OPTIMIZATION ON EXTRACTION AND STRIPPING OF BASE METAL IONS FROM WEEE LEACHATE BY LIQUID-LIQUID EXTRACTION

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ABSTRACT

Recovery of metals from Waste Electrical and Electronic Equipment (WEEE) has drawn a great attention of many researchers recently. Discharged electronic equipment is usually mechanically pre-treated to separate plastics from metal components, destined to further recycling. Hydrometallurgy is one of the most investigated methods to extract metals from WEEE by means of alkaline or acid media which promote the transfer of metals into solution. However, since WEEE contains different groups of metal ions (e.g. base metals, precious metals and rare earth metals) it is essential to investigate the treatment processes which are capable of selectively recover these group of metals from the leaching solutions. This study focuses on the extraction and stripping of base metals from WEEE leachate, with an investigation on the simultaneous effect of different factors such as pH, carrier, organic phase modifier and stripping agent concentrations. Initially, sulfuric acid and hydrogen peroxide were used for leaching process of base metals from WEEE, followed by an investigation on the effectiveness of different organic phases on WEEE leachate in terms of metal extraction. In this phase, Versatic 10 and tributyl phosphate (TBP) was used as carrier and phase modifier, respectively, while kerosene was used as the organic phase diluent. Extractions of silver, copper, cadmium, nickel, iron, lead, zinc and aluminum were achieved using 150mM of V10, loaded by 100mM of TBP in kerosene. Eventually, a study on extracted metals stripping was carried out in order to optimize the highest base metals stripping from the organic phase. For this purpose, different concentrations of sulfuric acid were used as stripping agent and the results revealed that 1.5M of H_2SO_4 successfully stripped the extracted metal ions.

Keywords: Base Metals, Leachate, Liquid-Liquid Extraction, Versatic 10, Waste Electrical and Electronic Equipment (WEEE).

INTRODUCTION

The Waste Electrical and Electronic Equipment (WEEE) production are increasing rapidly in recent years. About 30–50 million tons of WEEE is disposed of each year, with an estimated annual growth rate of 3–5% [1]. In 2014 around 9.5 million tons of WEEE were estimated to be generated in EU and 41.8 million tons worldwide. [2]. Amongst the various components existing in the WEEE (such as plastics, rubbers, ceramics etc.), the presence of base metals in huge proportion makes the WEEE simultaneously a noticeable source of hazardous materials [3] as well as a potential secondary source of metals [4]. Physical and chemical processes are generally employed for the recycling of metals from WEEE. The electronic waste is first mechanically treated in order to separate the non-metallic fraction from the metallic one. The latter is then further processed using high-temperature treatments, namely pyrometallurgical treatments, or leaching-based processes known as hydrometallurgical treatments. Due to its advantages in terms of lower costs and higher efficiency, hydrometallurgy has recently received a great deal of attention as an effective method to extract metals from WEEE. A hydrometallurgical process basically involves the dissolution of metals into solution and the extraction of the metals of interest from the leachate [5]. Sine WEEE contains a wide range of metals, the research is currently directed towards the optimization of these processes especially with regard to the treatment methods which are capable of the selective recovery of metals.

Liquid-Liquid Extraction (LLE) has been used for the recovery of metals from various waste sources [6, 7]. LLE system consists of two phases, named as the aqueous phase and the organic phase. Aqueous phase refers to the part of the system which is loaded (contaminated) by a solute (solutes) and the organic phase is an immiscible liquid (diluent) in which based on the liquid extraction classification contains an extraction facilitator (carrier, extractant) [8].

This study investigates the effect of the organic phase containing Versatic 10 (V10) as a carrier in kerosene, on base metal extraction from WEEE leachate. Eventually, an investigation on the effectiveness of various sulfuric acid concentrations on the base metal stripping from the loaded organic phase is also presented.

METHODOLOGY

WEEE shredding dust collected at a full-scale mechanical treatment plant was used for the experimental purposes. 20gr of the WEEE dust were subjected to a leaching process using 160mL of 2M H_2SO_4 and 40mL H_2O_2. A jar test machine was used to keep the solution stirred at 150 rpm. After 3 hours, the leachate was filtered and the aqueous phase was used for LLE experiments.

Decanoic acid (Versatic 10, ≥98% purity) and tributyl phosphate (TBP, ≥99% purity) supplied by SIGMA-Aldrich were used as the carrier and the phase modifier, respectively. Kerosene was used as a diluent and supplied by Honeywell. pH was adjusted using hydrochloric acid and ammonium solution (30%) while sulfuric acid was tested as a stripping agent. The organic phase was prepared by dissolving 50-250mM of Versatic 10 plus 50-150mM TBP in kerosene. Experiments involving the diluent without adding the carrier were carried out as well.

Preliminary studies were carried out to evaluate and estimate the influential factors that could play a major role in the metal extraction process: three factors (carrier concentration, feed phase pH and phase modifier concentration) were tested between two levels to determine the highest metal ion extraction condition by means of a factorial design.

For the extraction phase, a volume (10-50mL) of the prepared organic phase was mixed with the prepared aqueous phase at a specific organic to aqueous phase ratio (1:1) in a conical flask. The bottles were shaken by a magnetic stirrer. Samples were taken after 2 hours stirring from the aqueous phase to determine the metal uptake from the aqueous phase into the organic phase. The aqueous phase pH was measured before and after each run with a pH meter.
The extraction efficiency (E%) of metal ion was calculated according to the following equation:

$$\mathrm{E\%} = ([\mathrm{M}_{org,eq}^{2+}]/\mathrm{M}_{aq,ini}^{2+} \times 100 \qquad (1)$$

where $[M^{2+}]$ represents the concentration of metal ion and the subscripts *org*, *eq*, *aq* and *ini* denote organic, equilibrium, aqueous and initial states, respectively.

The organic phase with the highest extracted metal concentration was chosen for the further stripping studies in which different concentrations of H_2SO_4 were investigated to evaluate the highest stripping efficiency. The stripping procedure was similar to the extraction one, with the exception that the aqueous phase was the prepared aqueous stripping phase and the organic one consisted of the metal-loaded organic phase obtained after the extraction process. After the extraction process, the organic phase was thus separated and mixed with the stripping phase. 0.5, 1.0, 1.5 and 2M of H_2SO_4 were used as stripping agent. Unlike the extraction procedure, in the stripping procedure, the pH adjustment after mixing the two phases was omitted.
During each experiment, samples were taken from the aqueous phase, filtered and diluted with distilled water using appropriate dilution factors and were analyzed by inductively coupled plasma atomic emission spectroscopy for base metals (silver, copper, cadmium, nickel, iron, lead, zinc and aluminum) concentration measurements.

RESULTS AND DISCUSSION

Results achieved from preliminary studies on the LLE revealed that in highly acidic condition of the raw leachate, the metal extraction is not successful, while by increasing the pH value from 5 to 8 the metal concentration increased drastically, suggesting that the optimum pH value for metal-Versatic 10 complex formation is between 5 to 8: pH more than 8 caused metal hydroxide and precipitation formation whereas pH below 5 decreased the metal-carrier complex formation. These results are in good agreement with the general mechanism involving the chemical complexation of Versatic10 and metals.

Versatic 10 with a chemical formula of $C_{10}H_{20}O$ is a synthetic carboxylic acid containing an O-H branch in the chemical structure which makes it a suitable extractant in solvent extraction [9]. The general chemical reaction between metal divalent and Versatic 10 can be presented as below [10]

$$\mathrm{M_{aq}^{2+}} + \mathrm{n(RH)_2} \leftrightarrows [\mathrm{MR_2\,H_{2n-2}}]_{\mathrm{org}} + 2\mathrm{H_{aq}^{+}} \qquad (2)$$

Where RH represents the Versatic 10 molecular compound and n represents the number of carrier molecules involving in complexation reaction which for bivalent metals extraction is equal to 2.

According to Eq. 2, complexation between the metal ion and Versatic 10, which occurs at the aqueous /organic interface, leads to release of H^+ from the organic phase into the aqueous phase and as a consequence a drop in pH value is expected.

Eq.2 shows that feed phase pH plays an important role in the metal extraction process. However, it should be taken into account that since metal species show great intense for metal-hydroxide formation and precipitation, it is vital to determine the maximum pH value of the extraction process to avoid undesired metal-hydroxide formation. For this purpose, extraction reaction of a metal species by carrier loaded in aliphatic organic solvents can be presented as [11]

$$\mathrm{M_{aq}^{a+}} + \left[\frac{\mathrm{a+b}}{2}\right]\left(\mathrm{RH_{2(org)}}\right) \rightleftharpoons \mathrm{MR_a(RH)_{b(org)}} + \mathrm{aH_{aq}^{+}} \qquad (3)$$

where the valence of metal species (*a*) and the number of carrier molecules engaged in the reaction (*b*) are used as the stoichiometric coefficient of the Eq. 2. By increasing the pH, the equilibrium position moves to the right and, thus, produces more metal-organic complexes. On the other hand, as the H^+ concentration increases, the equilibrium position shifts to the left and less metal-organic complexes are produced. To avoid the formation of metal hydroxide at low H^+ concentrations, the maximum permissible pH of solution can be calculated based on the solubility product constant (Ksp) of metal hydroxides [12]

$$\mathrm{K_{sp}} = [\mathrm{M}]^{\mathrm{a+}}[\mathrm{OH}]^{-\mathrm{a}} \qquad (4)$$

For instance, the initial concentration of cadmium in the WEEE leachate was around 28mg/L (0.25mM). As the solubility product constant (K_{sp}) of cadmium hydroxides at 298 K° is 7.2×10^{-15}; by applying these factors in Eq.4, the concentration of $[OH^-]$ can be calculated as

$$[OH^-] = \sqrt{28.12 \times +10^{-12}} \qquad (5)$$

The [OH^-] obtained at a specific K_{sp} can be then used to determine the maximum permissible pH of the solution according to

$$pH = 14 + \log[OH^-] \tag{6}$$

which is equal to 8.73.

Figure. 1 shows the simultaneous effect of pH and [V10] on silver extraction. It was revealed that silver extraction from the WEEE leachate follows the same pattern for each stage. The highest extraction for silver occurred in all the experiment runs at the middle level of each factor (pH: 6.0 and [V10]: 150mM). Similar extraction behavior was observed for copper (Figure 2), according to the previous investigations reported in the literature [13] while the extraction behavior for aluminum and iron showed an opposite trend. As presented in Figure. 3, it was observed that once the initial pH of the aqueous phase is set at 7.0, the highest aluminium extraction takes place regardless of the carrier concentration (Figure. 3 B), while if both factors (pH and [V10]) are in their corresponding middle level (6.0 and 150mM, respectively), the aluminium extraction decrease drastically. These results suggest that the observed aluminum removal is basically due to pH change rather than extraction process. Similar findings are reported by using Versatic 10 as carrier and NaOH for pH adjustment [14]. Figure 3 shows that the highest extraction of nickel, zinc, lead and cadmium occurred in 6.0<pH<7.0 when [V10] is fixed at 150mM, with a relatively similar pattern of extraction.

Moreover, the results confirmed that using TBP as carrier individually has no effect on metal extraction efficiency, while on the other hand it was observed that in the case of using the organic phase without TBP, the emulsion formation practically disables the aqueous/organic phase separation. According to literature studies, TBP has shown relatively low extraction capacity for metal extraction [16] but it is mostly used as a phase modifier [17] by adduction with metal-carrier complexes in the organic phase [9]. Phase modifiers are used in order to eliminate or reduce the organic phase emulsification. An emulsification of the organic phase happens due to lateral shear forces and is counted as an important factor causing membrane instability [15].

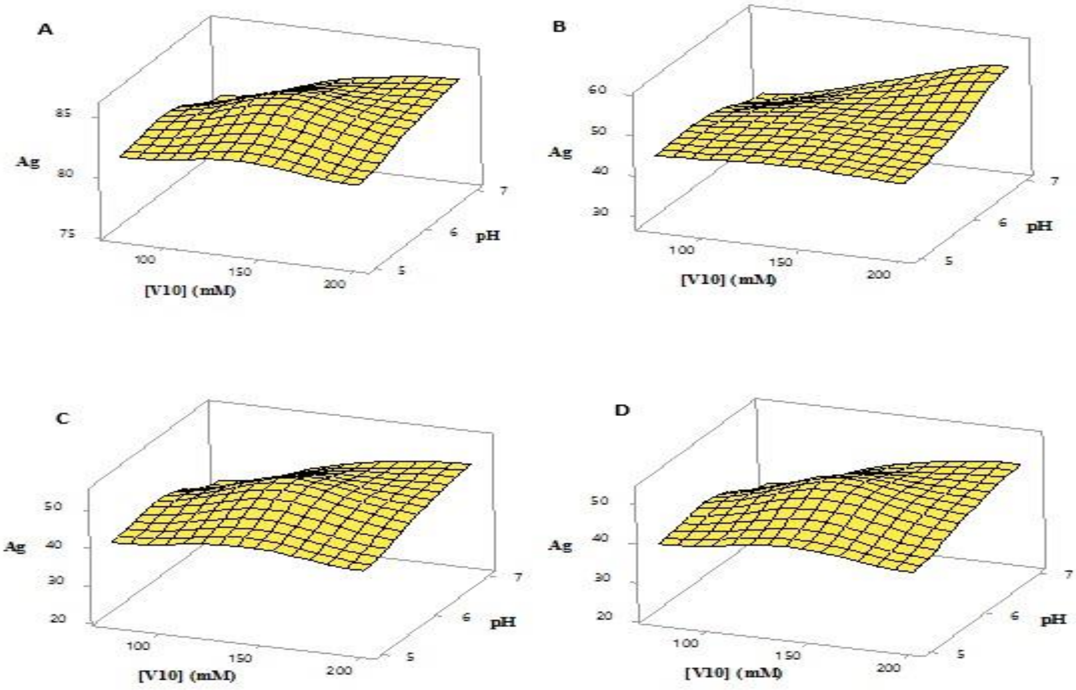


Figure 1 Silver extraction as a function of pH and [V10]

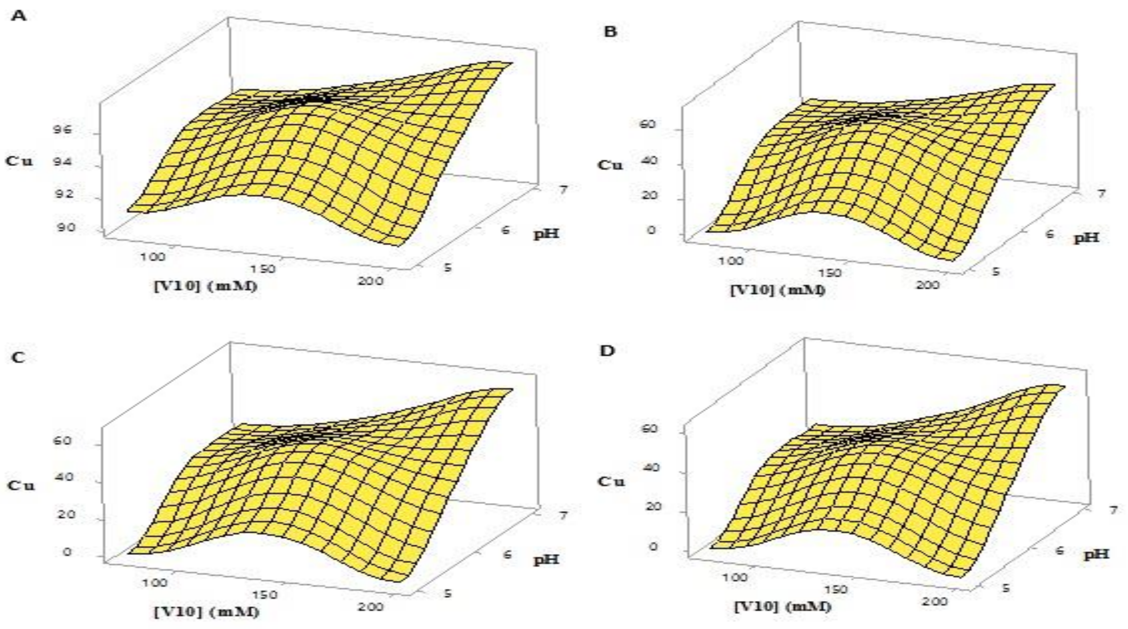
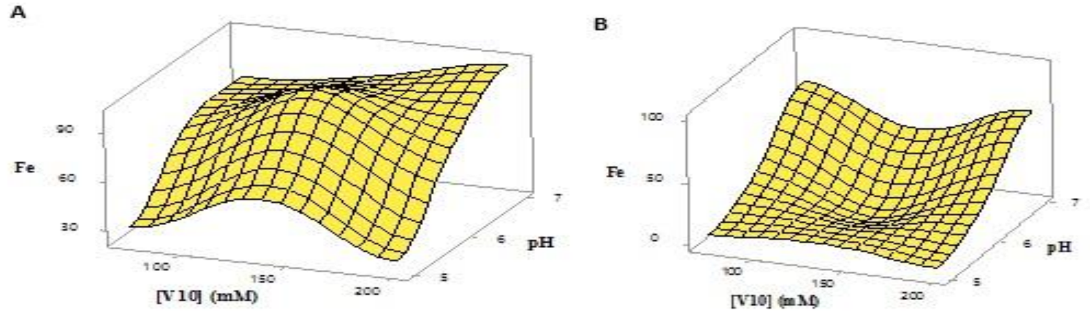
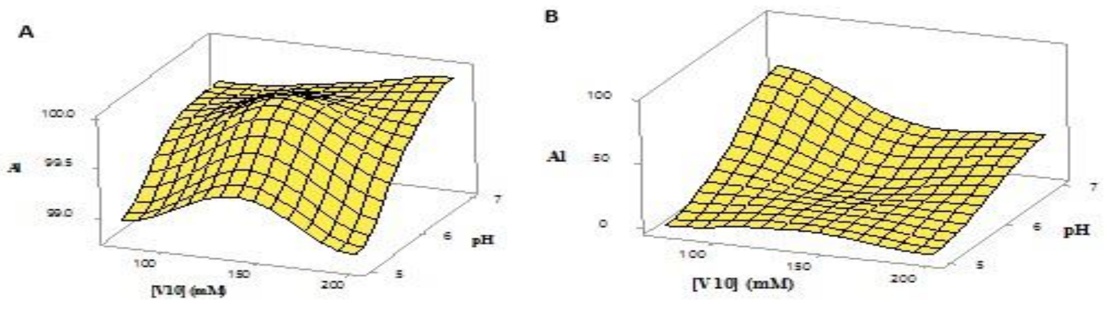


Figure 2 Copper extraction as a function of pH and [V10]





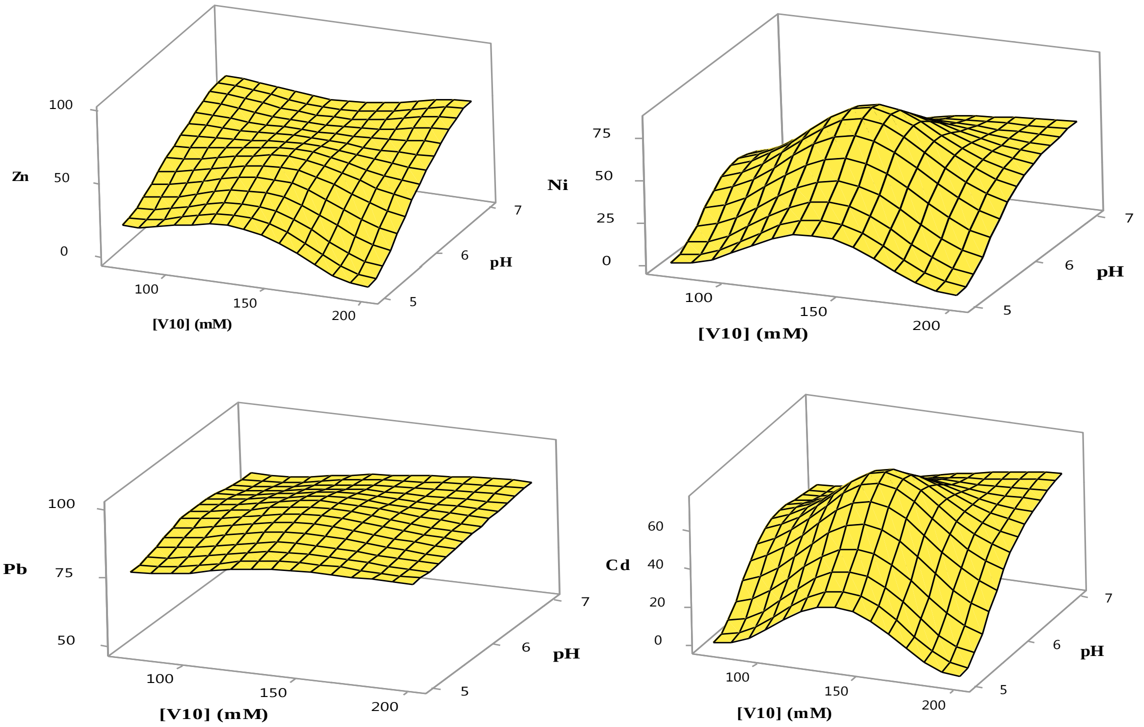


Figure 3 Three-dimensional plot of base metals extraction as function of pH and [V10]

Figure 4 shows the effect of sulfuric acid on metal stripping from the organic phase. Since sulfuric acid as a strong acid is capable of losing a proton (H^+) and being ionized (dissociated) in the stripping phase more than other mineral acids, hence the highest stripping percentage was obtained between 1M and 1.5M of H_2SO_4. The low concentration of H_2SO_4 (below 1.0 M) did not show enough strength to strip off the metals existing in the organic, while once the sulfuric acid is between 1M<[H_2SO_4]<2M it has the highest stripping efficiency.

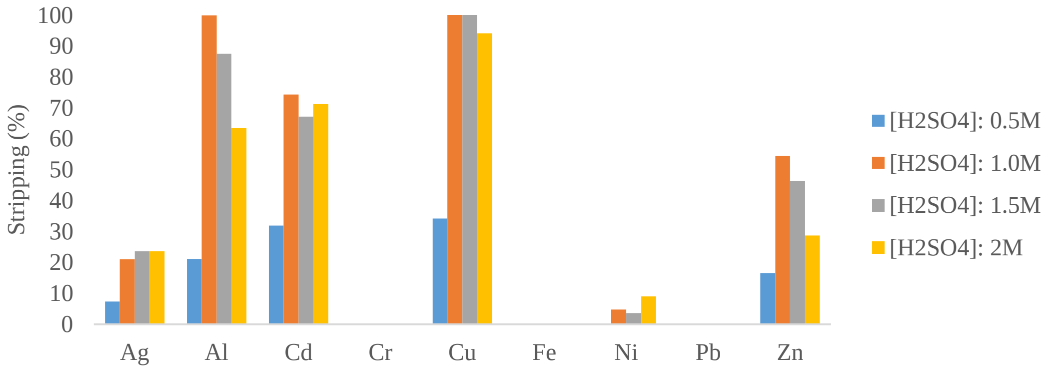


Figure 4 Metals stripping efficiency versus various stripping agent concentrations

CONCLUSION

A liquid-liquid extraction process was carried out in order to selectively recover base metals from WEEE dust leachate. The combination of Versatic 10, TBP and kerosene was investigated. Simultaneous effect of the carrier, phase modifier and aqueous phase pH were analyzed along with the efficiency of various sulfuric acid concentrations as the stripping agent. It was concluded that significant interaction between Versatic 10 and aqueous phase pH results in complete zinc, lead and copper recovery from the WEEE leachate solution Furthermore 85% of silver and 60% of cadmium were effectively extracted, using 150mM of Versatic 10, 100mM of TBP and at pH 6.0. It was also observed that during the extraction process and due to pH adjustment, massive quantities of aluminum and iron compound precipitated, resulting in a complete removal of both metals. It is suggested that TBP has a minor effect on metal extraction but has a significant role in preventing emulsion formation during the aqueous-organic stirring process. Finally, 1.5 M of sulfuric acid was found to strip the extracted metals at higher efficiencies.

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