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Effect of temperature on copper, iron and lead leaching from e-waste using citrate solutions

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ABSTRACT

E-waste is a potential source of large quantities of metals. The ability of citrate solutions to recover base metals from these materials has been demonstrated. In the present study, the effect of the temperature on base metal leaching capacity by the citrate solutions is determined. The material employed consisted of a mechanically prepared, gravity concentrated e-waste, with a metallic content greater than 90%. The leaching conditions were selected based on previous research performed by the authors (0.5 M sodium citrate, pH 4.5 and 20 g per liter e-waste concentrate). Leaching tests were performed at temperatures between 0° and 70 °C. The initial leaching rates for the three metals increased with temperature. However, these tapered off with time for temperatures above 30 °C, which can be associated to citrate destruction.

1. Introduction

In recent years, considerable effort has been invested in remediation of the environmental impact of human activities. The reutilization of waste materials on a large scale has attracted much attention, especially those generated in our everyday life (household effluents, e-waste, etc.). Specifically, the components of e-waste contain a complex array of metals in rich quantity, some of which are toxic to the environment and all of which are valuable resources (Priya and Hait 2017). These materials are especially difficult to treat because they usually contain three differentiable types: polymers (plastics), metals and an LED screen (Ongondo et al., 2011).

Economic factors and "programmed obsolescence" (continuous actualizations, new models, limited compatibility between manufacturers, etc.) have led to the ever-increasing generation of e-waste (Dannoriter, 2011). Nowadays, it is cheaper to replace an electronic apparatus than to repair it. Furthermore, these artifacts have been "massified" and form an integral part of daily life, independent of a person's socio-economic status; for example, in the year 2000, only 15 out of 100 people had cellphones, while in 2015, this figure had risen to 95 out of 100 (World Bank, 2015). There is a need for strategies that guarantee better control in consumption and the longer useful life of electronic devices (Breivik et al., 2014). In the meantime, the large amounts of these materials are susceptible to metallurgical treatment.

Extractive metallurgy is a field dedicated to the separation of metals from minerals and materials that contain them. Fortunately, many of the concepts employed in mineral treatment can also be applied to e-waste (Cui and Zhang, 2008; Tuncuk et al., 2012) and could contribute to the solution of environmental problems caused by the increase in potentially dangerous electronic residues (Kolias et al., 2014). Recently, there have many studies published on metal recovery from different types of waste material, most employing hydrometallurgical processes. These have centered on two aspects: (1) the recovery of base (Cu, Fe, Zn, etc.) and/or precious metals (Au, Ag, Pd), and (2) on the removal of toxic heavy metals (Pb, Cd, Hg, etc.) (Birloaga et al., 2014).

An extensive variety of base metal leaching processes have been proposed, principally employing inorganic acids at temperatures in the 70–100 °C range (Cui and Zhang, 2008; Akcil et al., 2015). The principal disadvantages of these systems are that the reagents cannot be reused and that the untreated waste leaching solutions become an environmental problem in themselves.

In contrast, processes that employ organic acid media can be used in several cycles (Jadhao et al., 2015) and produce acceptably degradable waste streams. The results presented in the present document are part of a broader study, carried out by the authors, in which inorganic acids are replaced in the leaching stage by solutions of sodium citrate (trisodium 2-hydroxypropane-1,2,3-tricar

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boxylate) to recover base metals from Electronic Waste from Printed Circuit Boards (EW-PCB). Citrate is a less corrosive and more selective than inorganic acids, because it is an effective complexing agent between pH 3 tand 8. Furthermore, the extraction percentages are better than those obtained using other organic acids, such as EDTA (diaminoetanotetraacetic acid), and inorganic acids (Torres and Lapidus, 2016). Leaching solutions containing sodium citrate can be considered an adequate alternative to conventional inorganic acid system and these solutions can be successfully reutilized in several cycles, once the metals are electrorecovered (Torres and Lapidus, 2017; Vegliò et al., 2003).

An inconvenience of hydrometallurgical processes, when compared to pyrometallurgical routes (incineration), is the slow kinetics (Sohn and Wadsworth, 1979). Higher temperatures are used to increase the leaching rate (Silvas et al., 2015; Smith, 1981; Sun et al., 2015), although, in some cases, the rise in temperature is not advantageous. For inorganic substances, such as ammonia and sulfuric acid, the leaching processes are operated at temperatures as high as 75 °C (Silvas et al., 2015; Sun et al., 2015). The present investigation contributes to the understanding the effect of temperature on base metal leaching contained in EW-PCB with sodium citrate solutions, especially considering the possible degradation that could result and its consequences on recyclability.

2. Materials and methods

The material employed in this study corresponds to a gravity concentrated EW-PCB (obtained from mobile phones), with a high metallic content. After size reduction and classification, the particle size fraction selected was $\geq 500\ \mu m$, containing 93.97% copper, 2.01% lead and 1.94% iron, in addition to minor quantities of other metals, including nickel and gold (Torres and Lapidus, 2016).

The leaching solutions were prepared using analytical grade trisodium citrate (0.5 M $Na_3C_6H_5O_7$, J.T. Baker) and deionized water (Millipore Milli-Q). The pH was adjusted to 4.5, with a dilute HNO_3 solution. A solid to liquid ratio of 2 g per 100 mL of solution was employed. Mechanical agitation was used and set at 125 rpm. The oxidant (hydrogen peroxide) was added each hour of the leach as a concentrated solution (30% w/v, J.T Baker) in an amount that corresponded to 0.1 M. Under these conditions, high extraction percentages of copper, iron and lead were achieved (Torres and Lapidus, 2016; Torres and Lapidus, 2017).

Since the principal objective was to analyze the temperature effect on base metal leaching, a 500-mL jacketed Pyrex® reactor was employed. The temperature was controlled by recirculating an ethylene glycol solution (30% v/v), heated or refrigerated in a constant temperature bath (Thermo-Haake K15/DC10). The reactor was also coupled to a Graham-type condenser to prevent any evaporation during the leach.

Samples of the leach solution were drawn each hour (5 mL) and diluted with deionized water at pH 4.5. The metal content in solution was quantify by atomic absorption spectrophotometry (AAS, Varian SpectrAA 220fs), using the lamps and procedures recommended by the manufacturer. After 5 h, the solid residue was separated from the leach liquor (by vacuum filtration) and digested to complete the metallurgical balance. Experiments at each temperature were performed in duplicate, or triplicate, if the relative error exceeded 5%.

Solution potential was measured initially and every hour before each peroxide addition using an ORP electrode with its corresponding potentiometer (Hanna Instruments, HI 4112). The ORP value reported for each experiment was the average for the entire leach and all are referenced to the standard hydrogen electrode (SHE). On the other hand, for the quantification of hydrogen peroxide degradation, leaching solutions were titrated with a standardized solution of potassium permanganate (Mattos et al., 2003; Ruiz-Sánchez and Lapidus, 2017).

To determine citrate degradation, Fourier Transform Infrared (FTIR) was employed. This technique provides the semi-quantitatively the vibrational spectrum of the citrate species at different concentrations compared to standard solutions prepared in a manner comparable to the leaching experiments, both in the absence and presence of added $CuSO_4$. FTIR measurements were performed on solutions of 0.5, 1.0 and 1.5 M sodium citrate at pH 4.5. To simulate leaching solutions and to determine if the copper present in a pregnant solution would cause interferences in the infrared spectrum, another series of measurements were carried with the addition of 6350 ppm copper, in the form of its sulfate salt. Only copper was considered since the maximum concentrations of lead and iron were very small in comparison (~200 ppm). For each solution, the spectrum represented an average of three scans with a resolution of 1 cm^{-1}.

3. Results and discussion

3.1. Leaching at ambient temperature (20 °C)

The leaching (oxidation/complexation) reactions for the three principal metals at pH 4.5 are shown below. As may be observed, an oxidant as well as a complexing ligand are necessary to achieve high solubility. Hydrogen peroxide was chosen since it is a relatively clean oxidant, leaving no products other than water.

$$2Cu^{\circ} + 2H_2O_2 + 2HCit^{2-} + H^{+} \rightarrow Cu_2(Cit)_2OH^{3-} + 3H_2O$$

$$Fe^{\circ} + H_2O_2 + HCit^{2-} + 2H^{+} \rightarrow FeHCit + 2H_2O$$

$$Pb^{\circ} + H_2O_2 + HCit^{2-} + 2H^{+} \rightarrow PbHCit + 2H_2O$$

where Cit^{-} is the citrate ion

The leaching behaviors for copper, iron and lead at 20 °C are shown in Fig. 1. During the entire experiment, the extraction of each metal is progressive, with no indication of cementation or precipitation. The trends are similar to those observed in previous studies (Torres and Lapidus, 2016), where lead is preferentially extracted, followed by iron and finally, copper. However, the pro-

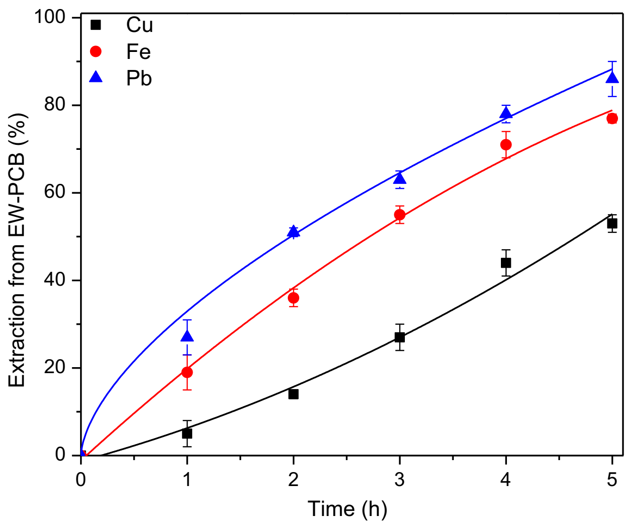

Fig. 1. Extraction of different metals from EW-PCB. All tests were performed at 20 °C and 125 rpm stirring rate, with a solid-liquid ratio of 20 g EW-PCB per liter of leaching solution (0.5 M sodium citrate at pH 4.5, with 0.1 M H_2O_2 additions every hour).

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