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Recovery of copper from scrap printed circuit board: modelling and optimization using response surface methodology

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ABSTRACT

The aim of the present investigation is to recover the copper, tin, lead and nickel from scrap printed circuit boards. Leaching and electrowinning have been employed to separate and recover these metals. Two stage leaching was employed wherein the first stage consisted of leaching the scrap board with 0.1 M $CuCl_2$ and 3.0 M HCl resulting in the dissolution of tin only. In the second stage leaching, the residue of the first stage was treated with 0.5 M $CuCl_2$ and 3.0 M HCl resulting in the dissolution of copper, nickel and lead from which lead is precipitated as $PbCl_2$ by cooling.

Next the electrowinning was employed to recover copper from a solution containing copper and nickel. Electrolysis was carried out in a two compartment cell divided by a cationic exchange membrane. A Box–Behnken experimental design has been applied to relate the current efficiency with current density, ratio of cuprous to cupric ion concentration, concentration of hydrochloric acid and electrolysis time. The current efficiency was found to increase with current density and concentration of cuprous ion.

1. Introduction

Electronic scrap like printed circuit board (PCB) is one of the most complex recycling materials among the wastes that contain copper. The metals present in the majority of cases are gold, silver, copper, tin and lead. At present only precious metals such as silver and gold are recovered from discarded boards. Other metals are precipitated as hydroxides and sent to the landfills. Mechanical recovery methods like density difference [1], air table separation [2], magnetic separation [3] and electrostatic separation [4] are employed for recovery of base metals. However these methods require high energy consumption and efficiencies are low. Pyrometallurgical process produces a large amount of gases and slag rich base metals. Hydrometallurgical processes have advantages such as low capital cost and flexibility of operation even on a small scale.

In hydrometallurgy, leaching is commonly used for the dissolution and recovery of metals. Acid extraction is a very effective means of leaching the metal contents because a low pH destabilizes numerous inorganic constituents. The effectiveness of the acids follows the order of nitric acid > hydrochloric acid > sulfuric acid [5]. Generally, leaching of copper from sulfide minerals is carried out by hydrometallurgical processes using cupric or ferric chloride ions as oxidant [5,6]. The leaching of copper in chloride media has some advantages, such as the high solubility of metal complexes, stability of monovalent copper and high leaching rates [7–9]. Ammonia is used as a leaching medium for the selective leaching of copper from copper scrap. A process for copper recovery from PCBs using ammoniacal leaching followed by electrodeposition has been reported [10,11]. This process uses an ammonia–ammonium salt solution containing Cu (I) and Cu (II) ammine complexes and consists of three steps of leaching, purification and electrowinning. Copper in the waste is leached as Cu (I) using Cu (II) as the oxidizing agent. Impurities in the solution are removed by solvent extraction and the purified Cu (I) solution is electrowon in a diaphragm cell. Cu(I) is reduced to metallic copper on the cathode and the remaining Cu (I) passes to the anode compartment where it is oxidized to copper (II). However the drawback of the ammoniacal system is the difficulty in leaching precious metals.

Kim et al. have reported a process for copper leaching from waste PCBs using electro-generated chlorine in hydrochloric acid [12]. Chlorine is generated from an acidic cupric chloride system in an electrochemical reactor at a Ti/RuO_2 anode. This chlorine is sent to a leach reactor where dissolution of metals takes place and the metals

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are recovered from solution by electro deposition [13]. This paper considers the possibility of recovering base metals such as copper, lead, tin and nickel from printed circuit boards scrap received from M/s NSB Electronics Ltd, Bangalore, by leaching with hydrochloric acid and cupric chloride system followed by electrowinning.

2. Materials and methods

All the chemicals used in the study were analytically pure. The etchant solution taken for the study was prepared synthetically using scrap Printed Circuit Board laboratory grade chemicals. To study the combined effect of operating parameter such as current densities, concentrations of cuprous, cupric ion and acid and at different time intervals on current efficiency Box–Behnken method of experimental design has been used.

2.1. Leaching experiments

Grounded powder of scrap printed circuit board materials received from M/s NSB Electronics Ltd, Bangalore as such was thermally treated at 500 °C for 1 h so that most of the organic matter are decomposed. This step is very important for further treatment since it removed the non metallic parts of the sample which improves the dissolution in the leaching step. The metal content of the board was determined by dissolving 5.0 g of the sample in aquaregia (50 mL) at ambient temperature and measuring the metal concentrations in the resulting solution by Atomic Absorption Spectrophotometer (Varian model spectra 220). An averaged metal composition of the scrap board is shown in Table 1. Leaching experiments were carried out by treating 25 g of dried PCB material with 300 mL of leaching solution in a glass reactor fitted with a water cooled condenser, a variable speed stirrer and a thermometer. The agitation speed was maintained constant at 500 rpm and the temperate was also maintained 25 °C constant. The flask was heated in a heating mantle fitted with a thermostat to maintain the temperature of the leaching solution at the desired level. For each run 300 mL of the leaching solution containing the required amount of $CuCl_2$, HCl and NaCl was charged into the reactor and the contents were stirred well with the help of a stirrer.

2.2. Electrowinning

The experimental set-up of the batch reactor used for electrowinning studies consisted of rectangular cell divided by a cation exchange membrane (Nafion 400 series) to separate the anode and cathode compartment. Rectangular graphite plates were employed as both anode and cathode. The plates (4 cm × 7.5 cm) were parallel to each other with a 10 cm inter-electrode gap. The electrodes were connected to a 5 A, 10 V DC regulated power supply, through an ammeter. A voltmeter was connected to measure the cell voltage. A solution containing the required amount of cuprous chloride, cupric chloride and hydrochloric acid served as both catholyte and anolyte. The electrodes were placed in the electrolyte in the cell such that 25 cm^2 of active surface of the cathode and anode was immersed. The solution was constantly stirred at 200 rpm using a stirrer to maintain uniform concentration. The electro-deposition was conducted under at different current densities. After the electrolysis is over, copper powder was scrapped from the cathode surface, washed with acetone, dried well and weighed. The current efficiency was determined from the weight of the copper powder collected under various conditions of current density, ratio of cuprous and cupric chloride concentration, HCl concentration and electrolysis time. For the electrowinning experiment the synthetic solution was prepared by dissolving appropriate amount of anhydrous cupric chloride salt and copper powder in desired acid concentration (HCl) and de-ionised water. The solution was stirred well until all the copper powder dissolves to obtain the desired concentration of the cuprous chloride solution, which is dark brown in color. To dissolve copper powder sometimes heating can also be done.

Table 1
Composition of scrap Printed Circuit Board.

S. no.	Element	Content % (w/w)
1	Copper	24.6
2	Lead	4.8
3	Tin	4.3
4	Nickel	1.5

2.3. RSM by Box–Behnken experimental design

Response surface methodology is one of the methods to design the experimental runs. In the present study the Box–Behnken method has been selected for the experimental design. Box–Behnken is a three level design with the central points. In general, the response of the experiment depends on the experimental conditions. This means that the experimental result can be described as a function of the experimental variables by the following polynomial equation

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i=1}^{k-1} \sum_{j=2}^{k} \beta_{ij} x_i x_j + \varepsilon \quad (1)$$

where y is the response variable, x_i and x_j are coded independent variables, $\beta_0, \beta_i, \beta_{ii}, \beta_{ij} (i = 1, 2.... k), \beta_{ij} (i = 1, 2,.... k; j = 1, 2,.... k)$ are regression coefficients for intercept, linear, quadratic and interaction terms respectively and ε is the statistical error. In the conventional experiment, the influence of the parameter on the output response is studied by varying the one parameter and keeping the other parameters constant. However, in the experimental design combined effect of operating parameters on output response can be studied simultaneously varying the other parameters. Experimental design is an effective and efficient optimization strategy to overcome this drawback, which has gained extensive applications in chemical engineering. The effects of combined variables are examined and optimization can be obtained with the help of RSM. [14]. In the present study, the RSM has been used to determine the relation between current efficiency with operating parameters. The levels of independent factors selected for present experiment are shown in Table 2. The uncoded variables are converted to coded variables using the following equation

$$x = \frac{X - [X_{max} + X_{min}]/2}{[X_{max} - X_{min}]/2} \quad (2)$$

where X = Natural variable and x = coded variable. A class of three level complete factorial design for the estimation of the parameter in a second order model has been developed by Box–Behnken. Table 3 gives the experimental runs for a three-level three factor Box–Behnken experimental design with three central points and the design was experimented using MINITAB 14(PA, USA).

Table 2
The level and range of variables chosen for photoelectrocatalytic-electrooxidation.

Factor	Variables	Unit	Range of actual and coded variables		
			−1	0	+1
X_1	Current density	A dm^{-2}	5	17.5	30
X_2	Cu^{2+}/Cu^{+} ratio	–	1	2	3
X_3	HCl concentration	g L^{-1}	160	205	250
X_4	Time	h	2	3.5	5