinafter TU). This reagent offers some advantages with respect to cyanidation or others systems cited previously (i.e., high leaching kinetics and the ability to be recycled after recovery of the precious metals). By contrast, TU has a great affinity for copper and requires very controlled operationing conditions (pH - Potential) to minimize degradation (Gurung et al., 2013; Poisot-Díaz et al., 2008; Syed, 2012).

Therefore, materials such as EW-PCB, which are processed for gold recovery, but contain large amounts of copper, cannot be leached directly by TU (Fig. 14). To avoid this disadvantage, the two most effective pretreatments studied in Parts I and II of this document were applied and their effect on the effectiveness of subsequent gold extraction was evaluated. For the complete processing tests, i.e. pretreatment for copper and subsequent TU gold

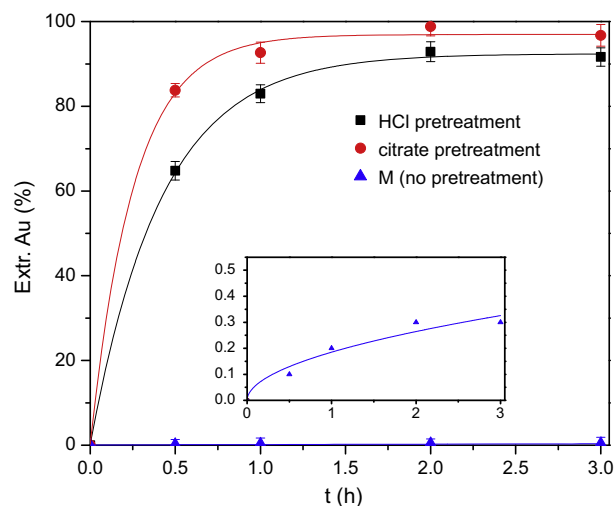


Fig. 14. Gold leaching from pretreated EW-PCB, using 0.4 M TU solutions at pH 1.5 during three hours. All tests were performed at 25 °C and 125 rpm stirring rate, with a constant solid-liquid ratio of 20 g EW-PCB per liter of leaching solution and particle size 177–400 μm . Pretreatment conditions: HCl: copper leaching for six hours with 0.5 M HCl solution and air sparging (1 L/min). Cit.: copper leach for six hours with 0.5 M citrate solution at pH 4.5 and addition of peroxide (0.1 M every hour). M: material without any preliminary treatment.

leaching, EW-PCB in the particle size range between 177 and 400 μm was employed since its gold content is the highest of size fractions analyzed (Table 1).

3.4.1. Suggested Route 1: Copper pretreatment with hydrochloric acid and air sparging, followed by gold leaching with TU

To study the pretreatment-leaching route process, the first stage consisted of a pretreatment for copper extraction from EW-PCB, using batches of 20 g per liter in contact with a 0.5 M hydrochloric acid solution and bubbling air during six hours. Subsequently, the solid filtrate from the first stage was leached with a 0.4 M TU solution at a pH of 1.5 for three hours (Fig. 14), obtaining a gold recovery equal to 83% in the first hour.

3.4.2. Suggested Route 2: Copper pretreatment with citrate and peroxide, followed by gold leaching with TU

In the second case, 20 g of EW-PCB per liter of leaching solution were used; the pretreatment was performed with a 0.5 M citrate solution and a 0.1 M peroxide dosage every hour for six hours. Similarly, the solid residue (including the filter) was leached with a 0.4 M TU solution for three hours (Fig. 14). In this case, a gold recovery of 93% was obtained after one hour of leaching.

It should be noted that the results of direct EW-PCB leaching (Fig. 14), i.e. without pretreatment to remove the copper, show an almost negligible gold extraction for all processing times.

These two possible routes demonstrate that it is possible to achieve gold recovery from EW-PCB at moderate temperatures ($\sim 25^\circ\text{C}$) with the application of a preliminary processing to remove as much copper as possible from the EW-PCB. Even though the two process routes studied in this investigation gave encouraging results, further studies can improve the applicability of different possible reagents combinations and/or even more favorable operating conditions. Although yields are similar between the two routes, the authors recommend the use of systems with citrate due to its superior handling characteristics, very low toxicity, recyclability and relative ease of scaling up.

4. Conclusions

Copper leaching from EW-PCB using with inorganic acid solutions at moderate conditions (25°C) is possible, but has very slow reaction kinetics; however the processing time can be shortened by adding auxiliary leaching agents as ozone injection, air sparging or peroxide dosing. In the conditions studied, solutions based on sulfuric or nitric acid were not effective for rapid removal of a considerable amount of copper from EW-PCB, independent of the auxiliary agent used. In the same conditions, chemical based systems employing hydrochloric acid and an auxiliary oxidant reagent, i.e. sparged air or additions of peroxide, produced copper extractions $\sim 80\%$.

Organic reagents, EDTA and citrate, promotes copper extraction from EW-PCB, but only when peroxide is added to the system. The EDTA-based solutions present some limitations in its ability to extract high metals concentrations in solution because of its low solubility. Citrate leaching is an interesting option for the recovery of base metals from EW-PCB. The extractions achieved with citrate are comparable with those obtained using hydrochloric acid, with the advantage of being much less toxic, more stable and safe for possible application. Additionally, the copper recovery from citrate leach liquors is much simpler than the analogous process when hydrochloric acid leached solutions are used.

Efficient and selective gold leaching from the EW-PCB may be achieved through alternative processing routes that include a preliminary removal of the copper and subsequent leaching of gold without the use of toxic reagents.

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Enhancement of simultaneous gold and copper recovery from discarded mobile phone PCBs using *Bacillus megaterium*: RSM based optimization of effective factors and evaluation of their interactions



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ABSTRACT

Bioleaching of Au from mobile phone printed circuit boards (MPPCBs) was studied, using *Bacillus megaterium* which is a cyanogenic bacterium. To maximize Au extraction, initial pH, pulp density, and glycine concentration were optimized via response surface methodology (RSM). Bioleaching of Cu, an important inhibitor on Au recovery, was also examined. To maximize Au recovery, the optimal condition suggested by the models was initial pH of 10, pulp density of 8.13 g/l, and glycine concentration of 10 g/l. Under the optimal condition, approximately 72% of Cu and 65 g Au/ton MPPCBs, which is 7 times greater than the recovery from gold mines, was extracted. Cu elimination from the MPPCBs having a rich content of Au did not cause a significant effect on Au recovery. It was found that when the ratio of Cu to Au is high, Cu elimination can considerably improve Au recovery. *B. megaterium* could extract the total Au from PCBs containing 130 g Au/ton MPPCBs.

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1. Introduction

In the 21st century, the electronic wastes or e-wastes have been a major solid waste in the world (Pradhan and Kumar, 2012). While e-wastes make less than 2% of the mass in united state landfill, they account for 70% of heavy metals (Jiang et al., 2014). Among e-wastes, mobile phones, with regard to their rich metal content (about 23% of the total weight), huge volume of production, and low life time (about four years), are the most important targets (Schluep et al., 2009; Kasper et al., 2011). A mobile phone contains at least 40 elements, including quite hazardous and highly precious metals such as copper, gold, platinum, silver, titanium, cadmium, mercury, lead, and tin. Mobile phone printed circuit boards (MPPCBs) are particularly the main carrier of metals in which precious metals make up more than 70% of their weight (Cui and Zhang, 2008; Jing-ying et al., 2012). Consequently, recycling, reusing, or finding true disposal ways of e-wastes are essential (Petter et al., 2014).

On the other hand, during the last four decades, a significant portion of gold has been utilized in electrical instruments because of its high electrical conductivity. Growing demand for gold makes its recovery from e-wastes crucial (Syed, 2012). Recycling e-wastes

is not only important for reducing environmental pollution but also it can save natural ores and promote the recovery of valuable metals (Jiang et al., 2014).

Pyrometallurgical and hydrometallurgical techniques are two traditional methods for recovering metals from e-wastes. These methods cause air pollution and are not recommended to be the most economical way for recovery of precious metals from e-wastes (Yang et al., 2014). Biohydrometallurgy solves old problems caused by conventional methods, using revolutionary solutions (Erust et al., 2013). Bioleaching techniques, a main area in biohydrometallurgy, suggest a natural way for solving environmental problems (Willner and Fornalczyk, 2013; Pradhan and Kumar, 2012). Using cyanogenic microorganisms in alkaline environments and biological process in acidic environments are two main areas in bioleaching techniques (Willner and Fornalczyk, 2013).

Cyanogenic microorganisms such as *Chromobacterium violaceum*, some *Pseudomonas* sp., *Bacillus megaterium*, and *Marasmius oreades* by producing cyanide in presence of various metals form cyanide complexes with high chemical stability and very good water solubility which mobilize many metals and metalloids (Syed, 2012; Brandl and Faramarzi, 2006). These microorganisms produce cyanide as a secondary metabolite, typically only during early stationary phase and only in glycine rich media (Brandl and Faramarzi, 2006). Glycine is a direct precursor and produces cyanide by oxidative decarboxylation (Shin et al., 2013). There are many physiochemical and biological parameters which affect

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bioleaching processes. Some little changes in these factors can create a huge variance in results (Willner, 2013). Accordingly, optimizing the process to reach the maximum metal recovery with minimum number of experiments is necessary (Amiri et al., 2012).

Natarajan and Ting (2014) studied pretreatment of e-waste and mutation of *C. violaceum* to promote gold recovery. The effects of pulp density and pH were examined. Chi et al. (2011) investigated bioleaching of Au and Cu from MPPCBs, using *C. violaceum* and examined supplementing oxygen and different pH ranges. Brandl et al. (2008) evaluated the potential of *C. violaceum*, *Pseudomonas fluorescens*, and *Pseudomonas plecoglossicida* for biological solubilization of Ag, Au, and Pt. In all of the above-mentioned researches on examining the effects of different selected variables, the optimization method of one factor at a time has been applied which is a conventional method with defined limitations.

MPPCBs and CPCBs are the most expensive e-wastes which can influence the economics of recycling. Knowing the details about extraction of gold from these two important e-wastes plays an essential role in recycling a mix collection of e-wastes. Since the production of cyanide by bacteria is limited, for having an economical recycling, it is necessary to have sufficient knowledge about bacterial behavior and the maximum metal recoveries from these two wastes. Previously, the authors examined Cu, Ni, and Au bioleaching from CPCBs (Arshadi and Mousavi, 2014, 2015a). Furthermore, extraction of Cu and Ni from MPPCBs was also studied (Arshadi and Mousavi, 2015b). The overall procedure of Cu, Ni and Au extraction from MPPCBs was presented in our previous work briefly (Arshadi and Mousavi, 2015c). In this study, simultaneous recovery of Au and Cu from MPPCBs was investigated. The overall obtained results can be useful in finding out a fully economical and suitable mixture of e-wastes with optimized gold recovery.

The main objective of this study was to evaluate the simultaneous gold and copper recovery from MPPCBs as a highly gold-rich waste. A pure culture of *B. megaterium*, a well-known cyanogenic bacterium, was utilized for gold solubilization via production of cyanide. RSM was also applied to optimize simultaneous Au and Cu biorecovery through identifying the optimal amount of initial pH, pulp density, particle size, and glycine concentration; important influencing parameters in the bioleaching process.

2. Management of e-wastes and the strategies on the issue

Increasing need of modern life for newer equipment and technology has led to a considerable proliferation in the volume of the waste in dumps and landfills. E-waste is physically and chemically distinct from other types of municipal and industrial waste; it comprises discarded electronic appliances mostly consisting of computer and mobile phones which have a short lifespan (Marques et al., 2013; Robinson, 2009). E-waste is currently one of the fastest growing waste streams in the world in terms of both quantity and toxicity (Chung et al., 2011). Correct handling of these wastes is indispensable for their further sustainable recovery, especially for maximum extraction of base, rare, and precious metals and also minimizing the environmental impact of the entire process chain (Palmieri et al., 2014). There are not adequate legislations worldwide on the efficient management of e-wastes. The rapid growth of e-wastes and the ineffectiveness of legislation have led to inappropriate management strategies in both developed and developing countries, resulting in profound impacts on the environment. Management of e-waste by recycling or disposal to landfills is followed by significant environmental risks (Robinson, 2009; Wong et al., 2007). Recently, in order to reduce the problems related to management of e-wastes at both national and international levels, comprehensive investigations have been conducted.

Several tools developed and applied for e-waste management are as follows: (1) Life cycle assessment (LCA) is a tool employed to design environmentally friendly electronic devices and minimize e-waste problems. (2) Material flow analysis (MFA) is a tool utilized in order to investigate the route of material (e-waste) flowing into recycling sites, or disposal areas and stocks of materials, in space and time. Exportation of huge amounts of e-wastes from developed countries to developing countries, particularly China, India, and South Africa, for reuse or recycling necessitated applying MFA strategy as a decision support tool for environmental and waste management. (3) Multi criteria analysis (MCA) is a decision-making tool developed for considering strategic decisions and solving complex multi-criteria problems, including qualitative/quantitative aspects of the problem. (4) Extended producer responsibility (EPR) is an environment policy approach that attributes responsibilities to manufacturers for taking back products after being used, and is based on polluter-pays principles. The findings indicate that each environment management tool has a specific information category. Thus, a combination of either LCA, MFA or MCA with EPR may be the optimal model to promote the management of e-wastes, irrespective of the nature of e-waste problem (Kiddee et al., 2013). Alternatively, due to the presence of precious metals in e-wastes, especially PCBs, there is a great motive for their recovery instead of simply disposing them. The purity of these valuable metals has been found to be 10 times greater than that of rich-content minerals (Hadi et al., 2015). Currently applied techniques for the recovery of metals from e-wastes have their own limitations and disadvantages (Pant et al., 2012). Pyrometallurgical treatment of e-waste raises concerns regarding the possible formation of brominated and chlorinated dibenzofurans and dioxins in burning processes due to the existence of halogens in plastic parts of the e-waste feedstock. Hydrometallurgical processes involve the dissolution and recovery of the target metals by means of acids, cyanide, halides, thiourea, or thiosulphate which can be hazardous for the environment and human health. Presently limited to rich countries, applying bio-metallurgical processing for the recovery of precious metals is more attractive because of its low-cost and high specificity for the target elements (Robinson, 2009; Tsydenova and Bengtsson, 2011).

3. Materials and methods

3.1. Source and preparation of mobile phone PCBs

MPPCBs were obtained from a collection center of e-wastes in Tehran, Iran. No physical or mechanical separation processes were applied before transporting them to the laboratory. To use PCBs in the experiments, first they were manually cut off to pieces of about 1 cm², and then the plastics were separated. They were crushed and fined by a satellite mill (Fristch, Germany). Finally, the classification of particle sizes from 37 to 149 μm was carried out, using a vibrator shifter and mesh numbers of 100, 200, and 400. The metal content of MPPCBs was determined via the inductively coupled plasma emission spectrometry (ICP-OES). Fig. 1 demonstrates the amount of some selected metals in the sample. More explanations can be found in our previous work (Arshadi and Mousavi, 2015b).

3.2. Plastic content of mobile phone PCBs

In order to reduce the error source in future analyses, the plastic content of the samples should decrease. To determine the amount of plastics in the remaining prepared MPPCBs, 110 g of the sample powder was mixed with 100 ml of brine (Wang et al., 2015).

The mixture was mixed well, and the heavy particles were allowed to settle down. The supernatant was discarded, and the

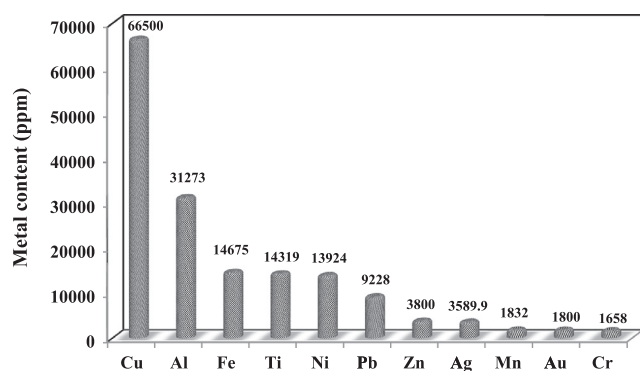


Fig. 1. Metal content of MPPCBs (ppm).

sediment was washed and then dried. Measurement of the sample weight before and after washing indicated that the amount of plastics was less than 0.5% (w/w).

3.3. Microorganism and culture condition

To extract gold, a cyanogenic bacterium is needed. Among cyanogenic bacteria, *B. megaterium*, which is found in widely diverse habitats, was used. While there are just few bioleaching researches using *B. megaterium*, the performance of this bacterium was examined in this study because of its ability in CN^- production and validation of a nearly 63% gold extraction from computer printed circuit boards by this species in our previous work (Arshadi and Mousavi, 2015a).

To conduct the experiments, *B. megaterium* (PTCC 1656) was provided in the lyophilized state from Iranian Research Organization for Science and Technology (IROST), Tehran, Iran. The nutrient broth medium with defined salt composition was utilized. The bacterial growth curve was plotted (data not shown), and it was found that approximately 10 h after inoculation, the bacterium almost reached the end of the logarithmic phase. The growth curve of *B. megaterium* has been presented in our previous research on CPCBs (Arshadi and Mousavi, 2015a).

3.4. Bioleaching experiments

In order to determine the best condition to reach the maximum simultaneous recovery of gold and copper, it was necessary to examine the effects of important parameters on the responses. In this study, the important factors including initial pH, initial glycine concentration, and pulp density (Andres and Colin, 1995; Jadhav and Hocheng, 2013; Gerayeli et al., 2013) were chosen to be investigated using statistical evaluation so as to present the appropriate models for Au and Cu recovery as the responses. RSM is a group of mathematical and statistical techniques, which is used in the development of an adequate functional relationship between interest responses and several variables that affect the response. Two important models, including first- and second-order models, are commonly employed in RSM. The purpose of considering RSM is to establish a relationship between the responses and the variables predicting responses value for a given setting condition and to determine the significance of the factors through hypothesis testing. Moreover, it determines the optimum condition of variables for having the maximum or the minimum value of response over a certain region. Among RSM principles, central composition design (CCD) is the most popular among all second-order design methods. The total number of experiments in CCD is equal to $n = 2^k + 2k + n_0$ in which k and n_0 are the number of variables and center points, respectively (Khuri and Mukhopadhyay, 2010). In the present research, Design-Expert software (version 7.1.4)

Table 1

Factors and their levels used for the bioleaching experiment.

Factors	Units	Low axial	Low factorial	Center point	High factorial	High axial ^a
A: Initial pH	–	7	7.60	8.50	9.40	10
B: Pulp density	g/l	2	5.7	11	16.4	20
C: Initial glycine Conc.	g/l	0.5	2.43	5.25	8.07	10

^a $\alpha = 2$.

was applied. The selected parameters and their levels are shown in Table 1.

3.5. Analytical methods and apparatus

An orbital shaker incubator (wise cube, South America) was used to shake and fix the temperature of the culture. To determine the metal content of MPPCBs as well as their concentration in the bioleached solution, ICP-OES (vista-pro, Australia) was applied. The pH variation of the solution was monitored by a pH meter (p25, ISTEK). The production of free and weak cyanide in terms of time was measured according to picric acid colorimetric method (Drochioiu et al., 2003), using a spectrophotometer (Optizen 3220UV, Korea).

4. Results and discussion

4.1. Fitting model

Experimental design was based on CCD with three-factors five-level. 19 suggested runs by CCD, including 8 (2^3) factorial points, 6 (2×3) axial points, and 5 center points were conducted. All experiments were done at 250 ml Erlenmeyer flasks containing 50 ml solution with 5% inoculum. The pH of the culture was not controlled during the process, while the environment temperature and shaking speed were adjusted at 30 °C and 170 rpm, respectively. The experimental condition and the responses related to each run have been shown in Table 2. It is worth mentioning that ignoring run#11 increased the model accuracy. CCD fitted the experimental results, suggesting two modified polynomial quadratic models for both Au and Cu recovery. Eqs. (1) and (2) resulted from 18 batch runs. The empirical relationships between Au and Cu recovery with selected parameters in coded units are as follows: for Au recovery

$$Y_{Au} = 1.37 + 0.41A - 1.96B + 0.20C - 0.03AB + 0.16AC - 0.55BC + 0.44A^2 + 1.31B^2 \quad (1)$$

for Cu recovery

$$Y_{Cu} = 51.99 + 6.71A + 12.00B + 16.04C + 11.02AB + 5.47BC + 5.73A^2 - 9.84B^2 \quad (2)$$

A, B, and C represent initial pH, pulp density, and glycine concentration, respectively. Multiple between two factors shows factor interactions. Eq. (1) demonstrates that pulp density was the most influential parameter with negative linear effect on gold recovery from MPPCBs; increasing the pulp density caused decreases in gold recovery, whereas for CPCBs the initial pH had the most influence on gold recovery (Arshadi and Mousavi, 2015b). Since MPPCBs are neutral, pH variation had a minor effect in comparison with the pulp density, while for CPCBs which have an alkaline nature, the solubility varied along with variation of pH. According to Eq. (2), for MPPCBs pulp density and glycine concentration, which have a positive linear effect, are the most important parameters in Cu

Table 2
Experimental plan and their response based on RSM.

Run	Factors			Response	
	A: Initial pH	B: Pulp density (g/l)	C: Glycine Conc. (g/l)	Au recovery (%)	Cu recovery (%)
1	7.60	5.65	2.43	4.23	31.6
2	9.40	5.65	2.43	4.43	25.0
3	7.60	16.35	2.43	1.87	20.91
4	9.40	16.35	2.43	1.29	69.1
5	7.60	5.65	8.07	5.80	47.2
6	9.40	5.65	8.07	6	44.7
7	7.60	16.35	8.07	0.61	69.1
8	9.40	16.35	8.07	1.33	100
9	7.00	11.00	5.25	1.01	57.4
10	10.00	11.00	5.25	3.99	70.3
11	8.50	2.00	5.25	–	–
12	8.50	20.00	5.25	1.58	35.7
13	8.50	11.00	0.50	1.11	13.5
14	8.50	11.00	10.00	1.57	75.7
15	8.50	11.00	5.25	1.97	51.4
16	8.50	11.00	5.25	1.41	59.5
17	8.50	11.00	5.25	1.21	56.8
18	8.50	11.00	5.25	1.16	48.6
19	8.50	11.00	5.25	1.01	51.4

recovery. This finding is similar to the results obtained for Cu recovery from CPCBs (Arshadi and Mousavi, 2014, 2015b).

4.2. Statistical evaluation

In order to investigate the effect of each parameter on Au and Cu recovery, the analysis of variance (ANOVA) is shown in Tables 3 and 4, respectively. ANOVA led to two modified quadratic models for both responses. According to Table 3, the F-value of Au model is equal to 21.73, indicating the significance of the model. P-value shows that the occurrence of error possibility is less than 0.01%, which validates the model. The parameters which have a p-value less than 0.05, including initial pH, pulp density, and interaction of pulp density-glycine concentration, affect Au recovery significantly. The lack of Fit of model is higher than 0.05 and is not significant; denoting that the model can fit experimental data with analytical data from the model. According to Table 4, lack of Fit and p-value of the model validate accuracy of model to estimate Cu recovery. Factors and most of pair interactions have a significant effect on Cu recovery.

Fig. 2(a)–(c) depicts the residual from each experiment vs. the amount of predicted factor respectively for pH, pulp density, and glycine concentration for Au. The points have been scattered randomly about the zero residual level. They have formed two parallel horizontal lines equidistant from the zero line and validate the

Table 3
ANOVA for Au recovery.

Source	ANOVA for Au recovery				
	Sum of squares	df	Mean square	F value	p-value
Model	48.08	8	6.011	17.16	0.0001
A: Initial pH	2.26	1	2.26	6.44	0.0317
B: Pulp density	35.04	1	35.04	100.0	<0.0001
C: Glycine Conc.	0.53	1	0.53	1.52	0.2493
AB	0.0085	1	0.0085	0.02	0.8800
AC	0.21	1	0.21	0.60	0.4573
BC	2.38	1	2.38	6.79	0.02852
A ²	2.55	1	2.55	7.28	0.02445
B ²	14.10	1	14.10	40.25	0.0001
Residual	3.16	9	0.35		
Lack of fit	2.60	5	0.52	3.71	0.1141
Pure error	0.56	4	0.14		

Table 4
ANOVA for Cu recovery.

Source	ANOVA for Cu recovery				
	Sum of squares	df	Mean square	F value	p-value
Model	7203.18	7	1029.03	16.28	0.0001
A: Initial pH	614.35	1	614.35	9.72	0.0109
B: Pulp density	1308.83	1	1308.83	20.70	0.0011
C: Glycine Conc.	3511.87	1	3511.87	55.55	<0.0001
AB	971.52	1	971.52	15.37	0.0029
BC	238.93	1	238.93	3.78	0.0805
A ²	441.98	1	441.98	6.99	0.0246
B ²	790.21	1	790.21	12.50	0.0054
Residual	632.23	10	63.22		
Lack of fit	553.28	6	92.21	4.67	0.0787
Pure error	78.95	4	19.74		
Cor total	7835.42	17			

model adequacy. Fig. 2(d)–(f) presents the residuals vs. parameters for Cu recovery. High R² values of 0.94 and 0.92 for Au and Cu, respectively, validate the fact that the models are capable of predicting the system behavior under given experimental conditions.

4.3. Response plots

4.3.1. Au recovery

In bioleaching processes, Au reacts with cyanide, and in electrochemical process gold is recovered in the form of dicyanoaurate [Au(CN)₂[−]] (Syed, 2012; Faramarzi et al., 2004). Pham and Ting (2009) examined gold extraction from an e-waste sample containing 4872 ppm Au and 28,320 ppm Cu. They reported that at pulp density of 0.5% the gold recovery was about 9.5%, while by increasing pulp density to 8% no Au was recovered. Additionally, they studied the pretreatment of e-waste by bio-oxidation using *Acidithiobacillus ferrooxidans*, which led to gold recovery of 11% and 3.5% at pulp density of 0.5% and 8%, respectively. Faramarzi et al. (2004) investigated gold recovery from PCBs using bio-oxidation process. The maximum amount of Au recovery by means of *C. violaceum* was 14.9%. Ting et al. (2008) evaluated gold biorecovery from an e-waste which contained 0.2% gold and more than 20% copper. They reached the maximum Au recovery of 30% using both *C. violaceum* and *P. fluorescens*.

In the current study, bioleaching of MPPCBs, which contained a high amount of Au about 1800 ppm, was investigated, and at a pulp density of 8.13 g/l, 3.35% of Au was recovered. Since there is a lack of enough information about the effects of different parameters on the process, optimization studies have been suggested in some literature.

4.3.1.1. Pulp density. As it was noted, the most effective parameter in Au recovery from MPPCBs is pulp density with a linear negative effect. Fig. 3(a) shows the interaction effect between glycine concentration and pulp density on Au recovery. At pulp densities of around 12.5 g/l, the effect of glycine concentration and pulp density interaction increases sharply. This indicates the fact that the effect of each of these parameters on Au recovery can be completely different in the presence or absence of the second factor. Part (b) demonstrates the important effect of pulp density on Au recovery, where by increasing pulp density the recovery dropped rapidly. When pulp density increases, the environmental toxicity increases as well, but subsequently the bacterial activity decreases (Natarajan and Ting, 2014; Pham and Ting, 2009). Moreover, by increasing pulp density in order to reach the same percentage of recovery, more amount of gold has to be released, and consequently a higher cyanide concentration is required, while the ability of bacterium in producing cyanide is limited. Natarajan and Ting (2014) also reported that by increasing pulp density, the gold

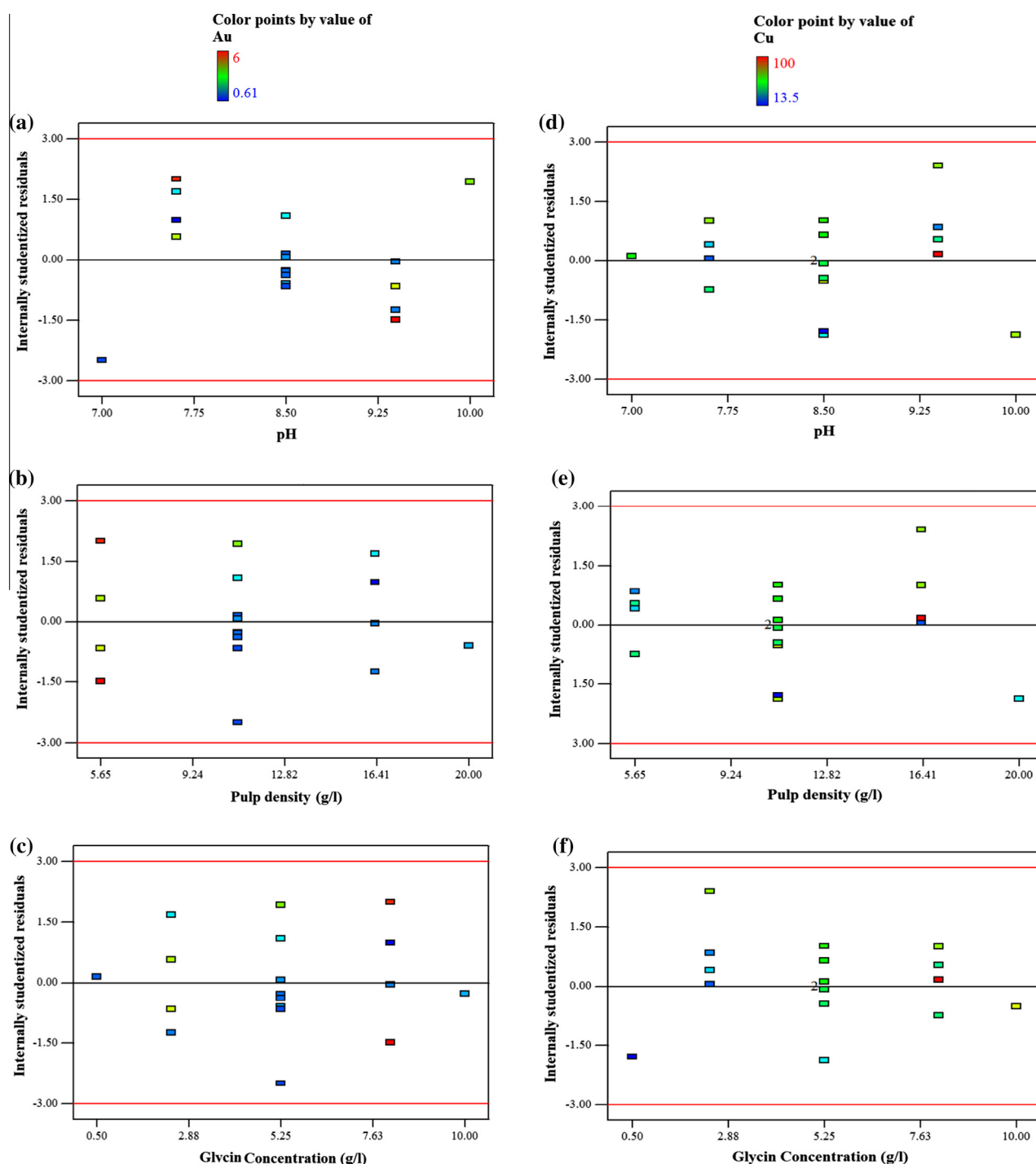


Fig. 2. Internally studentized residuals vs. factors (a–c) for Au recovery; (d–f) for Cu recovery.

recovery decreased. Fig. 3(c) shows the interaction effect of pulp density and initial pH on Au recovery from MPPCBs. As it is shown, there is no interaction between initial pH and pulp density at glycine concentration of 5.25 g/l. In other glycine concentrations, the same interaction was observed, too. As previously mentioned, at lower pulp densities regardless of the amount of initial pH, Au recovery increased.

It was also observed that for CPCBs, initial pH and pulp density had a sharp interaction which led to different results. These results arise from different natures of samples; CPCBs are highly alkaline, while MPPCBs are neutral.

4.3.1.2. Initial pH and glycine concentration. According to the suggested Au model, initial pH is the second important parameter on Au recovery. Fig. 4 shows the effect of initial pH and glycine concentration on Au recovery. Part (a) reveals that at pulp density of 6.5 g/l these factors did not have any interaction with each other, meaning that in the absence or presence of glycine the effect of initial pH is identical. However, when pulp density increases to 12.5 g/l, as shown in part (b), the interaction effect of initial pH and glycine concentration increases highly. In part (c), the contour plot of these two factors has been displayed. High initial pH leads to higher recovery. At $pK_a = 9.3$ and pH values higher than 9.3, the

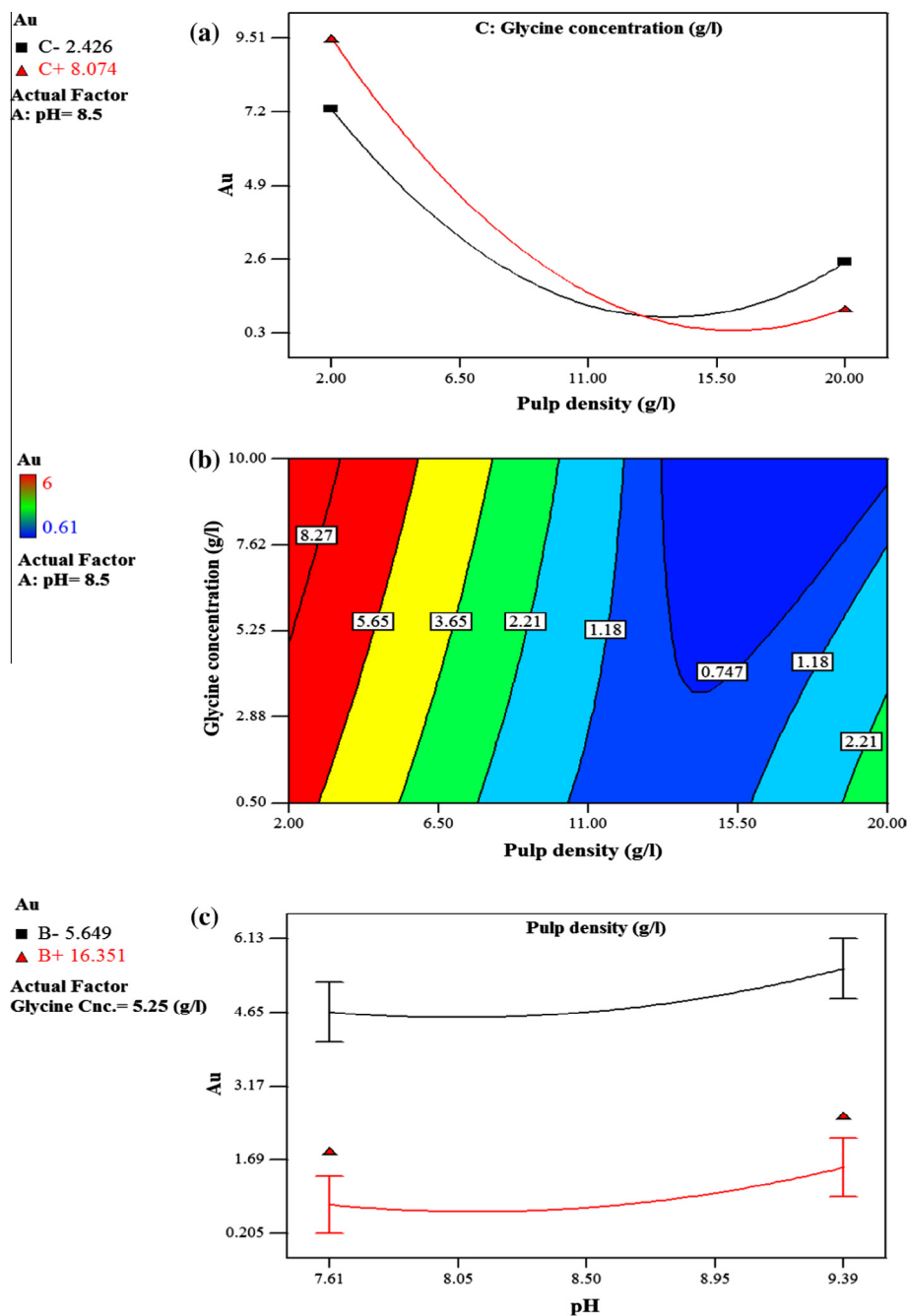


Fig. 3. Effect of pulp density on Au recovery (a) interaction plot with glycine concentration, (b) contour plot with glycine concentration and (c) interaction plot with initial pH.

dominant form of cyanide is CN^- which is stable in the solution and can attack the metals. At lower pH values, the dominant form of cyanide is HCN gas in which before reaction a high amount of gas is released out of the solution. On the other hand, it has been reported that the maximum amount of cyanide is produced at pH values of 7–8 (Natarajan and Ting, 2014). In addition, Shin et al. (2013) revealed that the maximum growth rate of *C. violaceum* occurs at pH of 8. These results can probably be promoted for *B. megaterium*.

As Fig. 4 illustrates, high amount of glycine is more effective on Au recovery. Shin et al. (2013) studied the growth of *C. violaceum* and cyanide production at glycine concentrations of 0.5–20 g/l. They reported that the maximum growth rate occurred at 0.5 g/l of glycine and that the maximum amount of cyanide was produced

at 5 g/l. The bacterial resistance and optimal amount of glycine concentration are probably interdependent. Increasing the amount of glycine as a direct metabolite in formation of cyanide, as long as it does not act as an inhibitor on bacterial growth, can lead to higher production of cyanide and subsequent enhancement of metal recovery yields.

4.3.2. Cu recovery

The effect of pulp density and initial pH at constant initial glycine concentration of 10 g/l has been shown in Fig. 5(a). Higher initial pH and pulp density lead to enhancement of Cu recovery. As formerly stated, at high initial pH the produced cyanide exists in the stable form of CN^- , and thus the free and available cyanide in the solution increases. Increasing pulp density causes an

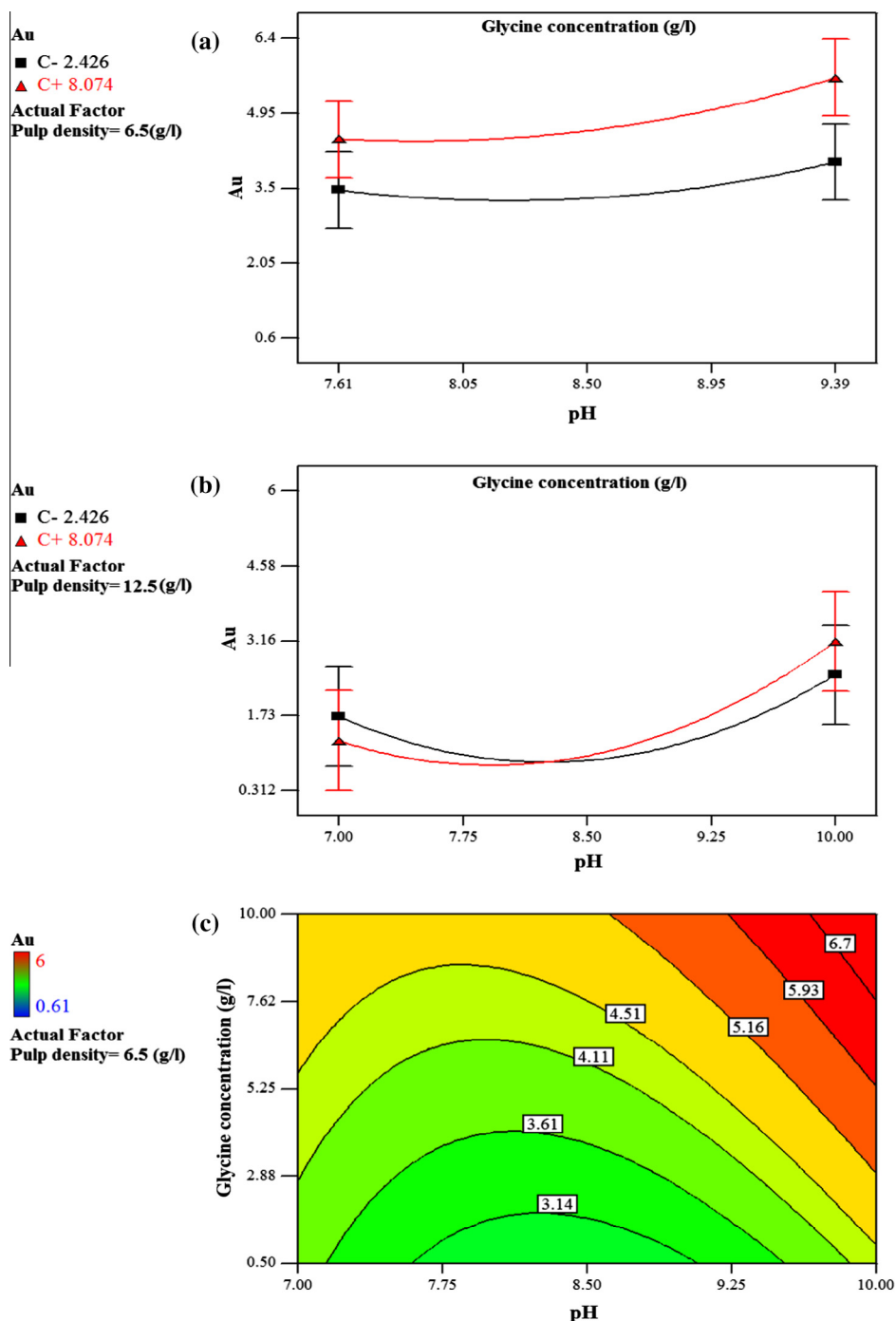


Fig. 4. Effect of glycine concentration and initial pH on Au recovery (a) interaction plot at pulp density of 6.5 g/l, (b) interaction plot at pulp density of 12.5 g/l and (c) contour plot at pulp density of 6.5 g/l.

increment in the number of particles and also the available surface for cyanide to form complexes with Cu and consequently improves Cu recovery. Probably by decreasing pulp density, the randomized collision between cyanide and Cu decreases.

In another research performed by the authors (Arshadi and Mousavi, 2015a), the same result was obtained. Investigation of Cu recovery from CPCBs using *B. megaterium* revealed that augmenting pulp density enhanced Cu recovery yield. In the first study (Arshadi and Mousavi, 2014), examining Cu extraction from CPCBs using *A. ferrooxidans* confirmed the fact that in some conditions increasing pulp density leads to higher Cu recovery.

The differences between part (a) and (b) in Fig. 5 depict the important role of glycine concentration on Cu recovery. By decreasing glycine concentration from 10 g/l to 0.5 g/l, Cu recovery dropped sharply. MPPCBs contain 6.65% (w/w) of Cu, which for reaching to a high recovery yield of Cu, a large amount of cyanide and, consequently, glycine is needed.

4.4. Optimal condition and confirmation test

To achieve the maximum simultaneous extraction of Au and Cu, the model suggested initial pH of 10, pulp density of 8.13 g/l, and glycine concentration of 10 g/l with desirability of 0.89. For

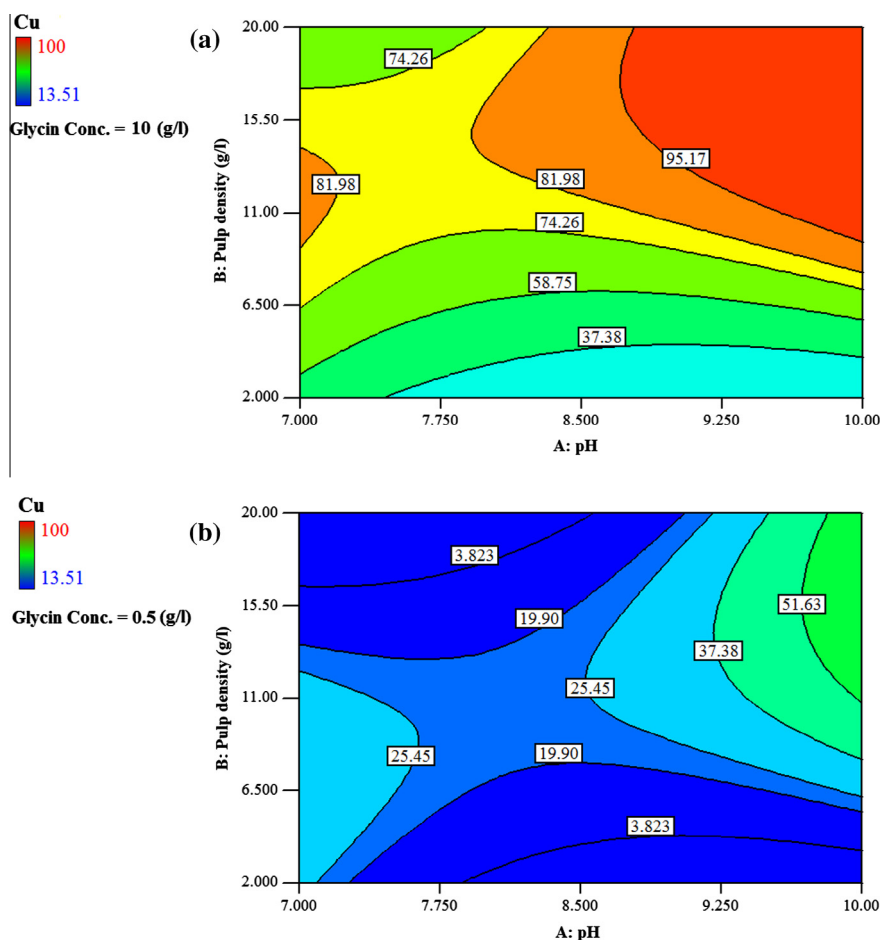


Fig. 5. Effect of pulp density and initial pH on Cu recovery at glycine concentration of (a) 10 g/l and (b) 0.5 g/l.

corroborating the accuracy of the model, an experiment was carried out under suggested optimal condition, confirming that 3.6% (65 g/ton) of Au and 71.45% of Cu were extracted. According to Table 5, the results of Au and Cu recovery obtained from the experiments were sufficiently near the amount of model expectance.

4.4.1. Effect of particle size and pretreatment on recovery

4.4.1.1. Particle size. In all of the conducted experiments, a homogeneous powder with particle sizes of 37–149 μm was used. To investigate the effect of particle size on metal recovery yields, an experiment was carried out in the same condition as validation test but using particles finer than 37 μm . Under this condition and within 10 days, 3.35% of Au and 85.22% of Cu were recovered. The important point here was that at pulp density of 8.13 g/l, by decreasing particle size the recovery remained constant. The same study on CPCBs revealed that at glycine concentration of 5 g/l and initial pH of 7, pulp density and particle size had an important interaction which was more intensive at pulp density of 12 g/l (Arshadi and Mousavi, 2015b). It is likely that under another condition, changing particle size could lead to a different result for recovery from MPPCBs. This testing established the importance

of using optimization which is ignored in most of the bioleaching studies on PCBs.

4.4.1.2. Effect of Cu elimination on Au recovery. As discussed earlier, most metals, especially Cu, have an inhibitory effect on Au recovery. In order to investigate the effect of elimination of Cu on Au recovery, the sample was pretreated. For this purpose, firstly Cu was totally extracted from MPPCBs using *A. ferrooxidans*, and then the sediment having remained from optimal condition of part I (Arshadi and Mousavi, 2015b) was washed, dried, and used. As a matter of fact, part I was a pretreatment to continue this research (for more details, the readers can refer to part I). In order to examine the effect of pretreatment on Au recovery, the second step of bioleaching of the Cu free pretreated sample of MPPCBs under the already obtained optimal condition for the normal sample was carried out using *B. megaterium*. The maximum amount of Au recovery under this condition was about 2.18%. Fig. 6 demonstrates pH variation vs. time which is almost the same for all of the samples. Since the startup point of pH is 10, the dominant form of cyanide is as HCN. Production of HCN by the bacterium causes pH reduction. When hydrocyanic acid reacts with the metals and makes cyanide complex, OH^- is released and, consequently, pH increases. Achieving the lowest value of pH occurred on the 6th day, meaning that the maximum amount of metals were bioleached on this day. The pH variation in MPPCBs solution was similar to that of CPCBs solution using *B. megaterium* so that there are two ups and downs on the figure. Motaghed et al. (2014) studied bioleaching of spent catalysts via *B. megaterium*, reporting that the pH increased from about 7 to 9 continuously within 4 days.

Table 5
Point prediction and verification of the models at the optimum conditions.

Response (%)	Target	Predicted recovery (%)	Confirmation experiment (%)
Au recovery	Maximize	6	3.60
Cu recovery	Maximize	82.3	71.45

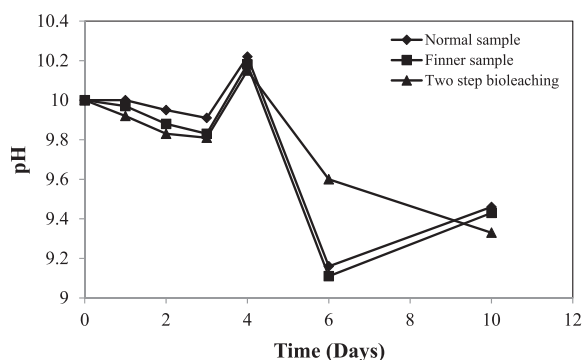


Fig. 6. The pH variation vs. time at optimal condition.

Pradhan and Kumar (2012) studied bioleaching of metals from e-wastes. They demonstrated that the pH increased from 7.2 to 9.2 by using *P. fluorescens* in for 7 days, describing that at pH of 7 cyanide is in the form of hydrocyanic acid and at pKa cyanide of 9.3 it is volatile. In the presence of salts, this amount diminished to 8.3 and the volatility decreased. By producing HCN and formation of complexes, the pH increased continuously. Chi et al. (2011) concluded that as a result of the growth of both *C. violaceum* and *P. fluorescens*, the pH increased continuously from 7 to 9 during 4 days and then remained constant. The same result achieved by Brandl and Faramarzi (2006) indicated that *C. violaceum* growth improved the pH continuously from 7 to 9 within 4 days which became constant afterwards. Faramarzi and Brandl (2006) showed that by increasing *P. plecoglossicida*, the pH augmented quickly from 7 to 9.5 and then declined to 8.5. It seemed that for cyanogenic bacteria when the startup point was 7, initially the pH raised up to 9, and then when reaching the values upper than 9.5, it dropped. In all of the explained researches, the startup point was about 7, while in this research the adjusted pH was 10, and that is why the pH variation was different. For CPCBs (Arshadi and Mousavi, 2015a), the startup point was 10, and the same plot was resulted.

There is a big difference between the results obtained for MPPCBs and CPCBs. It was shown that for CPCBs, Au recovery from the normal sample was about 36.81%, while approximately 63.8% of Au was recovered, using the pretreated sample (Arshadi and Mousavi, 2015a). There are two points which should be illustrated here. MPPCBs contain 1800 g/ton and 6.65% w/w of Au and Cu, respectively. The amount of Au in CPCBs is nearly 8.82 times less than that of Au in MPPCBs. The amount of Cu in CPCBs is about 6 times greater than that of Cu in MPPCBs. First, it can be concluded that to recover the same percentage of Au from MPPCBs as CPCBs, the amount of required cyanide must be more than 8.82 times greater than the amount needed to recover Au from CPCBs, while the potential of bacteria in producing cyanide is finite. It is expected that gold extraction from MPPCBs is less in comparison to CPCBs. Second, while since the amount of Au in MPPCBs is so much higher than CPCBs while the amount of Cu is a lot less, the inhibitory effect of Cu on Au recovery decreases sharply. Logically, by Cu elimination Au recovery from MPPCBs did not change significantly, whereas for CPCBs nearly 64% of Au was recovered. These results can be a golden key in bioleaching of PCBs of e-wastes.

5. Conclusion

To identify the interactions between parameters, the bioleaching process was statistically analyzed. Two modified quadratic models were suggested by the software for prediction of simultaneous Au and Cu recovery from MPPCBs. According to ANOVA, pulp

density and glycine concentration were the most important parameters on Au and Cu recovery, respectively. Under optimal condition suggested by the models, about 72% of Cu and 65 g Au/ton MPPCBs, 7 times greater than the recovery from gold mines, were extracted. The low ratio of Au/Cu in MPPCBs can improve Au recovery. To recover the total Au from MPPCBs, it is suggested that Au concentration in the original samples should be diluted before bioleaching.

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Greener approach for the extraction of copper metal from electronic waste



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ABSTRACT

Technology innovations resulted into a major move from agricultural to industrial economy in last few decades. Consequently, generation of waste electronic and electrical equipments (WEEE) has been increased at a significant rate. WEEE contain large amount of precious and heavy metals and therefore, can be considered a potential secondary resource to overcome the scarcity of metals. Also, presence of these metals may affect the ecosystem due to lack of adequate management of WEEE. Building upon our previous experimental investigations for metal extraction from spent catalyst, present study explores the concept of green technology for WEEE management. Efforts have been made to recover base metal from a printed circuit board using eco-friendly chelation technology and results were compared with the conventional acid leaching method. 83.8% recovery of copper metal was achieved using chelation technology whereas only 27% could be recovered using acid leaching method in absence of any oxidant at optimum reaction conditions. Various characterization studies (energy dispersive X-ray analysis, scanning electron microscopy, X-ray diffraction, inductive coupled plasma spectrophotometry) of Printed Circuit Board (PCB) and residues were performed for qualitative and quantitative analysis of samples. Significant metal extraction, more than 96% recovery of chelating agent, recycling of reactant in next chelation cycle and nearly zero discharge to the environment are the major advantages of the proposed green process which articulate the transcendence of chelation technology over other conventional approaches. Kinetic investigation suggests diffusion controlled process as the rate determining step for the chelate assisted recovery of copper from WEEE with activation energy of 22 kJ/mol.

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1. Introduction

Environmental management of hazardous wastes has become a major concern across the globe due to uncontrolled dumping of hazardous wastes into ecosystem in a cavalier manner. Significant potential risks associated with these hazardous wastes to the ecosystem are increasingly recognized. Nearly, 1.3 billion tonnes (1.2 kg/capita/day) of waste are generated every year across the globe (Hoornweg and Bhada-Tata, 2012), which will likely increase to 4.3 billion urban residents generating about 1.42 kg/capita/day of solid waste (2.2 billion tonnes per year) by the year 2025. Globally, solid waste management costs are also estimated to increase from today's annual \$205.4 billion to about \$375.5 billion in 2025. Developing countries such as China and India face a rapidly increasing amount of solid waste, from domestic generation and illegal imports. In addition, the lack of national regulation and/or lax enforcement of existing laws are promoting the growth of a

semi-formal or informal economy in industrializing countries. Improperly managed solid waste poses hazardous effects on human health and the environment. Uncontrolled dumping and improper waste handling may cause water contamination, increasing possibilities of flooding due to blocked drainage canals, greenhouse gas emission and consequently climate changes. Therefore, a strong need is felt to adapt the green innovative approaches for minimizing the global environmental impacts of solid wastes.

1.1. Greening the 'Waste'

This paper deals with the concept of "Greening the waste" which refers to a shift from less-preferred waste treatment (acid/alkali leaching, pyrometallurgical methods) and disposal methods (incineration, landfilling) toward greener technologies following the "Four R's" i.e. Reduce, Reuse and Recycle and Recovery. "Greening the waste" strategy is to move upstream in the waste management hierarchy as shown in Fig. 1, based on the internationally recognized approach of Integrated Solid Waste Management (ISWM) (ISWM, 2011). This concept includes

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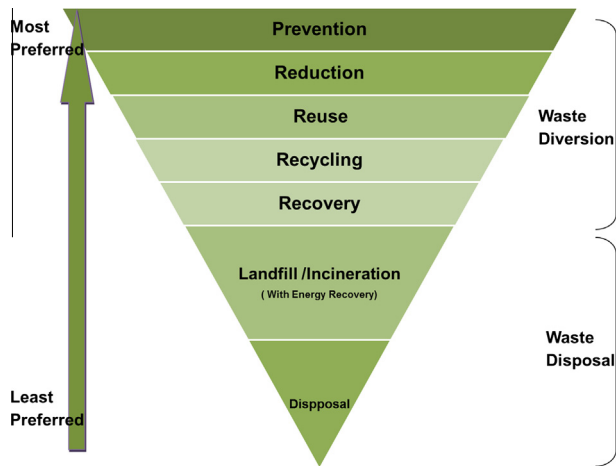


Fig. 1. Waste management hierarchy.

resource conservation and optimization, waste reuse and recycling, energy recovery, landfill avoidance and acquisition of novel green approaches for waste management. In this paper, “Greening the waste” concept has been explored in order to generate substantial economic, environmental and social benefits using waste electrical and electronic equipments (WEEE).

2. WEEE management

Revolutionary innovations in the functionality of information and communication technology certainly marked a new era of human civilization in past two decades. Though, negative shades of this revolution can also not be disregarded. With the rapid development and technology innovations, the useful life of consumer electronic products has been foreshortened. Thereof, generation of waste electronic and electrical equipments (WEEE) has been increased at a significant rate. According to the Basel Action Network, WEEE can be defined as:

“A broad and growing range of electronic devices ranging from large household devices such as refrigerators, air conditioners, cell phones, personal stereos, and consumer electronics to computers which have been discarded by their users”.

[Puckett and Smith, 2002]

WEEE contains valuable and hazardous metals which require special handling and recycling methods to minimize environmental contamination and hazardous effects on human health.

Globally, generation of WEEE is predicted to grow up to 65.4 million metric tons by year 2017 which is 34% higher than that of in year 2012 (Bidwell, 2013). It is also estimated that e-waste from old computers would raise by 500% and that of discarded mobile phone would be nearly 18 times higher by year 2020 than year 2007 levels in India (UNEP, 2010). Cobbing (2008) approximated production of almost 10 million tonnes of e-waste globally only from computers, mobile phones and television sets in year 2015. Hence, WEEE can be regarded as the most riotous solid waste stream which is growing at the rate of 3–5% annually (Tuncuk et al., 2012). Fig. 2 demonstrates the production of WEEE in different countries for the year 2012 which clearly demonstrates Europe and USA as the largest producer of e-scrap. Developing countries such as China and India are also moving at a fast pace in the technological world which can be estimated with the growing amount of WEEE in these countries.

Another sincere concern is the complexity of WEEE due to wide range of electronic products which differentiates WEEE from other

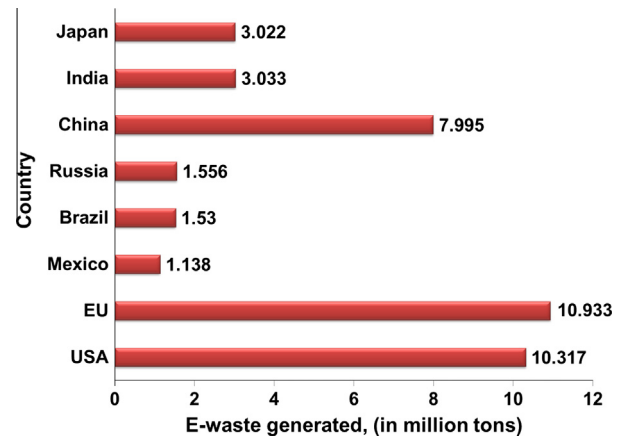


Fig. 2. Global generation of WEEE in year 2012. Source: StEP initiative, <http://www.step-initiative.org/overview-world.html>.

solid waste on the basis of their chemical and physical properties (Yla-Mella et al., 2004). WEEE contain large amount of metals, particularly Cu, Al, and Fe, mixed with various types of plastics and ceramics which reflects WEEE as a potential secondary resource to overcome the scarcity of metals. Nevertheless, presence of these metals may affect the ecosystem due to lack of adequate management of WEEE. Environmental effects of WEEE disposal are drawing increasing attention from the scientific community. Increasing number of research publications related to WEEE management has been analyzed for last 15 years by collecting the data from Scopus library (<http://www.scopus.com>). Scopus library enumerates that approximately 1221 reports have been published related to WEEE management out of which 584 are research articles, 124 are review article and 411 are conference papers. Also, more than 90 publications every year in the last decade (<http://www.scopus.com>) clearly illustrate the increasing concern of researchers toward economic potential and environmental consequences of WEEE.

Several initiatives have been made by the government and non-governmental organizations (NGOs). WEEE directive have made it mandatory for manufacturers to follow the concept of ‘Greener Electronics’ (Chen et al., 2011; Pant, 2010). The Restriction on the use of Hazardous Substances (RoHS) directive prohibits the use of Pb^{2+} , Cd^{2+} , Hg^{2+} , Cr^{6+} , polybrominated biphenyls (PBBs), and polybrominated diphenyl ethers (PBDEs) in new electronic devices (Chen et al., 2011). Incineration, landfilling and export to overseas are not allowed in recent years for WEEE management due to strict environmental legislations. Thus, environmental concerns and presence of reusable metals/components trigger the need to recover heavy and precious metals from WEEE, before disposing off these scrap material into the ecosystem. Some world initiatives for the WEEE management have been listed here in Table 1.

Incineration, landfilling and export to overseas are not allowed in recent years for WEEE management due to strict legislations. Thus, environmental concerns and presence of reusable metals/components trigger the need to recover heavy and precious metals from WEEE, before disposing off these scrap material into the ecosystem. Recovery of metals from WEEE using conventional hydrometallurgical and pyro-metallurgical processes is widely reported in literature; however, environmental consequences and high energy requirement are the major limitations which inhibit their use at large scale. Pyro-metallurgical methods are energy intensive and liberates hazardous dioxins which itself become secondary pollution possibility (Khalik et al., 2014; Cui and Zhang, 2008). Hydrometallurgical treatment of WEEE often uses cyanide, halide, thiourea and thiosulfate as leaching agent to extract

Table 1
Global initiatives for WEEE management.

Initiative	Details
Restriction of Hazardous Substances Directive (RoHS)	Enacted along with EU WEEE, restricts amounts of lead, mercury, cadmium, hexavalent chromium, PBB, and PBDE used in manufacture. Versions adapted by many other countries, including China and India
EU WEEE Directive	Adapted by all EU members by 2007. Establishes systems of collection and recycling based on producer take-back, for 10 categories of electrical goods
Solving the E-waste Problem (StEP)	Instituted formally in 2007 by UN agencies, StEP partners with prominent academic and govt. organizations (e.g., MIT, USEPA) on promoting reuse of recycled materials and control of e-waste contaminants
Reduce, Reuse, Recycle (3Rs)	Promoted by Japan. Seeks to prevent creation of waste, and to further cooperation on recycling with developing countries. Allows waste export for remanufacture
US State laws and the Responsible Electronic Recycling Act (HR2284)	25 US states have laws for e-waste collection, some stipulating consumer payment. HR2284 is a proposed national law to control e-waste export and certify used electronic goods for export
US NGOs—Basel Action Network (BAN), Silicon Valley Toxic Coalition (SVTC), Electronics TakeBack Coalition (ETBC)	These three act together for workable national e-waste collection and recycling programs. They internationally promote the “Basel Ban,” a more restrictive waste export amendment to the Basel Convention. BAN has produced documentaries, and much research
Bamako Convention	In force since 1998 in African Union countries. Sets more stringent waste import limits than the Basel Convention, and sets penalties. Seldom evoked

precious metals (Tuncuk et al., 2012; Peter et al., 2014; Akcil et al., 2015; Chen et al., 2015). These leaching agents may cause environmental problems due to high toxicity and therefore, cannot be considered safe alternative for metal extraction (Behnamfard et al., 2013). Thiourea, thiosulfate are potential carcinogen and have very low chemical stability. Corrosion problems, necessity of expensive material of construction to avoid corrosion, difficult handling of reagents and release of toxic gases are serious concerns, associated with acid-leaching process which make this process unworkable for metal extraction from waste material.

Bioleaching is another green alternative to extract metals from electronic and industrial waste and several authors have reported significant extraction efficiency using bioleaching methods (Bas et al., 2013; Willner and Fornalczyk, 2013; Madrigal-Arias et al., 2015; Panda et al., 2015a). Sequential bioreduction–bioleaching and bioreduction–chemical leaching hybrid experiments were performed to recover copper from an industrial waste (Panda et al., 2015b). Recovery of copper was observed to be higher in case of chemical leaching methods, still eco-friendly attribute substantiates the applicability of bioleaching methods. Chalcopryrite bioleaching using heap-leach technology is current advancement in order to process low grade and difficult-to-enrich ores for copper extraction (Panda et al., 2015c). Though bioleaching methods are established as green alternative in order to minimize environmental pollution; longer leaching time, contamination possibilities and limited acceptability of microorganisms at high temperatures still confine the applicability of biotechnological approaches.

Therefore, a strong need of an effective solution is perceived which addresses the limitations of conventional approaches and provides an eco-friendly alternative to this growing problem. Chelation–dechelation concept, a modern research trend, was coined by our research group to extract heavy metals from spent catalyst. Chelation is defined as the formation of stable metal–ligand complexes which are soluble in water (Chauhan et al., 2015c). Building upon our previous research work (Chauhan et al., 2012, 2013a, 2015a), chelation technology has been proven an efficient green approach for metal extraction from contaminated media, though this technology has not been explored yet in the literature (to the best of our knowledge) for metal extraction from WEEE. Present study is a novel research effort to investigate the applicability of chelation technology in recovery of metals from electronic waste. Experiments were also performed using conventional acid leaching method and extraction efficiency of chelation technology was compared with acid leaching to acknowledge the more efficient approach. Reaction parameters were optimized under atmospheric reflux conditions at moderate reaction temperature.

Significant recovery of metal, successful recovery and recycling of chelating agent in subsequent chelation cycle, mild reaction conditions and noncorrosive nature of the extraction process offer wide applicability of chelation technology in WEEE management.

3. Raw material and reagents

Printed Circuit Board (PCB) of desktop computer was employed as the metal source in present study. Elemental composition of the sample PCB was determined by the inductive coupled plasma optical emission spectrometry (ICP-OES) using aqua regia which suggests presence of 20 wt% copper with trace amount of other precious metals (Au – 41 ppm, Ag – 159 ppm, Pd – 28 ppm). Ethylenediaminetetraacetic acid (EDTA) (Fisher Scientific) was used as a reactant for the chelation experiments whereas sulfuric acid (H₂SO₄, 98% pure) (Merck) was employed as an acid leachant in the present study. Double distilled water of high purity (millipore apparatus) was employed in all the experiments. Various characterization techniques (scanning electron microscopy ((SEM) EVO50), energy dispersive X-ray analysis ((EDX) EVO50), X-ray diffraction (XRD, Philips X'pert-1 X-ray diffractometer)) were performed to study the morphology and metal phase distribution in PCB sample and residues. Cary 5000 Varian UV spectrophotometer was used to determine the metal concentration in solution.

4. Experimental procedure

4.1. Dismantling of PCB

The electronic component (e.g. capacitors, batteries and resistors) and plastic materials of spent PCB were removed manually using pliers. PCB was, then, shredded into the pieces approximately of size 2 × 2 cm. These pieces were crushed using grinder and then sieved to form the homogenous powder of the desired particle size of 150 µm.

4.2. Acid leaching experiments

Leaching experiments were conducted for the extraction of copper from sample PCB. 5 g of homogeneous powder of spent PCB was added to the aqueous solution of sulfuric acid (varied from 10% to 30%) in order to maintain desired molar concentration of reactant and liquid to solid (L/S) ratio in slurry. Reaction was

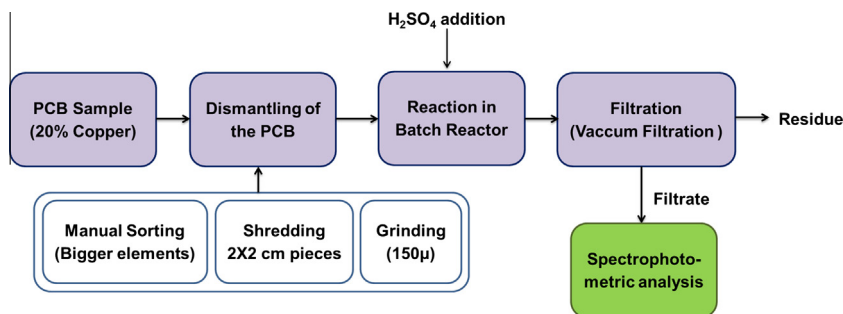


Fig. 3. Block diagram for the acid leaching process.

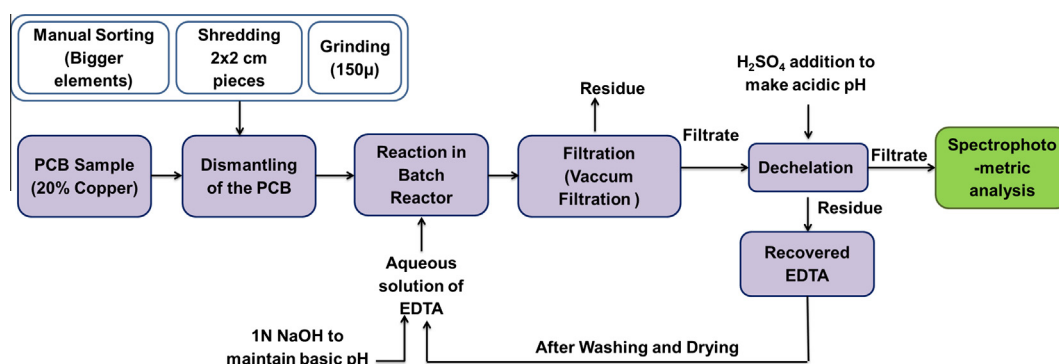


Fig. 4. Block diagram of chelation–dechelation experiments.

performed in a batch reactor under atmospheric reflux condition and continuous stirring was provided for proper mixing. A condenser was attached to the flask to prevent vaporization loss. Block diagram for the leaching process is given in Fig. 3.

Temperature, reaction time, solid to liquid ratio, concentration of leachant and stirring speed were varied for a wide range in order to optimize the leaching efficiency. Once the reaction is complete, the resulting slurry was filtered on sintered glass. Cary 5000 varian UV spectrophotometer was employed to determine the copper content in the filtrate. All the experiments were carried out in triplicates and the average deviation among the replicates was observed to be within $\pm 5\%$.

4.3. Chelation–dechelation experiments

Chelation experiments were performed in the similar manner as described in literature (Chauhan et al., 2012). Aqueous solution of chelating agent EDTA was prepared to obtain the desired molar concentration of the EDTA. As the chelating agent EDTA is dissolvable in alkaline medium, therefore sodium hydroxide (NaOH, 0.1 N) was added dropwise to maintain the basic pH of the solution. 5 g of PCB sample was added to the chelating agent solution and a certain L/S ratio was maintained during the chelation reaction. Slurry was transferred to the reactor for chelation experiments at certain reaction temperature. Once the reaction was complete, slurry is filtered using vacuum filter and the filtrate was sent for the dechelation experiments. The insoluble leach residue was washed thrice with distilled water (60 °C) and dried at 100 °C for 4 h. Fig. 4 demonstrates the block diagram of the chelation–dechelation experiments for copper recovery and EDTA recycling.

Dechelation of Cu–EDTA complex was carried out at acidic pH, therefore sulfuric acid was added to the filtrate to attain pH 2–3. Precipitation time of 6 h was provided to allow the maximum

precipitation and settling of EDTA and more than 96% EDTA was recovered in the residue. After washing with distilled water and drying at 100 °C for 2 h, this recovered EDTA could be recycled in the subsequent chelation cycles. The filtrate obtained after dechelation experiment was analyzed using UV spectrophotometer. Spectrophotometric calibration was performed by preparing aqueous solutions of known concentration of copper sulfate (100–500 ppm). The peak of the Cu was observed at 356 nm wavelength. Calibration equation was developed by plotting graph between absorbance and amount of Cu (ppm) present in solution and amount of Cu (ppm) in solution of unknown concentration was determined using Eq. (1):

$$Y = 0.0012X - 0.034 \quad (1)$$

where Y is the absorbance at 356 nm wavelength (Cu peak) and X is the amount of Cu present in filtrate (ppm). All the experiments were carried out in triplicates and the average deviation among the replicates was observed to be within $\pm 5\%$. Percentage (%) extraction of copper is given as the ratio of amount of Cu present in the solution to the initial amount of Cu present in PCB sample which can be represented as shown in Eq. (2):

$$(\%) \text{ Extraction of Cu} = \frac{\text{Amount of Cu in filtrate}}{\text{Initial amount of Cu in PCB}} \times 100 \quad (2)$$

5. Results and discussions

5.1. Effect of molar concentration of reagent

Effect of molar concentration of H_2SO_4 and EDTA on the % Cu extraction from PCB was studied. H_2SO_4 concentration was varied in the acid leaching experiments from 10% to 30% (i.e. 0.28 M to 0.84 M). Leaching experiments were performed under atmospheric reflux condition at 100 °C for 4 h. Continuous stirring was provided

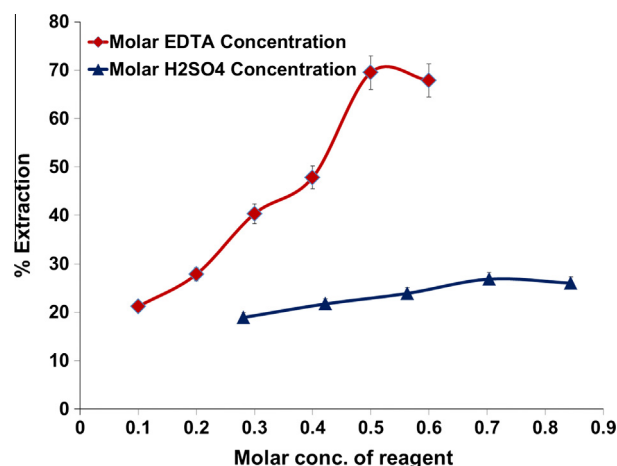
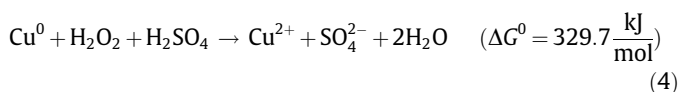
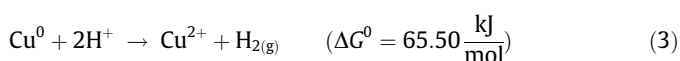


Fig. 5. Effect of molar concentration of reagent on Cu extraction. Reaction conditions: L/S ratio = 15:1 (v/w), stirring speed = 700 rpm, reaction temperature = 100 °C, reaction time = 4 h, particle size = 150 µm (pH = 11 in case of chelation experiment).

at 700 rpm and L/S ratio was kept constant at 15:1 (v/w). It can be depicted from Fig. 5 that as the acid concentration increases in the reacting solution, the % Cu extraction increases up to 0.7 M, and beyond 0.7 M, it became nearly constant. Therefore, 0.7 M (i.e. 25% acid concentration) was considered optimum to perform acid leaching experiments. It is worthy to mention here that very limited (not more than 30%) Cu extraction was achieved using sulfuric acid as an acid leachant. Lack of any oxidant in the present work could be the possible reason for low extraction of Cu from PCB. Deveci et al. (2010) observed less than 2% Cu extraction using H₂SO₄ in absence of any oxidant while, more than 60% Cu was recovered using H₂O₂ along with H₂SO₄. Literature suggests that oxidative leaching is an efficient way to recover base metals and can be explained by following Eqs. (3) and (4) (Tuncuk et al., 2012), however in order to minimize hazardous handling of chemicals, oxidants were not used in present study.



Since, the major objective of this study was to explore a green technology for Cu extraction from WEEE, performance of leaching experiments was compared with the emerging green chelation technology. EDTA concentration was varied for a wide range from 0.1 M to 0.6 M. Other process parameters (reaction temperature, L/S ratio, stirring speed, particle size) were same as that for acid leaching except that chelation experiments were performed at alkaline pH = 11. Increase in extraction efficiency was observed with the increases in molar concentration of EDTA as shown in Fig. 5. 0.5 M molar concentration of EDTA was considered as the optimum to maximize Cu extraction and beyond this concentration, no significant increase in the extraction efficiency was observed. Nearly 70% Cu was extracted from PCB sample at optimum molar concentration of EDTA.

Results were found to be in agreement with our previous observations for metal extraction from spent catalyst (Chauhan et al., 2013a, 2013b) which suggests that higher concentration of chelating agent pushes the reaction in forward direction due to the reversible nature of the reaction.

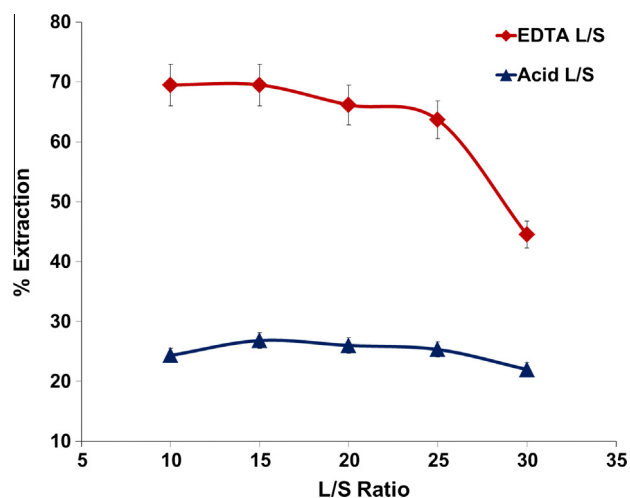


Fig. 6. Effect of L/S ratio on Cu extraction. Reaction conditions: H₂SO₄ concentration 0.7 M, stirring speed 700 rpm, reaction temperature 100 °C, reaction time 4 h, EDTA concentration 0.5 M (pH = 11 in chelation experiments).

5.2. Effect of liquid to solid ratio

L/S was varied for a wide range from 10:1 (v/w) to 30:1 (v/w) to perform leaching and chelation experiments. Optimum molar concentration of acid and chelate, obtained in previous section (0.7 M H₂SO₄, 0.5 M EDTA) was employed in further experiments while other process parameters were kept same as mentioned in Section 4.1. Fig. 6 demonstrates the effect of L/S ratio on metal extraction efficiency. No significant change in extraction efficiency was observed with increase in L/S ratio in case of acid leaching experiments as shown in Fig. 6. It can be explained by the fact that reactant is present in the solution more than the required for leaching reaction and therefore, variation in L/S ratio did not affect the extraction efficiency. Kim et al. (2003) also studied the effect of L/S on lead extraction from soil and explained that no effective increase in extraction efficiency can be observed beyond a certain L/S value when the concentration of reagent is enough for the metal extraction and only a small fraction is being effectively utilized in the leaching process.

Extraction efficiency was observed to be nearly constant for L/S = 10:1 (v/w) and 15:1 (v/w) as shown in Fig. 6 while performing experiments using EDTA. Beyond 15:1 (v/w), increase in L/S ratio exhibited a negative effect on extraction efficiency. More than 20% decrease in Cu extraction was observed while increasing L/S ratio from 15:1 (v/w) to 30:1 (v/w). Chauhan et al. (2015a) suggested that increase in L/S ratio can be attributed to a decrease in the reactant concentration at constant MR (molar ratio of reactant to metal), and therefore, metal recovery decreases after achieving optimum L/S ratio for efficient mixing as can be seen beyond 15:1 (v/w) in Fig. 6. However, if the L/S ratio is too low to minimize the external resistance in absence of efficient mixing, then the extraction efficiency will be less. In the present study, the mixture of PCB sample and aqueous solution of EDTA was not viscous and therefore, proper mixing could be achieved even at low L/S ratio i.e. 10:1 (v/w).

5.3. Effect of reaction temperature and reaction time

Reaction temperature and reaction time was varied for a wide range from 40 °C to 120 °C and from 1 h to 5 h respectively to investigate the effect of temperature and time on the extraction of Cu from PCB. It can be observed from Fig. 7 that extraction of Cu increases with the increase in reaction temperature which

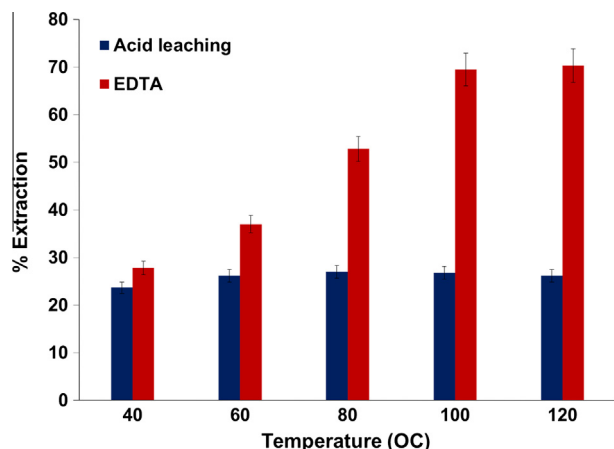


Fig. 7. Effect of reaction temperature on Cu extraction. Reaction conditions: H_2SO_4 concentration 0.7 M, liquid to solid ratio 15:1, stirring speed 700 rpm, reaction time 3 h, EDTA concentration 0.5 M (pH = 11 in chelation experiments).

could be related directly to the enhanced reaction kinetics. At high temperature, molecules collide frequently and thus reaction rate increases which may cause improvement in extraction efficiency. In case of acid leaching, 60 °C was considered as the optimum reaction temperature whereas, chelation reaction showed increase in Cu recovery with the increase in temperature from 40 °C to 100 °C. Therefore, 100 °C was considered as the optimum reaction temperature for chelation experiments. Results are in concordance with the literature where reaction temperature significantly affects the recovery of metals from contaminated sites due to the Arrhenius behavior of reactants.

Effect of reaction time on extraction efficiency was studied for a wide range from 1 h to 5 h. It can be depicted from Fig. 8 that amount of metal extracted increases with increase in reaction time. An asymptotic value of Cu recovery was attained at 3 h reaction time for leaching and chelation experiments, therefore, 3 h was considered as the optimum reaction time in present study for Cu extraction from PCB.

5.4. Mass transfer limitations

Effect of external mass transfer on the recovery of Cu was studied by varying stirring speed for a wide range of 100–900 rpm.

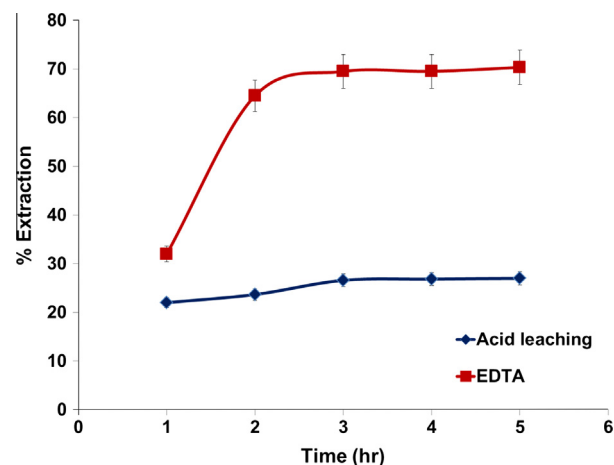


Fig. 8. Effect of reaction time on Cu extraction. Reaction conditions: H_2SO_4 concentration 0.7 M, liquid to solid ratio 15:1, stirring speed 700 rpm, reaction temperature 100 °C, EDTA concentration 0.5 M (pH = 11 in chelation experiments).

Internal mass transfer was assumed to be negligible as fine powder of PCB sample (150 μm) was employed in the present study. Below this particle size, filtration problems were observed during experiments. It can be depicted from Fig. 9 that external mass transfer could be minimized with increase in stirring speed, therefore significant increase in % extraction of Cu was observed with the increases in stirring speed. Beyond 700 rpm, extraction efficiency almost remains constant for both chelation and acid leaching experiment, therefore, 700 rpm was considered as the optimum stirring speed. Nearly 10% increase in Cu recovery was attained while increasing stirring speed from 100 rpm to 700 rpm. Chelation experiments showed 40% high extraction efficiency than acid leaching experiments at optimum stirring speed as demonstrated in Fig. 9.

5.5. Effect of reaction pH

As the chelating agent EDTA was dissolvable in distilled water at alkaline pH, the effect of reaction pH was studied in the alkaline range of pH = 7 to pH = 11 for chelation experiments. It is reported in literature that % distribution of various protonation stages strongly affects the effective pH range for a chelating agent (Chauhan et al., 2015a), therefore increase in extraction efficiency was reported with the increase in reaction pH in literature (Goel et al., 2009; Chauhan et al., 2013a). However, results obtained in present study for Cu extraction from PCB samples contradict to the available literature. Highest extraction efficiency was obtained at neutral pH while, with the increase in reaction pH, extraction efficiency starts to decrease as shown in Fig. 10. 15% decrease in extraction efficiency was observed while increasing reaction pH from pH = 7 to pH = 11. It could be explained by the presence of other competing metal cations present in PCB sample which may interfere with the formation of Cu–EDTA complex at alkaline pH and thus affect the Cu recovery. Decrease in extraction efficiency with increased pH could be due to the accumulation of insoluble copper hydroxide at alkaline pH (excess of NaOH). Still further experimental investigations are required to find out the major interfering metal cations in the present study. Literature suggests lower pH values to be more favorable for Cu extraction in presence of competing ions (Ko et al., 2010; Kakitani et al., 2009).

It is clear from all the experimental observation that higher extraction of Cu from WEEE can be achieved using chelation technology than the conventional acid leaching method. 58% higher amount of Cu was extracted using EDTA than H_2SO_4 at optimum

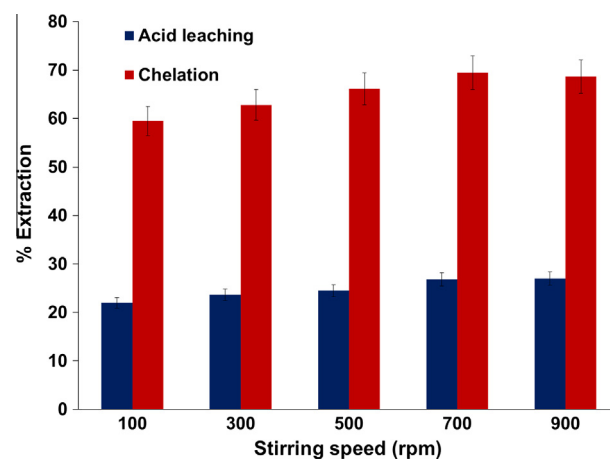


Fig. 9. Effect of reaction time on Cu extraction. Reaction conditions: H_2SO_4 concentration 0.7 M, L/S ratio 15:1 (v/w), stirring speed 700 rpm, reaction temperature 100 °C, EDTA concentration 0.5 M (pH = 11 in chelation experiments).

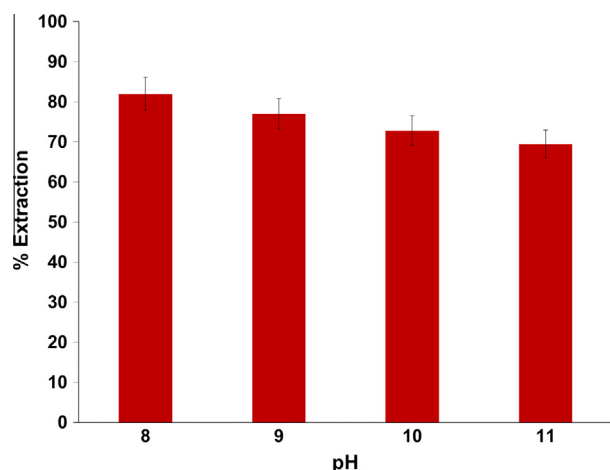


Fig. 10. Effect of pH on Cu extraction. Reaction conditions: EDTA concentration 0.5 M, (L/S) ratio 15:1 (v/w), stirring speed 700 rpm, reaction temperature 100 °C, reaction time 3 h.

reaction conditions i.e. molar concentration of EDTA = 0.5 M, L/S = 15:1 (v/w), stirring speed = 700 rpm, reaction time = 3 h, reaction temperature = 100 °C, particle size = 150 µm and reaction pH = 7. Mild reaction pH in case of chelation experiments affirms the easy handling, non-corrosive and less hazardous reaction environment.

6. Recovery and recycling of chelating agent

Successful recovery of chelating agent by employing dechelation process is an added incentive to the proposed novel green technology. Details of the dechelation process are given in Section 4.3. The major aim of the present study is to recycle 100% of the EDTA. However, prior to that, it is necessary to carry out a material balance of EDTA and also to verify whether the recovered EDTA (from the precipitation/dechelation step) shows similar efficiency in complexing Cu as compared to the fresh EDTA. Literature suggests (Vuyyuru et al., 2010; Chauhan et al., 2012, 2013a) that recovered EDTA can be recycled in subsequent chelation cycles for significant metal extraction and thus, reflects the economic constancy of the process.

In the present study, extraction efficiency of the recovered EDTA was compared with fresh EDTA over a wide range of operating conditions at atmospheric reflux conditions. 700 rpm stirring speed, 150 µm mean particle size, fresh EDTA solution pH of 8, 0.5 M concentrations of fresh and recovered EDTA, 100 °C reaction temperature and 3 h reaction time were obtained as the optimum process parameters for the chelation experiments using recovered EDTA. Fig. 11 demonstrates that the recovered EDTA consistently showed lower Cu recovery than the fresh EDTA.

Nearly 67% Cu was extracted at optimum reaction conditions after three subsequent cycles. Nevertheless, after the fifth cycle operation, approximately 30% less extraction efficiency was observed than with fresh EDTA; consequently, no further experiments were carried out using recovered EDTA. Loss in extraction efficiency with repetitive use of recovered EDTA can be attributed to factors such as increase in impurities with each recycling operation of EDTA (Chauhan et al., 2013a), Na-EDTA (fresh) vs protonated EDTA (subsequent), different moisture contents between the two samples which may distort the molarity (Vuyyuru et al., 2010). Therefore, it is advisable not to recycle EDTA after three chelation cycles to maintain the economic consistency of the process.

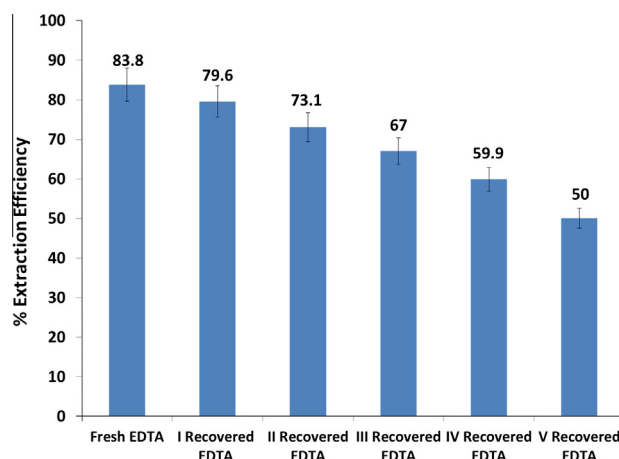


Fig. 11. Recovery of Cu from PCB using recovered EDTA: loss in performance from 83.8% to 67% over three EDTA recovery cycles.

7. Characterization of PCB sample and residue

Various characterization techniques were used for the evaluation of physicochemical properties of PCB and residues. Surface morphology of the PCB sample and the residue was studied by Scanning electron microscopy (SEM) analysis as shown in Fig. 12. Pellets of the PCB sample and residue were prepared in the similar manner as described in literature (Chauhan et al., 2012). The difference in the morphology of PCB and residue was investigated by performing the SEM analysis at the magnification of 20,000×. Fig. 12(A) clearly demonstrates the clog formation and rough surface in the SEM image of PCB sample. The bright spots (encircled to highlight) in the Fig. 12(A) denotes the ample presence of metal particle in the PCB sample. Fig. 12(B) represents the SEM image of the residue obtained after the acid leaching experiment at optimum leaching conditions. Void formation, scattering of particles and relatively less clog formation indicates the removal of metal ions from PCB sample. However, still significant amount of metal could be present in the residue. SEM image of the residue obtained after the chelation experiments performed at optimum reaction conditions is shown in Fig. 12(C). A clear surface without presence of any impurities or metal ions could be seen which clearly demonstrates efficient removal of metal ion from PCB samples.

Along with morphological changes during the experiments, quantitative determination of metal ions was also performed for PCB sample and residue using Energy Dispersive X-ray (EDX) analysis. EDX spectra for the PCB sample, leaching residue and chelation residue are shown below in Fig. 13. Peak for Cu metal has been encircled in Fig. 13(A)–(C) which demonstrates the presence of Cu metal ions in the PCB, residue obtained after leaching and residue obtained after chelation cycle respectively. It could be clearly seen in Fig. 13(B) and (C) that intensity for Cu peak is less in residues than PCB sample. Chelation residue showed the smallest peak (encircled in yellow) which indicates the highest removal of Cu during chelation treatment.

X-ray diffraction (XRD) analysis was performed over the range $10^\circ < 2\theta < 80^\circ$ at a step size of 0.05° and a count time of 1 s per step to identify the crystalline phases of PCB and residue samples. Phases were identified using the Joint Committee on Powder Diffraction Standards (JCPDS) software.

XRD patterns for PCB, leaching and chelation residues at different molar concentration of reactants are shown in Fig. 14. A strong peak at 2θ of 44.08° representing the (111) cubic face centered plane of Cu metal ion, was observed in XRD spectra of PCB samples as shown in Fig. 14(A). In addition, two small peaks near 2θ of 51°

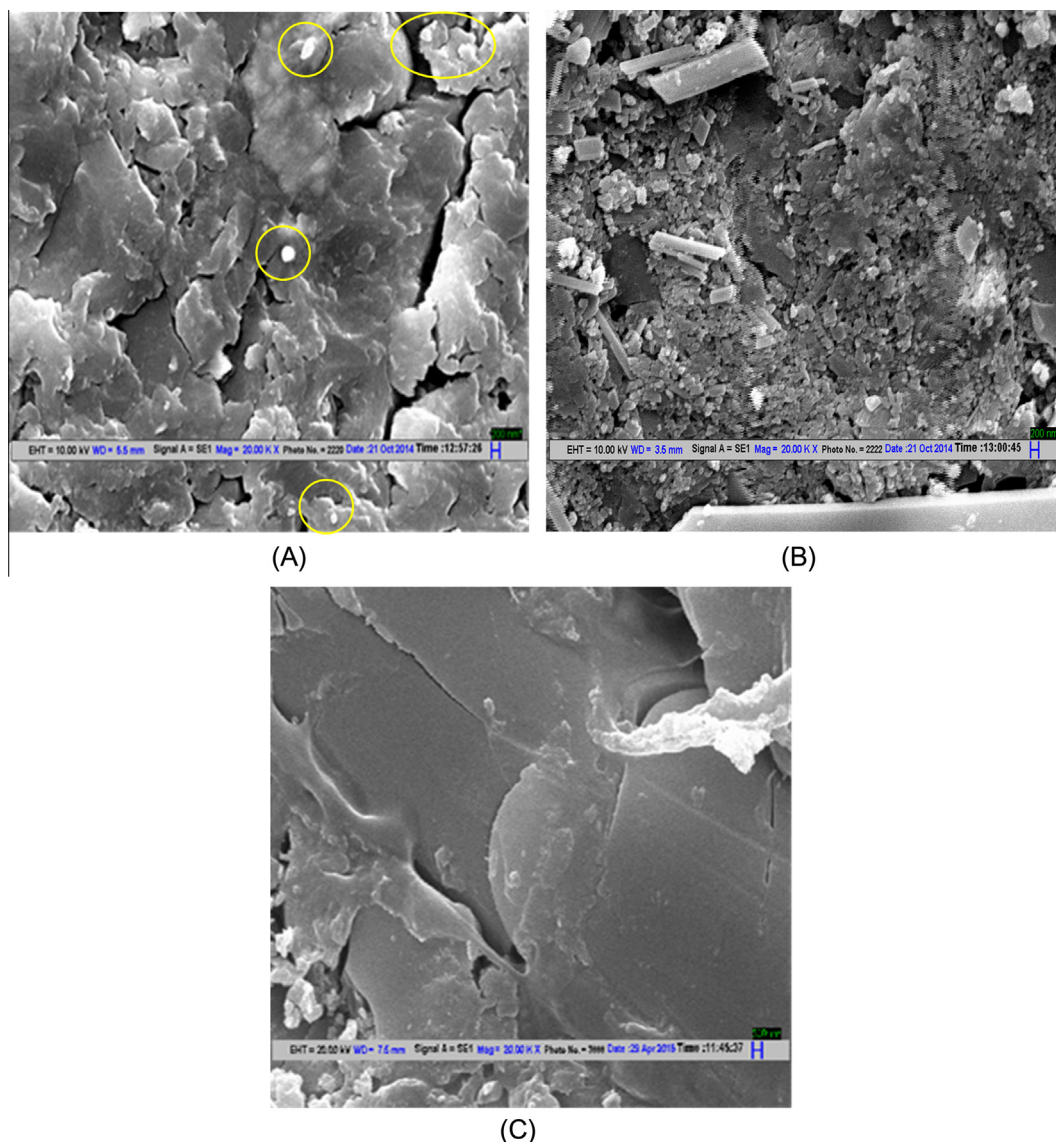


Fig. 12. SEM images of (A) PCB sample. (B) Residue obtained after acid leaching experiments. (C) Residue obtained after chelation experiments performed at optimum reaction conditions.

and 74.56° was also observed for Cu metal which can be attributed to the diffraction of (200) and (220) plane. Fig. 14(B) and (C) represents the XRD pattern for residue obtained at 15% (0.42 M) and 25% (0.7 M) H_2SO_4 concentration respectively.

Relatively weak diffraction peak in Fig. 14(C) than (B) suggests the higher (%) removal of Cu ion at high molar concentration of acid. Weakest intensity for the Cu peak was observed in Fig. 14 (E) when chelation experiments were performed at 0.6 M molar concentration of EDTA. Results obtained in XRD spectra clearly corroborate the results obtained at different molar concentration of reactant. These characterization results also suggest the high extraction efficiency using chelation technology than acid leaching experiments.

8. Kinetic investigation of chelation technology for Cu recovery

Recovery of metals using chelation technology involves dissolution of metal particles in the aqueous solution of chelating agent (solid–liquid extraction) where rate of dissolution is controlled by the resistance generated either by the transport rate of

molecules, diffusion of reactants and products through the porous product layer and rate of reaction at the surface of unreacted core (Chauhan et al., 2015b).

In the present manuscript, it is assumed that little amount of metal ions are present on the particle surface while major fraction of metal ions is at the core of the particle. As the reaction proceeds, chelation agent solution extracts Cu from the reaction zone (PCB inner zone). Over the time, reaction zone starts to shrink and eventually, the reaction zone moves inwards to the solid, leaving behind extracted metal in the chelating agent solution and inert solid without metals. Therefore, shrinking core model was employed in the present study to determine the rate controlling step for Cu recovery from PCB sample. The shrinking core model for the reaction controlled by the chemical reaction at the particle surface is given as Eq. (5):

$$k_c t = 1 - (1 - x)^{\frac{1}{3}} \quad (5)$$

where k_c is reaction rate constant (min^{-1}), t is the reaction time (min) and x is reacted fraction of copper. The plot of $1 - (1 - x)^{\frac{1}{3}}$ vs time at different reaction temperatures is shown in Fig. 15. It

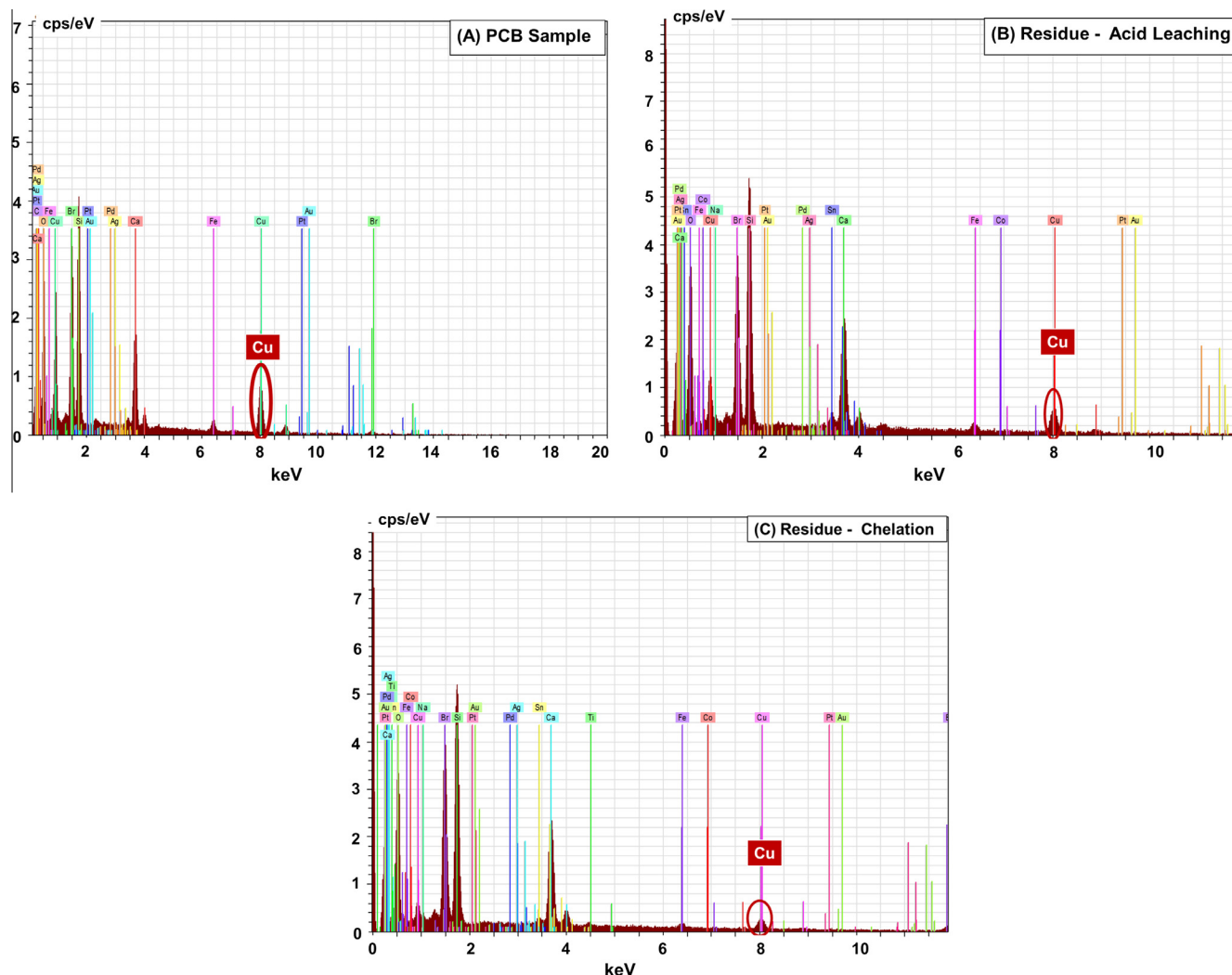


Fig. 13. EDX spectra for (A) PCB. (B) Residue obtained after leaching. (C) Residue obtained after chelation cycle.

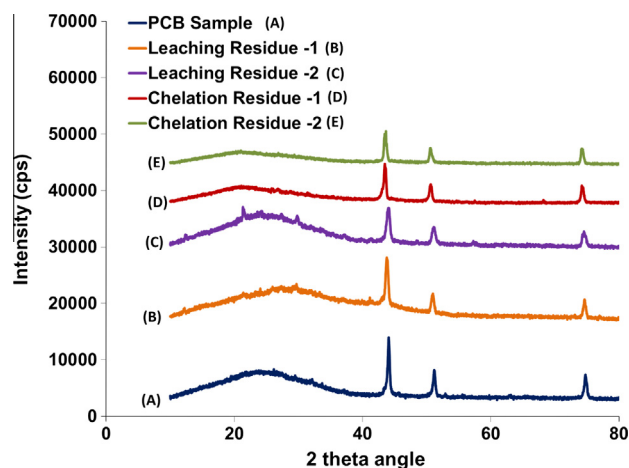


Fig. 14. XRD pattern of PCB sample, residue obtained after acid leaching and chelation experiment.

can be observed from Fig. 15 that experimental data do not fit a straight line for Eq. (5) and therefore, extraction process could not be controlled by chemical reaction model in present study.

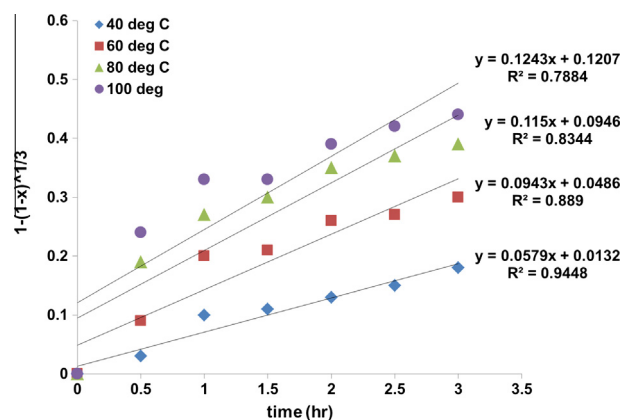


Fig. 15. Plot of $1 - (1 - x)^{1/3}$ against time at various reaction temperatures.

The shrinking core model was also studied for rate control by internal diffusion. The equation used for the diffusion controlled reaction is given in Eq. (6):

$$k_p t = 1 - \left(\frac{2}{3}\right)x - (1 - x)^{2/3} \quad (6)$$

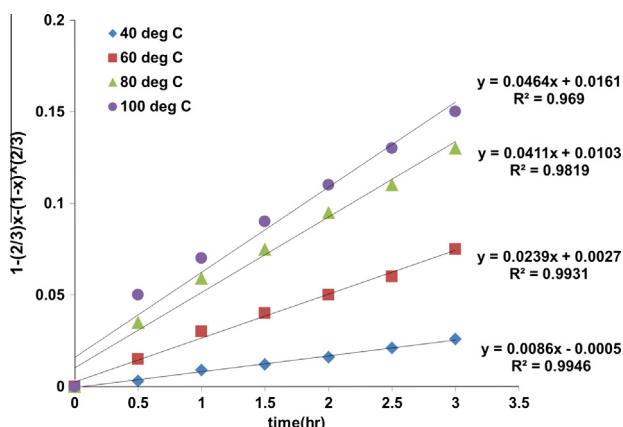


Fig. 16. Plot of $1 - (2/3)x - (1 - x)^{2/3}$ vs time at various reaction temperature.

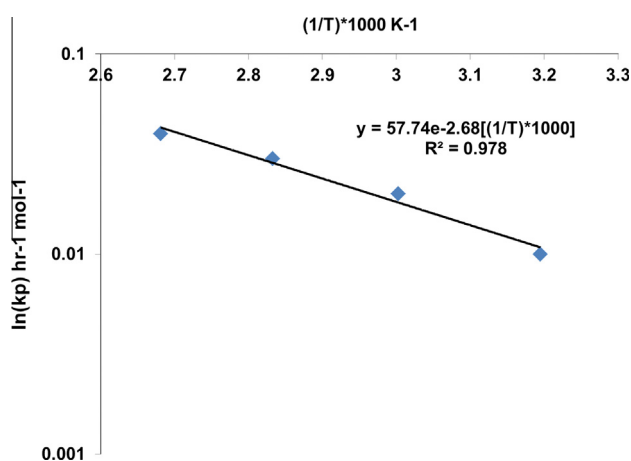


Fig. 17. Arrhenius plot for calculating activation energy.

k_p is rate constant (min^{-1}), t is the reaction time (min) and x is reacted fraction of copper. A plot of $1 - (2/3)x - (1 - x)^{2/3}$ against reaction time was plotted using experimental data and shown in Fig. 16. Straight lines and nearly zero intercepts were obtained for Eq. (6) as shown in Fig. 16 which indicates that the reaction is controlled by the internal diffusion. This observation can be justified by the fact that all the experiments were conducted at 150 μm particle size. Though, further reduction in particle size could be achieved to minimize the mass transfer limitation, but difficulty in filtration arises with very fine particle size. The value of correlation coefficients (R^2) shown in Fig. 16 are also closer to 1 which confirms the well fitted regression model for diffusion controlled extraction process. Therefore, it was concluded that the extraction of Cu from PCB is mainly controlled by the diffusion through product layer.

The activation energy for a diffusion controlled extraction of Cu was calculated using the Arrhenius equation. Curve was plotted using $\ln(K)$ as ordinate and $1/T$ as abscissa for extraction process in Fig. 17. The value of rate constant k_p was calculated as the slope of the straight line from Fig. 16. Linear correlation coefficient for the Arrhenius curve of copper metal is more than 0.97. The activation energy of the copper recovery using EDTA is calculated as 22.2 kJ/mol. Results are in well agreement with the literature values. Kim et al. (2011) studied the leaching kinetics of copper from waste PCB by electro-generated chlorine in HCl solution and calculated activation energy as 24.5 and 20.7 kJ/mol in combined and separate reactors respectively. Lambert et al. (2015) calculated activation energy as 20.4 kJ for copper dissolution from waste

electric cables by biohydrometallurgy. Huang et al. (2014) also studied the leaching behavior of copper from waste PCB with Bronsted acidic ionic liquid and found that the leaching process controlled by the diffusion through the product layer with activation energy 25.3 kJ/mol.

9. Conclusion

Present study is a pioneering effort (to the best of our knowledge) to extract Cu metal from PCB using an emerging green chelation technology. Nearly 84% copper was recovered using EDTA at optimum reaction conditions i.e. EDTA concentration – 0.5 M, liquid to solid ratio – 15:1 (v/w), temperature – 100 °C, reaction time – 3 h, stirring speed – 700 rpm and pH – 7. Comparative evaluation of the conventional acid leaching method with chelate assisted extraction of copper suggest that leaching of PCB could not recover more than 30% Cu in absence of any oxidant. Use of any oxidant is avoided in present study in order to look for a safe alternative. Hazardous handling of acids, corrosion problems and secondary pollution possibilities are other reasons which elude acid leaching method for metal extraction. Recycling of recovered chelating agent is another aided advantage to the chelate assisted extraction process which offer economic incentives to the industrial practice. Kinetic investigation suggests diffusion inside pores as the rate-controlling mechanism for copper extraction with activation energy of 22.2 kJ/mol. Proposed technology for metal recovery from WEEE may prove its utility in waste recycling and eco-management.

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High temperature transformations of waste printed circuit boards from computer monitor and CPU: Characterisation of residues and kinetic studies



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ABSTRACT

This paper investigates the high temperature transformation, specifically the kinetic behaviour of the waste printed circuit board (WPCB) derived from computer monitor (single-sided/SSWPCB) and computer processing boards – CPU (multi-layered/MLWPCB) using Thermo-Gravimetric Analyser (TGA) and Vertical Thermo-Gravimetric Analyser (VTGA) techniques under nitrogen atmosphere. Furthermore, the resulting WPCB residues were subjected to characterisation using X-ray Fluorescence spectrometry (XRF), Carbon Analyser, X-ray Photoelectron Spectrometer (XPS) and Scanning Electron Microscopy (SEM). In order to analyse the material degradation of WPCB, TGA from 40 °C to 700 °C at the rates of 10 °C, 20 °C and 30 °C and VTGA at 700 °C, 900 °C and 1100 °C were performed respectively. The data obtained was analysed on the basis of first order reaction kinetics. Through experiments it is observed that there exists a substantial difference between SSWPCB and MLWPCB in their decomposition levels, kinetic behaviour and structural properties. The calculated activation energy (E_A) of SSWPCB is found to be lower than that of MLWPCB. Elemental analysis of SSWPCB determines to have high carbon content in contrast to MLWPCB and differences in materials properties have significant influence on kinetics, which is ceramic rich, proving to have differences in the physicochemical properties. These high temperature transformation studies and associated analytical investigations provide fundamental understanding of different WPCB and its major variations.

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1. Introduction

Worldwide production of Electrical and Electronic Equipment's (EEE's) is increasing at an alarming rate, which apparently at their End-of Life (EoL) yields to Electronic Waste (e-waste). It has been estimated that the annual global production of e-waste is around 20–50 million tonnes (mt) (Bastiaan et al., 2010; Rajarao et al., 2014) and increasing at the rate of ~4% per year (Cui and Forssberg, 2003). Annual generation of e-waste in European Union (EU) is 7–8 mt; United States (US) is 6–7 mt; United Kingdom (UK) is 1–2 mt; Japan accounts for 3–4 mt and China around 0.5–1 mt (Widmer et al., 2005). UNEP predicts that the blithe approach of developing countries would raise the e-waste quantity up to 500 percent in a decade's time (United Nations Environmental Program (UNEP), 1989). However in the last two decades few countries like US, EU, UK, Australia, Taiwan and Japan have established environmental directives, treaties and conventions in concern to

the manufacturing, disposal and recycling protocols for all classifications of EEE wastes. In spite of these protocols, Environmental Protection Agency (EPA) estimates that only 15–20% percent of e-waste has been recycled, whereas the remaining indefinite statistics states that e-waste is either subjected to landfilling or incineration processes or exported illegally to Asian countries (Mayers, 2001).

European Topic Centre on Resource and Waste Management (ETC/RWM) states that the EEE is mostly metallic (iron and steel) and accounts to half of the weight percentage whereas the non-metallic (plastics) holds to nearly 21% leaving the remaining as non-ferrous metals (Directive 2002/95/EC). EEE is considered as a source of hazardous Volatile Organic Compounds (VOC) and Semi Volatile Compounds (SVC) such as brominated organic pollutants and polycyclic aromatic hydrocarbons. (Herat, 2008). Environmental hazards caused due to e-waste disposal raises a major concern in legislating a protocol for safe handling of EEE globally. Apart from environmental issues, these toxin releasing elements or compounds causes serious damage to human brain cells, skin allergies and cancer when exposed (Menad et al., 2013). Many countries

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have drafted legal measures directed to the both industrial sector and consumer world to act responsibly in handling EEE (Dalrymple et al., 2007), considering all the facts in conjunction to its increase in production, usage, domestic and commercial outcomes and recycling. The integral part of almost all the EEE is a Printed Circuit Board (PCB), which acts as a platform upon which the mounting and designing of all the microprocessors, capacitors, semiconductor units and circuits are built. EoL of all EEE includes PCB which generally contains 40% of metals, 30% of organics and 30% ceramics (Schlummer et al., 2007).

1.1. Single/double-sided and multi-layer PCBs

PCBs are broadly classified as single/double (commercially referred as FR-2) sided and multi-layered (commercially referred as FR-4) (Zeng et al., 2012), which are non-conductive boards which creates conductive connections between the electronic components mounted on the PCBs. Single sided is the least complex PCB as it contains only one substrate (board) above which all the macro electronic components are fabricated connected with the wires (copper traces) on the other side. In case of double sided PCB the mounting of electronic components are attached on both sides of the substrate. These substrates are interconnected through bridges/vias to the copper traces by Plated-Through Hole (PTH) construction assembly processing. As far as Multi-layered PCB is concerned the substrates are insulated by several layers of conglomeration which may extend up to 100 layers. Similar to double-sided PCB, sandwiching of the multi-layered boards are interconnected by PTH or by using pads (Hall and Williams, 2007a; Duan et al., 2011). In general most of the single/double-sided PCB substrates platforms are polymer rich often manufactured with cellulose paper laminated phenolic resins. While multi-layered PCB boards contain multifunctional epoxy resins or cyanate resins or ceramic fills. Single/double sided PCB is applicable in domestic sectors in contrast multi-layered PCB is suitable for more complex dynamic industrial and commercial sectors. Dismantling a Waste PCB (WPCB) assembly is the first step in the recycling process; various conventional and advanced techniques have been in use to extract valuable elements and predominantly to eliminate of hazardous materials (Ongondo et al., 2011; Kiddee et al., 2013). In particular, reprocessing of WPCB is tedious due to its complexity of materials and possible emission of toxic substances in the form of gases. Generally, recycling of WPCBs (single/double and multi layered) is carried on through manual methods, mechanical processing, chemical methodologies (leaching), and pyrolysis (slow and rapid) (Scott et al., 1990; Guo and Xu, 2009; Mankhand et al., 2012). Further in addition there are other metallurgical separation techniques such as pyrometallurgy, hydrometallurgy and biometallurgy which are vast in its application and use in the WEEE recycling world. Out of all the above mentioned methods, pyrolysis is of significant interest for its application of decomposing the organic matters in e-waste at elevated temperatures (Hall and Williams, 2007b; Chiang et al., 2007; Cui and Zhang, 2008; Li et al., 2010) (generally in the absence of inert atmosphere).

Pyrolytic recycling approach is widely researched for its numerous industrial and technological applications. Characterisation and kinetic behaviour of WPCB under various conditions using numerous parameters have been studied (Chen et al., 1999; Mangut et al., 2006; Das et al., 2009; Zhao et al., 2011). However, it is understood that the recycling methods of WPCB is studied considering it as one single entity of the entire e-waste stream (Veit et al., 2005; Cui and Forssberg, 2007). So while recycling WPCBs, both the types of WPCBs should be considered as two different wastes. It is essential to study the residual and kinetics of both single/double-sided and multi-layered WPCB. Thermogravimetric analysis (TGA) is a

well-established and widely used technique in which the mass of a sample is monitored as a function of temperature or time. TGA involves the thermal degradation of the sample in an inert atmosphere with uniform heating rate and simultaneous recording the mass loss of a sample with temperature. TGA is inherently quantitative, and therefore an extremely powerful thermal technique.

This current study deals with residual and kinetic studies of both single-sided and multi-layer PCB. ThermoGravimetric Analyser (TGA) and vertical TGA techniques were used to understand the thermal degradation behaviour of single-sided and multi-layer WPCB powders obtained from cryomill grinding. The change in behaviour and weight loss of both single-sided and multi-layered WPCB powders were observed and recorded using the TGA/DTA analysis under nitrogen atmosphere. The obtained data's are used to plot TGA/DTG curves through which kinetic patterns are calculated. Furthermore, obtained residues after pyrolysis are characterised by using carbon analyser, scanning electron microscope (SEM) and X-ray photoelectron spectroscopy (XPS) techniques.

2. Experimental

2.1. Materials

Random PCB of EoL monitor (Single-sided) and Central Processing Unit (CPU/multi-layer) of a computer was picked up from the recycling unit of the UNSW Australia, Sydney for this study. The schematic diagram of single-sided and multi-layered PCB including pictures of different substrates used in PCB are shown in Fig. 1. The multifarious WPCB was then physically dismantled from its units with the help of mechanical devices. Majority of transistors, capacitors, semiconductor circuits, battery, ceramic projections and microchips were removed in order to avoid the complexity of toxic levels. The dismantled WPCB board from CPU and monitors was further truncated into possible smaller sizes (~1 cm) and then used accordingly.

2.2. CryoMill grinding

Homogenisation of the truncated WPCB was achieved by converting them into fine powders with the application of CryoMill (Mixer Mill – Retsch®) grinding technique under the Liquid Nitrogen (Dewar LN2 Auto fill 501 – Retsch®) atmosphere.

2.3. Elemental analysis

WPCB powders and the residue after pyrolysis were examined using the XRF (X-ray Fluorescence) spectrometry measurements, which were performed on the PANalytical PW2400 Sequential Wavelength Dispersive X-ray Fluorescence spectrometry (WDXRF) to determine the composition of various elements present. Table 1 shows the results of both SSWPCB and MLWPCB performed by the X-ray fluorescence spectrometer. Further it presents the proximate and ultimate analysis of both types of WPCB's. Proximate analysis of WPCB samples in this study was carried out based on ASTM standard methods. Fig. 2 shows the elemental distribution of the SSWPCB (Monitor) and MLWPCB (CPU). Carbon Analyser is used to study the elemental percentage of carbon, nitrogen and sulphur present in WPCB powders and in the residue which was obtained after TGA-slow pyrolysis experiments.

2.4. TGA – pyrolysis technique

ThermoGravimetric Analyser (TGA, Perkin Elmer STA 8000) was used to perform the slow pyrolysis of WPCB powders obtained from both single and multi-layered PCB. Slow pyrolysis was

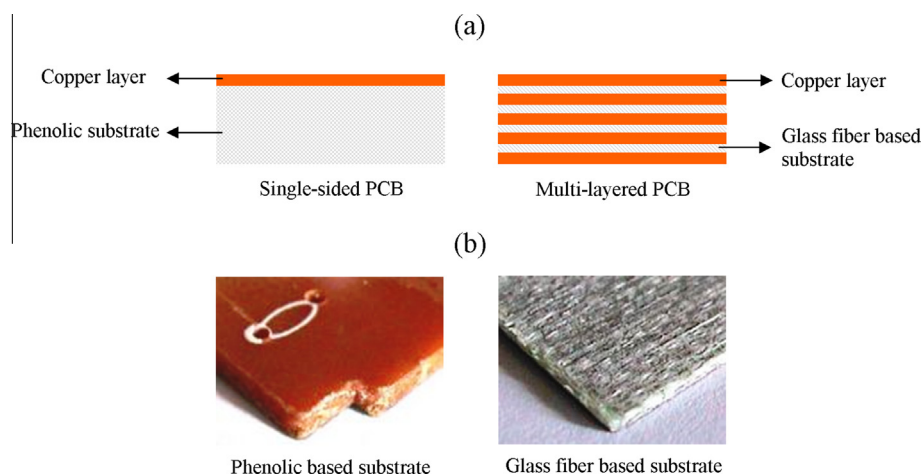


Fig. 1. (a) Schematic diagrams of single-sided and multi-layered PCBs and (b) pictures of different substrates used in PCBs.

Table 1

Proximate, ultimate and elemental analysis of SSWPCB and MLWPCB.

	SSWPCB	MLWPCB
<i>Proximate analysis (wt.% as received)</i>		
Moisture	1	0
Ash	13.50	69.44
Volatile matter	61.11	27.63
Fixed carbon	24.75	2.48
<i>Ultimate analysis (wt.% as received)</i>		
C	36.16	11.29
S	0.26	0.25
N	1.72	0.27
<i>Elemental analysis (X-ray fluorescence studies, %)</i>		
MgO	0.174	0.139
Al ₂ O ₃	0.85	5.344
SiO ₂	2.194	20.192
P ₂ O ₅	0.561	0.043
SO ₃	0.031	0.00
CaO	0.859	8.049
TiO ₂	0.07	0.355
Cr ₂ O ₃	0.042	0.038
MnO	0.017	0.00
Fe ₂ O ₃	4.356	0.491
NiO	0.195	0.099
CuO	30.556	45.238
ZnO	0.722	0.168
As ₂ O ₃	0.011	0.008
Ag ₂ O	0.11	0.00
SnO ₂	5.448	1.735
BaO	0.1123	0.157
PbO	0.19	0.014
Cl	0.065	0.084
Br	5.372	4.369
I	1.33	0.452
Au	0.00	0.03
K ₂ O	0.00	0.038
ZrO ₂	0.00	0.02
SrO	0.00	0.042
PtO ₂	0.00	0.022

performed from temperature range of 40–700 °C at different heating rates of 10, 20 and 30 °C/min. Experiments were carried out under the nitrogen gas atmosphere with the gas flow rate of 20 ml/min.

2.5. VTGA – vertical thermogravimetric analyser

The VTGA consists of a mechanically operatable vertical tube furnace, analytical balance, mass flow controller, data logging computer and furnace controller. The control of the furnace

temperature is conducted using a thermocouple external to the reaction tube and examined the sample temperature is controlled using inside thermocouple to the reaction tube below sample tray. The sample weight loss is recorded during the reaction at controlled intervals. The result TG analysis allows the understanding of some important properties of certain materials such as reactivity and pyrolysis behaviour.

Fig. 3 shows the customised VTGA set up and it is similar to that for conventional pyrolysis. The kiln reactor was an AISI 310 steel column (length: 650 mm, inner diameter: 28 mm) indirectly heated by electric elements surrounding the reactor chamber. Tests were conducted in batch mode; a sample was introduced in the hot zone (corresponding to the position of the resistances) at ambient temperature and the heating rate was determined by tension applied through a voltage regulator at the heads of an electrical resistance ranging from 220 to 380 V. Some preliminary tests were carried out to set the furnace heating rate in order to obtain a sample heating rate of 5 °C/s. The solid residence time was ~1–5 min.

Experiments were conducted under a purging gas system and the gas used for this particular work is nitrogen. Rapid high temperature transformations for three different temperatures (700 °C, 900 °C and 1100 °C) are performed and its resulting parameters are recorded.

2.6. Characterisation of pyrolysis residue

2.6.1. Elemental analysis

Carbon Analyser is used to study the percentage of elemental carbon, nitrogen and sulphur present in the residue which was obtained after pyrolysis experiments.

2.6.2. SEM technique

Scanning Electron Microscope (SEM) is used to describe the physical structure of the residue. The samples were then examined and imaged using a TM 3000 Hitachi Scanning Electron Microscope (SEM). The energy dispersive spectrum (EDS) was also recorded to determine the elemental composition.

2.6.3. XPS technique

XPS analysis was carried out on residues obtained by WPCBs using Thermo ESCALAB250i X-ray Photoelectron Spectrometer. The Al K α line was used as the X-ray source. For measurements, samples were loaded into ultra-high vacuum (about 2×10^{-9} mbar) chamber of the XPS apparatus.

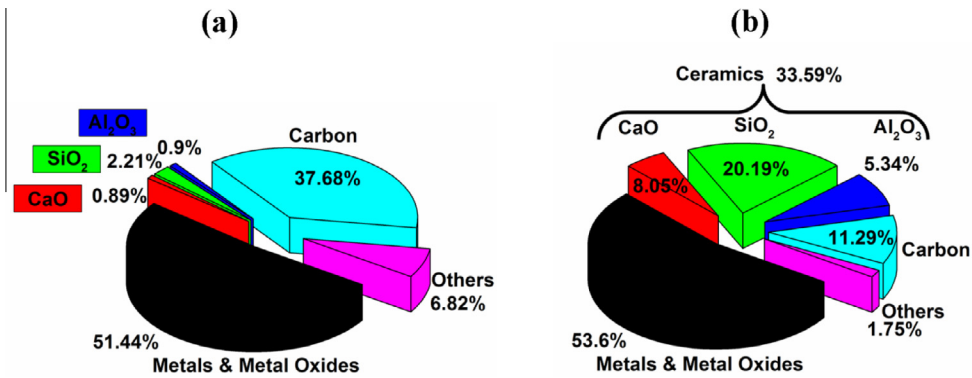


Fig. 2. XRF analysis of (a) SSWPCB and (b) MLWPCB powders.

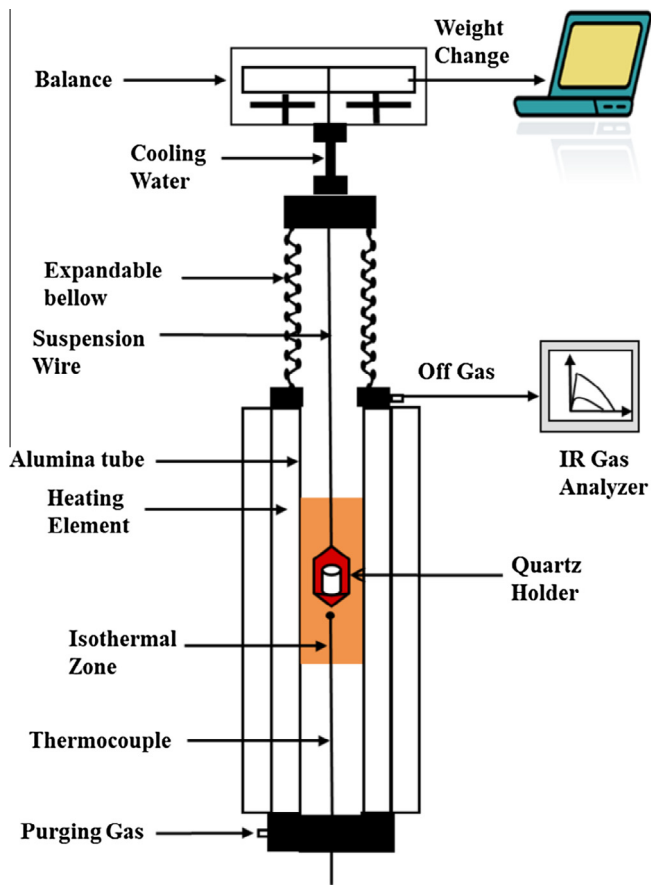


Fig. 3. Schematic representation of customised vertical thermo-gravimetric analyser.

2.7. Pyrolysis kinetics theory

Pyrolysis of WPCB is generally a complex process. It is possible to describe the pyrolysis behaviour of PCB scraps under different conditions by different pyrolysis mechanisms (De Marco et al., 2008; Guan et al., 2008). The reaction mentioned in this study is one of the commonly used arbitrary functions, equations and considerations to determine the decomposition rate of the pyrolysis reactions. The general reaction can be represented as given below.



where (k) is the rate constant of the reaction following the Arrhenius law. It was assumed that the total reaction accords with

the following conventional equation: It is very tedious and complex to determine a complete kinetic analysis of sandwiched PCB systems (composites), but some kind of “effective” or “average” kinetic description is still required. In the below description, the overall rate of the Pyrolytic reactions of WPCB is described by the following equation:

$$\frac{dX}{dt} = k(T)f(x) \quad (1)$$

(General Law in order to undergo kinetic study)

where x , t , $k(T)$, $f(x)$ represents the degree of conversion of the pyrolysis process, the time, the rate constant with respect to temperature and the reaction model respectively. Reaction model is a function depending on the decomposition mechanism (slow or rapid pyrolysis), which can be in the form of an n th order of reaction: $f(x) = (1 - x)^n$ and x which in particular can be defined as follows:

$$x = \frac{m_i - m_t}{m_i - m_\infty} \quad (2)$$

where m_i is the initial mass of the sample, m_t is the mass at time t in seconds and m_∞ is the mass of the sample at the end of the reaction (all expressed in gms).

It is assumed that constant (k) obeys the Arrhenius correlation:

$$k(T) = A \exp\left(-\frac{E}{RT}\right) \quad (3)$$

where E is the activation energy (J mol^{-1}), A is the pre-exponential factor ($1/\text{s}$), T is the absolute temperature (K) and R is the universal gas constant ($\text{J mol}^{-1} \text{K}^{-1}$). For a constant heating rate β during pyrolysis process, $\beta = dT/dt$.

Eq. (3) can be written as:

$$\ln(k) = \ln(A) - \frac{E}{R} \left(\frac{1}{T}\right) \quad (4)$$

The equation above can be intercepted with the equation of straight line which is $y = mx + c$ where $y = \ln(k)$; $m = E/R$; $x = 1/T$ and $c = \ln(A)$ respectively.

For further understanding the following calculation can be studied.

By combining and rearranging the Eqs. (1) and (3), the reaction rate can be written as:

$$\frac{dx}{dT} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) (1 - x)^n \quad (5)$$

Integrating the Eq. (5) we get

$$\int_0^x \frac{dx}{(1 - x)^n} = \frac{A}{\beta} \int_{T_0}^T \exp\left(-\frac{E}{RT}\right) dT \quad (6)$$

Based on Eq. (6), Coats-Redfern's method was derived for the analytical determination of the kinetic parameters, as Eqs. (7) and (8):

When $n \neq 1$, we get:

$$\ln \left\{ \frac{1 - (1-x)^{1-n}}{T^2(1-x)} \right\} = \ln \left\{ \frac{AR}{\beta E} \left(1 - \frac{2RT}{E} \right) \right\} - \frac{E}{RT} \quad (7)$$

When $n = 1$ then we get:

$$\ln \left\{ \frac{-\ln(1-x)}{T^2} \right\} = \ln \left\{ \frac{AR}{\beta E} \left(1 - \frac{2RT}{E} \right) \right\} - \frac{E}{RT} \quad (8)$$

When $2RT/E$ is negligible to be ignored then the above Eqs. (7) and (8) can be transformed to Eqs. (9) and (10) as follows:

When $n \neq 1$, we get:

$$\ln \left\{ \frac{1 - (1-x)^{1-n}}{T^2(1-x)} \right\} = \ln \left\{ \frac{AR}{\beta E} \right\} - \frac{E}{RT} \quad (9)$$

When $n = 1$, we get:

$$\ln \left\{ \frac{-\ln(1-x)}{T^2} \right\} = \ln \left\{ \frac{AR}{\beta E} \right\} - \frac{E}{RT} \quad (10)$$

Since we assumed the pyrolysis reaction obeys the Arrhenius equation (Eq. (3)), by using Eq. (4) a slope plotted between $\ln k$ versus $1/T$ and by equating that to $-E/R$, activation energy of the reaction can be determined. Furthermore, Iterative method and the least squares method can be implemented to the Eq. (9) to determine the values of n and A .

3. Results and discussion

3.1. Characterisation of waste PCBs

Through XRF results of both the WPCB's it is very much evident through that both the sample shows different compositions as SSWPCB is rich in carbon content owing to 37.68% with lower level of silica of 2.21% whereas on the other hand MLWPCB is glass fibre rich in total of 33.59% which includes CaO (8.05%), SiO₂ (20.19%) and Al₂O₃ (5.34%) respectively. Similarly, studies through carbon analyser also provide two different elemental weight percentages of carbon with only sulphur having closer values. In addition to the ultimate analysis, proximate analysis is performed which includes moisture, volatile matter, fixed carbon and ash showing varied weight percentages of both SSWPCB and MLWPCB confirming that the source of waste PCB's are entirely different in their elemental composition.

Due to the differences in results of the WPCB's it is understood that further physical and kinetic properties of SSWPCB and MLWPCB are essential. In order to study, both slow and rapid pyrolysis experiments were chosen to compare and analyse the thermal degradation behaviour of WPCBs.

3.2. TGA/DTG profiles

3.2.1. Slow pyrolysis of SSWPCB and MLWPCB

TG experiments determine the weight percentage of the sample used with respect to the temperature; on the other hand the DTG profile is the derivative measurement of the TG curve (Aboulkas et al., 2008; Moltó et al., 2009), which corresponds the major degradation stages of the TG-curve. Both the curves obtained enables to configure the understanding of the thermal process deployed within the different PCB samples.

Fig. 4(a) and (b) shows the TGA and DTG curves obtained from the slow pyrolysis process of the SSWPCB recorded at the three different heating rates of 10, 20 and 30 °C/min under nitrogen

atmosphere. Table 2 shows the weight loss, residual weight and maximum degradation rate of the samples calculated at temperatures between 40 °C and 700 °C. In addition, Table 3 also shows the three levels of degradation such as the initial (T_i), maximum (T_{max}) and final (T_f) temperatures of the sample weight loss. From the TGA/DTG plots it can be understood that the mass degradation levels of the samples occurs between 250 °C and 380 °C temperature range and subsequently the decomposing rate is slow and steady until the designated temperature of 700 °C. The percentage of weight is 55.81, 60.28 and 62.10 for 10, 20 and 30 °C/min respectively. It is observed that the weight of the sample decreases with increase in the heating rate. Maximum weight percent is observed at 325 °C, 336 °C and 340 °C at 10, 20 and 30 °C/min respectively. Increase in the heating rate gives a paradigm shift as noted in the DTG curve which shifts to higher temperature regions. This result is in agreement with the work of other researchers (where the WPCB is considered to be a single WEEE sample and not as a single-sided PCB) (Kowalska et al., 2006; Font et al., 2011; Zhan and Qui, 2011). The process observed here from the DTG curve could have multi-level decomposition. Further understanding of this is necessary.

Likewise in order to determine maximum decomposition rate for MLWPCB, TGA experiments with similar parameters is performed and its respective TGA and DTG profiles were recorded. In case of MLWPCB, percentage of weight is 24.62, 25.40 and 25.91 for 10, 20 and 30 °C/Min respectively, which is lower than that of SSWPCB. Fig. 5(a) and (b) shows the effect of heating rate on the TGA and DTG behaviour; increase in heating rate shifts the thermal degradation values towards the higher temperatures. Maximum weight percent for MLWPCB is observed at 337 °C, 349 °C and 358 °C at 10, 20 and 30 °C/min respectively, which is slightly higher than the SSWPCB recordings.

In comparison to both the TGA/DTG pyrolysis experiments it is observed that the weight loss is more in the SSWPCB than the MLWPCB. The reason being the thermal stability in the SSWPCB is weak because of its high polymer content whereas the thermal stability is high in the case of ceramic rich MLWPCB. Flames retardants present in SSWPCB degrades at high temperatures releasing the brominated compounds followed with TG curve returning to a smooth decrease, decomposing the phenolic resin and the end product char is formed accounting to an average of 40%. In the case of MLWPCB the presence of glass fibre ceramics impregnated along with the brominated epoxy polymer resin inhibits the heat flow and retards the combustion process resulting in lower mass loss with the char averaging about 75%, proving that these two types of PCBs are of completely different properties and needs individual pyrolysis treatments for its effective recycling.

3.2.2. Rapid pyrolysis of SSWPCB and MLWPCB

Fig. 6 shows the TG/DTG curves acquired which allows the understanding of the samples reactivity and its rapid behaviour when exposed to high temperature pyrolytic furnace. Unlike slow pyrolysis, rapid pyrolysis thermal degradation of a material is calculated by keeping the pyrolytic temperature constant. Table 4 shows the time, amount of weight loss and percentage of residue of samples corresponding to constant set temperature. For SSWPCB the average weight loss percentage is 60.81 whereas for MLWPCB is 24.40. These results are consistent in behaviour to the results that are obtained through slow pyrolysis, proving the consistency in the differences of these two WPCB samples.

Rapid pyrolysis TGA/DTG profiles shown in Figs. 6(a) and (b) and 7(a) and (b) explains that the samples losses its weight immediately within few minutes after it is exposed to the reactors. Major thermal degradation happens during the early minutes (~3–8 min) of the rapid pyrolysis experiments. The maximum mass degradation time taken for SSWPCB samples at the temperatures 700 °C,

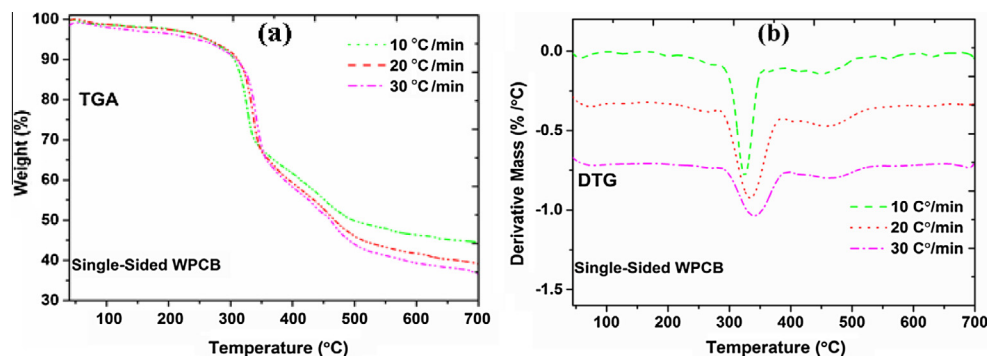


Fig. 4. Slow pyrolysis – (a) TG and (b) DTG curves of SSWPCB.

Table 2

Slow pyrolysis – degradation temperatures, weight loss%, amount of residue and maximum degradation values of SSWPCB and MLWPCB.

Sample	Heating rate β ($^{\circ}\text{C min}^{-1}$)	Degradation temperatures ($^{\circ}\text{C}$)			Weight loss% at 700 $^{\circ}\text{C}$ (wt.%)	Char residue% at 700 $^{\circ}\text{C}$ (wt.%)	Maximum degradation rate (wt.% min^{-1})
		T_i	$T_{\max}$	T_f			
SSWPCB (Monitor)	10	256	325	352	55.81	44.04	23.55
	20	290	336	370	60.28	39.71	12.07
	30	303	340	378	62.10	37.89	8.47
MLWPCB (CPU)	10	279	337	386	24.62	75.37	27.66
	20	307	349	404	25.40	74.59	14.91
	30	318	358	405	25.91	74.08	10.22

Table 3

Kinetic evaluation of SSWPCB and MLWPCB.

Sample	Heating rate β ($^{\circ}\text{C min}^{-1}$)	Order of the reaction n	Activation energy E_A KJ mol^{-1}	$\ln A$	Correlation co-efficient R^2
SSWPCB	10	1.81	50.96	5.39	0.999
	20	1.49	59.59	7.56	0.982
	30	1.56	58.16	7.57	0.987
MLWPCB	10	1.27	99.08	13.33	0.929
	20	1.05	88.59	11.58	0.951
	30	1.28	78.60	10.14	0.967

900 $^{\circ}\text{C}$ and 1100 $^{\circ}\text{C}$ are 85, 80 and 35 s respectively. In case of MLWPCB samples it is 50, 25 and 20 s which shows the trend of decrease in residence time in increase in the temperature of the furnace.

3.3. Pyrolysis kinetics

3.3.1. Slow pyrolysis kinetics

Materials used for the TGA/DTG study showed that the decomposition (90% weight loss) rate occurred majorly between

the temperatures ranging from 256 $^{\circ}\text{C}$ to 405 $^{\circ}\text{C}$ (in both SSWPCB and MLWPCB). The kinetic study and thermal behaviour in that particular region is chosen to study. The kinetic parameters such as E_A and A of the SSWPCB and MLWPCB for heating rates of 10, 20, and 30 $^{\circ}\text{C/min}$, assuming that the powder pyrolysis is a first order reaction are determined using the integration method and are presented in Table 3. The estimated activation energy mainly depends on the reaction rate mechanisms during the pyrolysis reactions.

Fig. 8 shows the Arrhenius plots of $\ln(k)$ versus $\ln(1/T)$ for the samples studied using the one step integral method for the different degradation temperatures. The corresponding R^2 values obtained from the equation of straight line appears to be in the range of 0.98–0.99 for the SSWPCB and 0.92–0.96 for the MLWPCB, showing that the n^{th} order chemical reaction model assumed was suitable to describe the slow pyrolysis reactions. The estimated activation energy for SSWPCB is in the range of 50.96–59.59 KJ mol^{-1} with an average of 56.24 KJ mol^{-1} (a slightly higher value compared to the value reported by Sun et al., which is based on microwave induced pyrolysis) (Sun et al., 2012). In case of MLWPCB, E_A is in the range of 78.60–99.08 KJ mol^{-1} with an average of 88.75 KJ mol^{-1} .

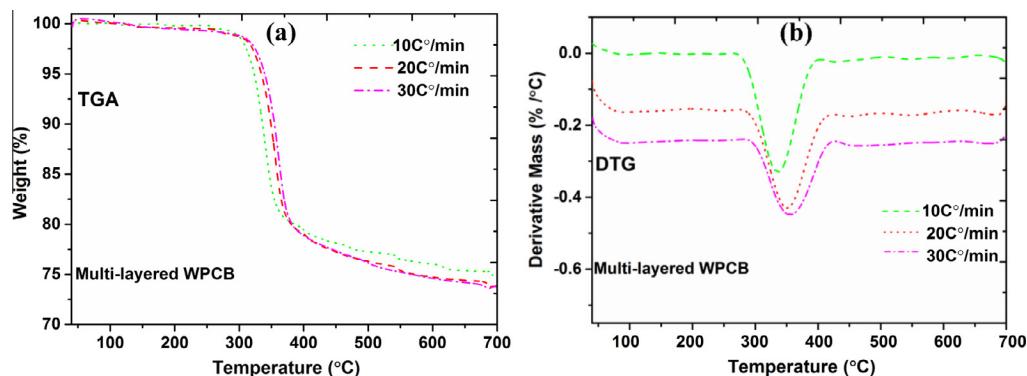


Fig. 5. Slow pyrolysis – (a) TG and (b) DTG curves of MLWPCB.

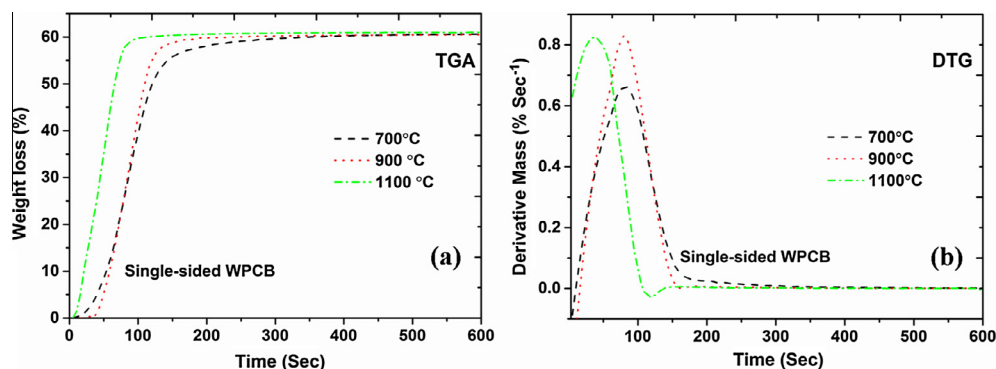


Fig. 6. Rapid pyrolysis – (a) TG and (b) DTG curves of SSWPCB.

Table 4

Rapid pyrolysis – degradation time, weight loss%, and amount of residue.

Sample	Furnace temperature (°C)	Degradation time (secs)			Weight loss% (wt.%)	Char residue% (wt.%)
		t_i	t_{max}	t_f		
SSWPCB	700	5	85	170	60.76	39.24
	900	5	80	160	60.67	39.33
	1100	5	35	115	61.02	39.08
MLWPCB	700	5	50	105	24.98	75.02
	900	5	25	70	24.39	75.61
	1100	5	20	60	23.83	76.17

In SSWPCB, E_A value between 50 and 60 KJ mol^{-1} is mainly because the degradation happens mostly in the temperature range of 250–400 °C with only a minor DTG shift irrespective of the heating rates. In this work is observed that the value of E_A and A for the SSWPCB is lower than the MLWPCB owing to the difference in its chemical composition and thermo physical structural properties.

The reaction mechanism refers to the difference in resin arrangement system present in the SSWPCB and MLWPCB, which irreversibly undergoes physical and chemical degradation with the thermal destruction of polymer links, resulting the change in activation. High temperature transformation associated with the SSWPCB and MLWPCB has a significant variation in the material properties. The exposure in SSWPCB results in the formation of porous like structure. In case of MLWPCB there is an increase in glass-fibre density of the epoxy matrix hindering the decomposition rate leading to higher activation energy.

3.3.2. Rapid pyrolysis kinetics

Through rapid pyrolysis experiments it is understood that the increase in temperatures and variations in residence time will have

considerable change in the kinetic parameters of the WPCB, which is in agreement to slow pyrolysis as well. The resulting SSWPCB DTG curve through VTGA has a decreasing peak starting from 700 °C to 1100 °C with increase in the derivative mass, whereas the time taken for maximum degradation decreases with increase in temperature. It is further noted that the DTG curves shifts with decreasing intensity at constant 700 °C, 900 °C, and 1100 °C temperatures respectively. In case of MLWPCB the DTG curves shows that increase in onset temperature increases the decomposition rate requiring minimum residence time than SSWPCB. This phenomenon is due to the dissolution of higher organic matters with volatiles present in SSWPCB leading to higher residence time for material degradation than in MLWPCB.

3.4. Characterisation of residue

Fig. 9 shows the XRF results of both SSWPCB and MLWPCB. The residue obtained after pyrolysis is composed of both metallic and non-metallic fractions. In this study, non-metallic fractions were separated manually from metallic fractions and was further char-

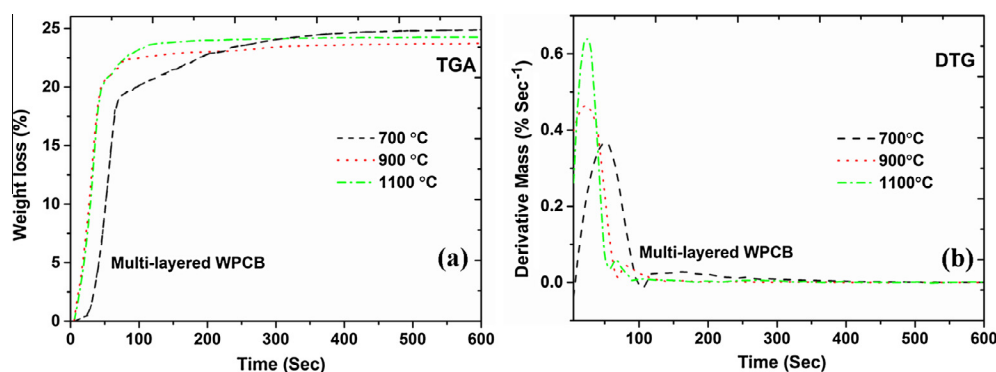


Fig. 7. Rapid pyrolysis – (a) TG and (b) DTG curves of MLWPCB.

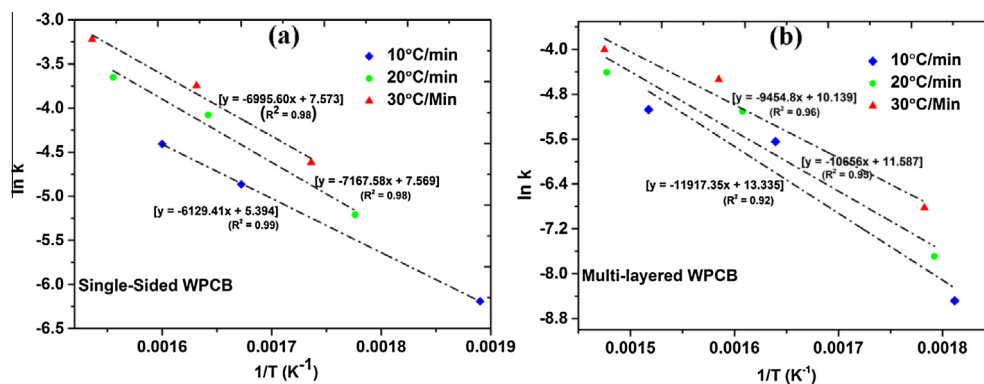


Fig. 8. Slow pyrolysis – Arrhenius plots of $\ln(k)$ versus $\ln(1/T)$ of (a) SSWPCB and (b) MLWPCB.

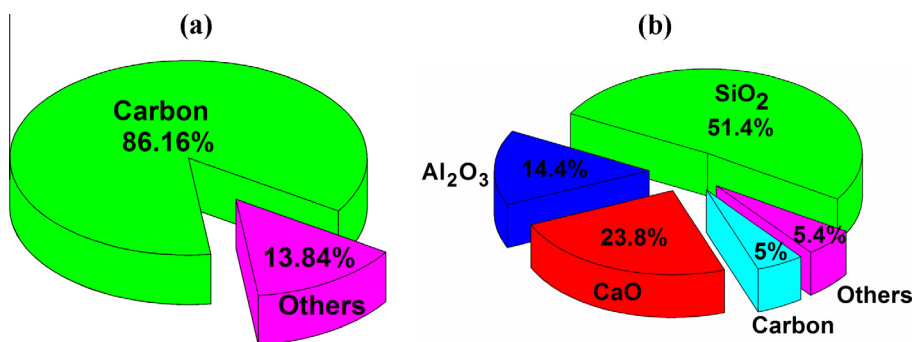


Fig. 9. XRF residue analysis of (a) SSWPCB and (b) MLWPCB.

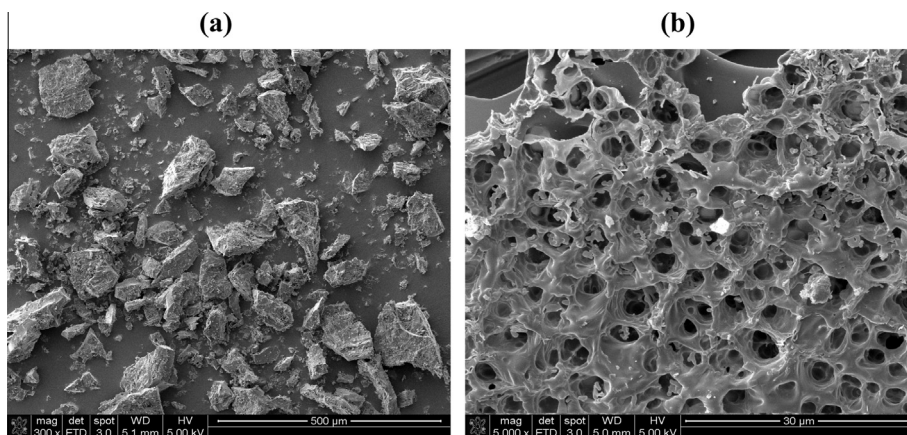


Fig. 10. SEM images (a) black residue of SSWPCB and (b) porous structure of SSWPCB.

acterised. The non-metallic fraction of SSWPCB appears to be black residue Fig. 10(a). The obtained char was lower in density and rich in carbon with 86.16%. The structural morphology of the residue was observed by using SEM technique and result is represented in Fig. 11. Further the EDS image confirms and goes in agreement with the physicochemical properties of SSWPCB with large portions of carbon print. The SEM image clearly indicates the presence of porous structures Fig. 10(b), which were formed due to the release of gases during decomposition of polymers. To study the chemical nature and surface analysis of the residue XPS analysis were carried out. Table 5 shows the XPS data of SSWPCB which clearly signifies the presence carbon in higher quantities of the residue such as start binding energy (BE), peak BE, end BE, full

width half maximum (FWHM), area and atomic compositions (at. %). A small amount of silica was also observed from XPS results.

The physical property of non-metallic portions of MLWPCB after pyrolysis was layered white grey hard residues Fig. 12. The elemental residual analysis represents non-metallic fraction of MLWPCB found to be around 90% (SiO_2 -CaO, Al_2O_3) of glass woven content with SiO_2 concentration of around 51%. Carbon, metal oxides and non-metals attributes to 10%. A representative SEM image of PCB residue is shown in Fig. 13, which evidently shows that the residue is mainly composed of glass, woven micro fibres with diameter of around 10 μm . XPS data of MLWPCB which shows the presence of silicon, aluminium and calcium along with carbon on the surfaces of the residue. The SEM image also indicates that

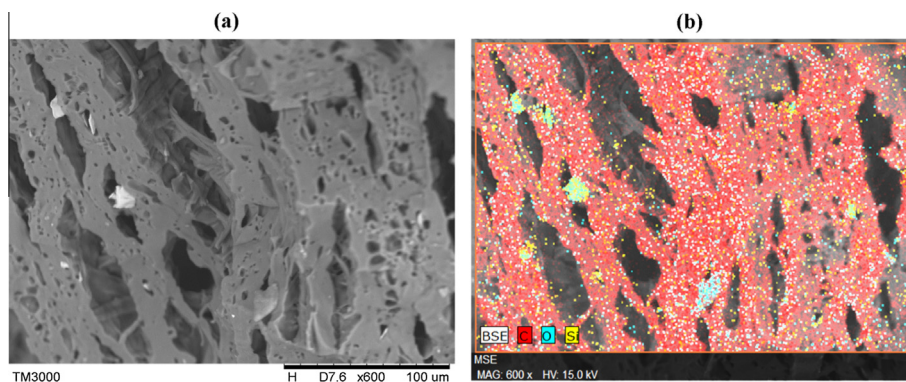


Fig. 11. (a) SEM and (b) EDS images of SSWPCB.

Table 5

XPS data of SSWPCB and MLWPCB.

Name	Start BE	Peak BE	End BE	FWHM eV	Area (P) CPE. eV	At. %
SSWPCB						
Mg1s	1312.08	1306.05	1300.48	2.58	1643.92	0.56
C1s	293.68	284.98	281.38	1.19	37551.02	85.95
Na1s	1076.08	1072.12	1068.88	1.41	531.65	0.18
O1s	540.08	532.79	527.38	2.81	12055.60	9.7
Si2p	109.88	102.18	98.58	1.50	534.39	1.48
Zn2p3	1027.38	1022.99	1018.68	1.92	1113.42	0.16
P2p A	137.68	134.61	130.58	2.78	142.53	0.27
N1s A	404.58	401.81	395.28	1.32	222.80	0.29
N1s B	404.58	398.79	395.28	1.32	505.96	0.69
N1s C	404.58	400.81	395.28	1.32	592.81	0.76
MLWPCB						
C1s	293.68	284.98	281.38	0.95	42631.47	79.59
O1s	540.08	533.38	527.38	3.18	20577.79	13.51
Si2p	109.88	104.7	98.58	3.04	1516.87	3.42
Zn2p3	1027.38	1022.74	1018.68	1.28	660.03	0.08
N1s A	404.58	401.42	395.28	2.58	349.37	0.37
N1s B	404.58	399.10	395.28	2.58	289.50	0.3
Cu2p3	948.48	953.16	928.88	1.19	1402.68	0.18
Ca2p3	356.38	349.61	344.78	3.05	2356.24	1.32
Al2p	81.18	76.34	73.28	1.14	279.9	0.96
F1s	691.88	686.88	680.88	0.38	598.72	0.27

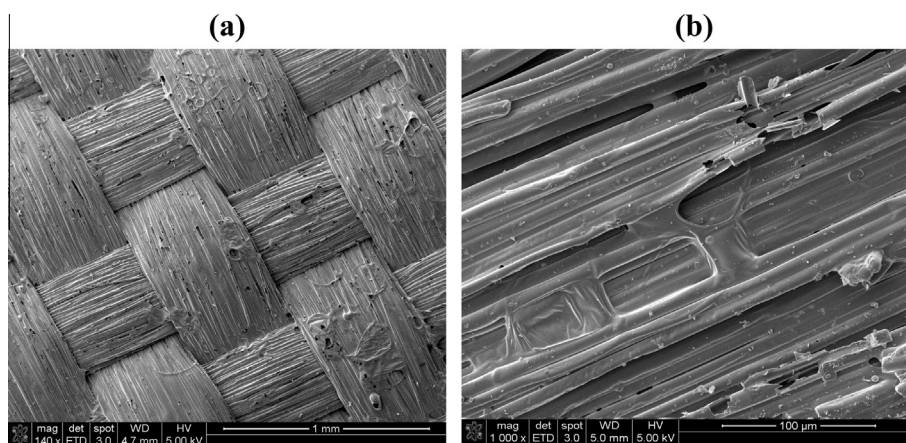


Fig. 12. SEM images (a) white grey hard residue of MLWPCB and (b) glass-fibre structure of MLWPCB.

the obtained residue is relatively clean and free from metallic particles. Furthermore, EDS analysis shows that surface is mostly covered with carbonaceous materials.

Both slow and rapid pyrolysis studies indicate that very high valuable carbon product (90% carbon in residue) and ceramic product (90% – SiO_2 -CaO, Al_2O_3) from WPCB's is achievable. These

chars can be effectively used as major source of raw materials for the synthesis of activated carbon, carburiser material in alloy making industries, hydrogen storage materials and also as feedstock for various industrial purposes. Synthesizing composites through WPCB and finding applications using the same is of interest for future work.

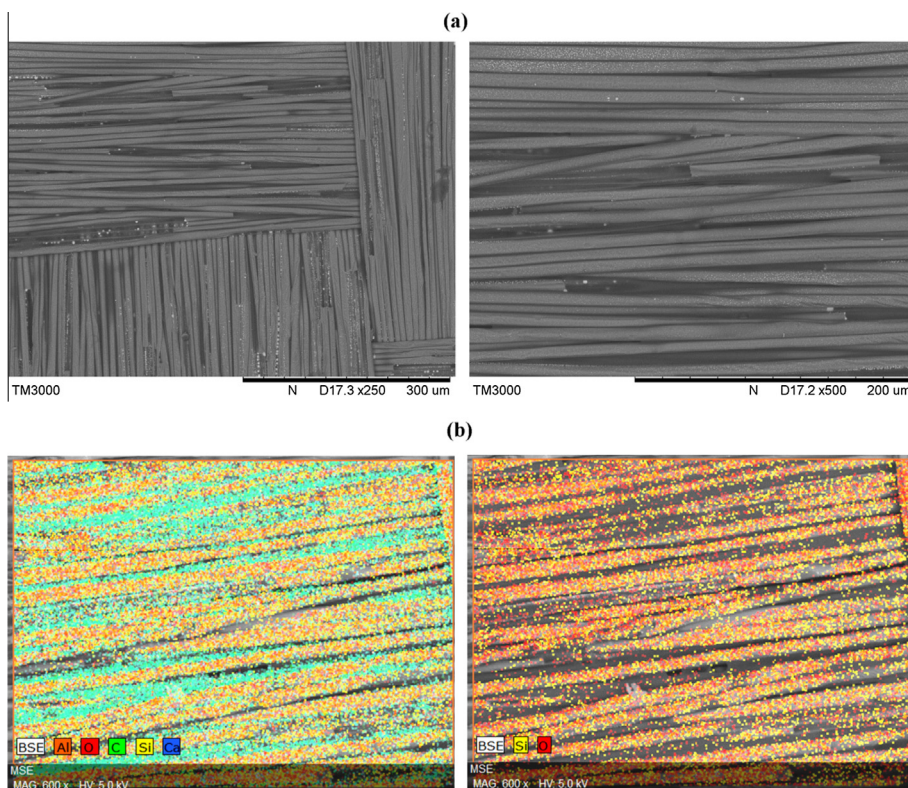


Fig. 13. (a) SEM and (b) EDS images of MLWPCB.

4. Summary and conclusions

In this present work, TGA-pyrolysis (slow and rapid) experiments and elemental characterisation has been performed for WPCB obtained from monitor and CPU to understand the kinetic behaviour and transformations at high temperatures. The resulting data highlights the significant differences in the WPCB from monitor and CPU. The main observations in this study are concluded and summarised below:

1. TGA-slow pyrolysis experiments show that the major material decomposition of both SSWPCB and MLWPCB is between the range 250–405 °C. The average weight loss for SSWPCB is 59.39% and for MLWPCB is 25.31%. The pyrolysis processes are assumed to be of first order reaction rates with the average solid residue of 40.54% for SSWPCB and 74.68% for MLWPCB.
2. VTGA-rapid pyrolysis experiments shows that the major degradation takes places in between the initial 5–85 s. The average weight loss for SSWPCB is 60.81% and for MLWPCB is 24.4%. Post rapid pyrolysis the average solid residue left in SSWPCB is 39.21% and 75.60% for MLWPCB. Thus both the results shows the differences in the two sources of WPCB which is consistent to the data obtained using slow pyrolysis.
3. In TGA – slow pyrolysis experiments the estimated activation energies for SSWPCB are in the range of 50.96–59.59 kJ mol⁻¹ and for MLWPCB are in the range of 78.60–99.08 kJ mol⁻¹ respectively. It is due to major presence of organic content in SSWPCB; lower energy is required to trigger the reaction whereas higher energy is required in the case of MLWPCB due to its ceramic rich contents.
4. The powder-residual elemental properties of WPCB are studied using XRF, Carbon Analyser, XPS and SEM techniques. The results obtained indicate the presence of high carbon content in SSWPCB and high silica content in the MLWPCB. The polymer rich SSWPCB decomposes more to higher temperatures with

the shift in the derivative mass at higher heating rates. On contrary MLWPCB shows minimum decomposition at higher temperatures due to its presence of SiO₂, Al₂O₃ and CaO (ceramic) content alongside glass fibres which is again confirmed using SEM. Results obtained shows SSWPCB as an important carbon source and MLWPCB as a material source for composites industry, therefore reducing the manufacturers demand for conventional raw materials.

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