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Recovery of metals from pyrolysed PCBs by hydrometallurgical techniques

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ABSTRACT

Present paper is a part of developed novel process to recover various metals (Cu, Fe, Ni and Pb) environmentally from waste printed circuit boards (WPCBs). The process consists of pyrolysis-physical beneficiation-leaching-solvent extraction-electrowinning-cementation. The PCBs were pyrolysed at a temperature of 300 °C and the obtained poly-cracker ash of PCBs was subjected to comminution for the separation of metallic from non-metallic fractions using scutter crusher and grinding mills. Further, the ground poly-cracker ash of PCBs was scrubbed/washed with water without using any additives to enrich the metallic concentrate up to 98%. The scrubbed sample was further screened to separate low and high metal concentrates. Further, the high metal concentrate (+10 mesh i.e. >2 mm size) was leached in 4 M HNO_3 at 90 °C for 60 min maintaining pulp density 30 g/L and stirring speed 250 rpm. Result showed the complete dissolution of the metals viz. Cu, Fe, Pb and 57.5% Ni etc. present in the concentrate. Systematic scientific studies were also carried out to recover acid and metal from leach liquor of the poly-cracker ash of PCBs. To recover nitric acid from the leach liquor, the experiments were carried out using 60% TBP diluted in kerosene, which resulted in the extraction of 98% HNO_3 in three stages at O/A ratio 3/1 in 12 min. Subsequently, air sparging was performed to separate and recover Fe as precipitate. After the recovery of acid and iron, the leach liquor was further processed to recover Cu using 25% LIX 84IC diluted in kerosene. The copper was found to be extracted 99.99% in two stages at pH 2.5, O/A ratio 1/1 in 20 min, leaving Ni and Pb in the raffinate. Cu solution was stripped from loaded organic using 10% H_2SO_4. Cu metal sheet was obtained from the strip solution by electrowinning process in 4 h at temperature 30 °C using a cathode current density of 200 A/m^2. Further, the raffinate was processed for the recovery of Ni and Pb. Based on the experimental results a process flow-sheet is proposed for the extraction of all major metals (Cu, Fe, Ni and Pb) from the waste PCBs. The process has the potential to be commercialized after scale-up studies.

1. Introduction

Printed circuit boards are the essential components of electrical and electronic equipments (EEEs). Due to technological modernization and improvement in quality, EEEs are being replaced with faster rate (Kang and Schoenung, 2005). Worldwide production of printed circuit boards (PCBs) and semiconductor was estimated to be $10–15 billion in 2009 (Kumari et al., 2013) and it has reached nearly $60 billion in 2012, which was 1.7% real growth over 2011 (Kumar et al., 2014) and the UN estimate of the global WEEE production was 20–50 million tons per year (Hadi et al., 2015). These waste printed circuit boards (WPCBs) contain valuable, hazardous and precious metals. The recovery of these metals from electronic waste is necessary, both from economic point of view as well as to conserve the natural resources. These materials could be processed either by pyrometallurgical or hydrometallurgical method after pre-treatment process. The recovery of metals by hydrometallurgical processes is efficient compared to pyrometallurgical processes because of environmental protection and cost effectiveness. However, pyrolysis is one of the thermal pre-treatment processes, which are carried out in the absence of oxygen. During pyrolysis, dismantled component of spent PCBs are treated in an oxygen free atmosphere which decompose the organic part to low molecular weight products of liquids or gases that can be used as fuel. The pyrolysis process is more proficient as both char and metallic constituent obtained can be easily recycled. Base metals such as Cu, Fe, Ni and Pb are generally the industrial metals which oxidize easily. These are used in a wide variety of applications from electrical wiring (Cu) to batteries (Pb), strengthen and harden metal alloys (Ni) and to coat and protect more reactive metals, such as Fe.

Several authors studied the pre-treatment and physical beneficiation process followed by hydrometallurgical process to recover metals from waste PCBs (Long et al., 2010; Havlik et al., 2010; Mankhand et al., 2012; Kumari et al., 2013; Kumar et al., 2014). The recovery of metals from waste PCBs using vacuum pyrolysis followed by mechanical processing is reported (Long et al., 2010). In continuation of the above text, recovery of copper and tin from waste printed circuit boards

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after thermal treatment (300–900 °C) is also studied (Havlik et al., 2010). Efforts have been made to recover copper in nitric acid from waste PCBs after thermal treatment in air and nitrogen atmosphere (Mankhand et al., 2012). Metals such as Cu, Pb, Ni etc. recovered from pyrolysed PCBs using 2 M HNO_3 at 85 °C for 75 min maintaining a pulp density of 100 g/L (Kumari et al., 2013). Recycling of valuable metals such as Cu, Pb, Ni etc. from pyrolysed PCBs using physical beneficiation and hydrometallurgical treatment is also reported (Kumar et al., 2014).

Various authors reported the extraction of acid and metals using different extractants (Shin et al., 2009; Bell et al., 2012; Jaiswal et al., 2015; Le et al., 2011; Zhang et al., 2010). Extraction and recovery of nitric acid from waste etching solution using TBP as an extractant are investigated (Shin et al., 2009). Bell et al. (2012) reported the extraction of nitric acid into tridentate diglycolamide ligand, TODGA. Recovery and reuse of nitric acid from effluents containing free nitric acid in the absence and presence of metal nitrates are also reported (Jaiswal et al., 2015). Further, extraction of copper from nitrate leach liquor of printed circuit boards by solvent extraction using 10% LIX 984 N at pH 1.9 is reported (Le et al., 2011). Separation of copper, iron, zinc and nickel from nitrate solution by solvent extraction using LK-C2 is also reported (Zhang et al., 2010).

Several authors studied the recovery of lead from e-waste by cementation process (Volpe et al., 2009; Makhloufi et al., 2000; Farahmand et al., 2009). Recovery of lead from the paste of lead-acid battery using leaching with urea acetate and cementation is reported by researchers (Volpe et al., 2009). Another process for removal of lead ions from acidic solutions by cementation on rotating iron disc is also investigated by researchers (Makhloufi et al., 2000). Further optimization and kinetics of lead cementation with aluminum powder are also reported (Farahmand et al., 2009). Electrowinning of copper is studied by different authors (Pedro et al., 2014; Veglio et al., 2003). Pedro et al. (2014) optimized the parameters for copper electrowinning from synthetic copper sulfate solution using a pulsed bed electrode. Another process is also reported for recovery of valuable metals from electronic and galvanic industrial wastes by leaching and electrowinning techniques (Veglio et al., 2003). After the literature review, it is noticed that combined process of pyrolysis-physical beneficiation-leaching-solvent extraction-electrowinning-cementation is not reported. So, present work reports novel process flow sheet for the extraction of all major metals (Cu, Fe, Ni and Pb) from the waste PCBs.

Present paper reports that a novel process flow sheet comprises pyro-hydro hybrid metallurgical process for the recovery of metals from waste PCBs. The process is environmental and based on zero waste concepts. The systematic scientific studies were carried out to recover copper and other metals from waste PCBs using pyrolysis followed by physical beneficiation and hydrometallurgical process. The enriched metal concentrate obtained after beneficiation was leached in acid and generated leach liquor was further put to solvent extraction process. Various process parameters viz. effect of pH, extractant concentration, O/A ratio, loading capacity etc. were studied to optimize favorable conditions for recovery of acid and copper solution. Copper metal was obtained from the leach liquor by electrowinning processes. This process carried out on lab scale is feasible technique and can be used for industrial applications.

2. Experimental

2.1. Preparation of the sample

Printed circuit boards were dismantled from obsolete computers and the small components such as batteries, capacitors etc. populated on PCBs were removed by IR heating (235 °C). This results in desoldering (by IR heating) of all the populated parts of PCBs. At this temperature, Sn present in solder material melts due to its low melting point while other metal remain intact in the PCBs sheets. These depopulated sheets were crushed and processed for pyrolysis. Poly-cracker ash of PCBs obtained after pyrolysis were used for experimental purpose which contains metallic and non-metallic constituents. The poly-cracker ash of PCBs was further beneficiated to separate the pyrolysed epoxies and metallic concentrates. This metallic concentrate having +10 mesh (BSS) (i.e > 2 mm size) is focused here for the recovery of metals.

2.2. Methods

A novel process consists of pyrolysis-physical beneficiation-leaching-solvent extraction-electrowinning-cementation has been studied for the recovery of Fe, Cu, Ni and Pb metals from waste PCBs.

2.2.1. Thermal pre-treatment followed by physical beneficiation

Electronic components of the PCBs such as batteries, capacitors etc. were removed by desoldering to get depopulated sheets of the boards. The depopulated sheets of the PCBs boards were reduced in size using scutter crusher. The crushed PCBs were put to vacuum pyrolysis process at a temperature 300 °C, which required 60 min and with a settle time of 3–4 min. The generated fumes get condensed to obtain LDO (Low density oil) and poly-cracker ash (pyrolysed) of PCBs was obtained. The poly-cracker ash of PCBs was subjected to physical beneficiation for the separation of metallic from non-metallic fractions using scutter crusher and grinding mills. Further, the ground poly-cracker ash of PCBs was scrubbed/washed with water without using any additives to enrich the metallic concentrate up to 97.8%. The scrubbed sample was further screened to separate low metal concentrate (−10 mesh i.e. <2 mm size) and high metal concentrate (+10 mesh i.e. >2 mm size). This metallic concentrate having +10 mesh (BSS) (i.e. >2 mm size) is focused here for the recovery of metals.

2.2.2. Hydrometallurgical treatment

The metallic components were leached using different acidic medium in a temperature controlled closed three necked Pyrex glass reactor fitted with condenser where the sample pieces were put in the leachant after reached desired temperature in a particular ratio and heated using hot plate. Mechanical agitation during the experiment was maintained using a stirrer which was adequate to eliminate the mass transfer effect on dissolution. The samples were drawn at a desired time interval and were analyzed. Satisfactory mass balance was obtained with a maximum deviation of ±2%. Leach liquor generated would be then pumped to solvent extraction as a feed solution where equal volume of aqueous and organic solution were mixed for a specified time to extract acid and copper. Prior to Cu extraction, air sparging was carried out to remove Fe content in the form of precipitate from the leach liquor to intensify the extraction of Cu. After that Ni was left in the raffinate, which was extracted by solvent extraction also. Electrowinning of copper was performed at lab scale by maintaining certain parameter in a glass tank employing unalloyed cathode of Titanium of grade 1 and 2 anode of Lead-Antimony alloy (antimonial lead) containing antimony in range of 2–6 wt.%. Copper electrowinning from the purified leach liquor (strip solution) has been studied to generate copper metal sheets. Recovery of lead by cementation process was carried out from leached solution (free from acid, iron, copper and nickel) in a Pyrex reactor. The recovery of metallic lead by cementation with aluminum is an electrochemical process involving the oxidation of aluminum and the reduction of lead nitrate.

2.3. Chemicals and reagents

All the chemical reagents such as nitric acid, hydrochloric acid, sulfuric acid, etc. used for experiment were of laboratory reagent grade (Grade: GR, supplied by Merck, India). Tri-butyl phosphate (TBP) was supplied by Luoyang Aoda Chemical Ltd., China). 2-hydroxy-5-nonylacetophenone oxime (LIX 84IC) was supplied by M/s Cognis