Developing Feasible Processes for the Total Recycling of WEEE to Recover Rare Metals

Jae-chun Lee, Manis Kumar Jha, Rekha Panda, Pankaj Kumar Choubey, Archana Kumari, and Tai Gyun Kim

Abstract The present paper reports several application-oriented processes developed for the recovery of various non-ferrous (Cu, Ni, Al, Pb, Sn), rare (Li, Co, In), precious (Au, Ag, Pt, and Pd), and rare earth metals (Nd, Ce, La, Y, Eu) from various urban ores, i.e., waste electrical and electronic equipments (WEEE), liquid crystal displays (LCD), batteries, magnets, fluorescent tubes, etc. Initially, the WEEE and various wastes were classified and dismantled. Further, the materials were pretreated to separate plastics, epoxy, ceramics, rubber, iron cover, and metallic concentrates. Based on their properties, plastic, epoxy and rubber could be either pyrolysed for production of marketable low-density oil and saleable activated carbon or directly recycled. The pre-treated metallic concentrates were processed by hydrometallurgical techniques, i.e., leaching, solvent extraction, ion-exchange, electro-winning for maximum recovery of metals. Various flow sheets discussed for rare metal extraction and processing strictly comply with environmental regulations.

Keywords Rare metals · E-waste · Recycling · Hydrometallurgy

Introduction

Nowadays, lots of electrical and electronic wastes (e-waste) are being generated with alarming rate worldwide and around 80% of the valuables present in these wastes end up in landfills. Although, strict regulations are being imposed by government in many countries for proper treatment of these electronic scraps but only 20% of that

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is being recycled in an organized manner. In developing countries, lack of proper collection system, illegal recycling by unorganized sector as well as lack of cost-effective simple technology for processing e-waste, adversely affect the environment. Therefore, a feasible technology with minimum environmental impact is required for the recovery of metals from such scraps. Recycling is the imperative solution to the growing e-waste problem and it has become a significant economic activity. Major fraction of e-waste constitutes personal computers, mobile phones, batteries, magnets, fluorescent tubes, etc. PCBs of personal computers contain Cu, Ni, Sn, Pb, and precious metals; however, mobile phone PCBs/connectors contain metals of economic interest mainly the precious metals(Au, Ag, Pt, Pd) and Cu. The magnets present in various electronic goods contain Nd (rare earth) whereas the lithium-ion batteries (LIBs) is composed of rare and strategic metals such as Co, Li, Ni, etc., which should be recovered in an eco-friendly manner.

The conventional technology for the recycling of e-waste has been based on the pyrometallurgical process, which has the advantage of accepting any physical form of e-waste. However, it is associated with certain drawbacks such as a long-term recovery options, air pollution, and loss of the noble metals with low recovery of critical metals. Accordingly, in recent years, we have made concerted effort to develop the hydrometallurgical routes for the total recycling of metallic and other components from a variety of e-wastes. The total recycling of e-waste particularly requires elaborate mechanical pretreatment including the pyrolysis as well as the chemical processing because of the complicated structures and compositions, whereas for the selective recovery of metals, chemical leaching followed by advanced separation techniques viz., solvent extraction/ion-exchange techniques are considered appropriate. Thus the present research reports various novel, feasible, and scientifically validated hybrid pyro-, chemical-, and hydro-metallurgical processes developed for the total recycling of metal values such as rare, rare earths, and precious and non-ferrous metals from a variety of e-wastes.

Pre-treatment of E-waste

E-waste is mixture of plastics, epoxy resins, ceramics, and metals requires pre-treatment prior to the hydrometallurgical processing. Initially, the e-wastes are dismantled, classified, and pre-treated to collect/remove metals present in it. Direct leaching of e-waste coated or encapsulated with plastics and ceramics rarely accomplishes effective extraction of valuable metals. Thus, metallic fractions have to be liberated from the non-metallic parts (plastics and ceramic, epoxy, etc.) before hydrometallurgical treatment. Methods of mechanical pre-treatment/chemical processes, i.e., organic swelling [1], pyrolysis [2, 3], etc. used for pre-treatment of e-waste have been described below.

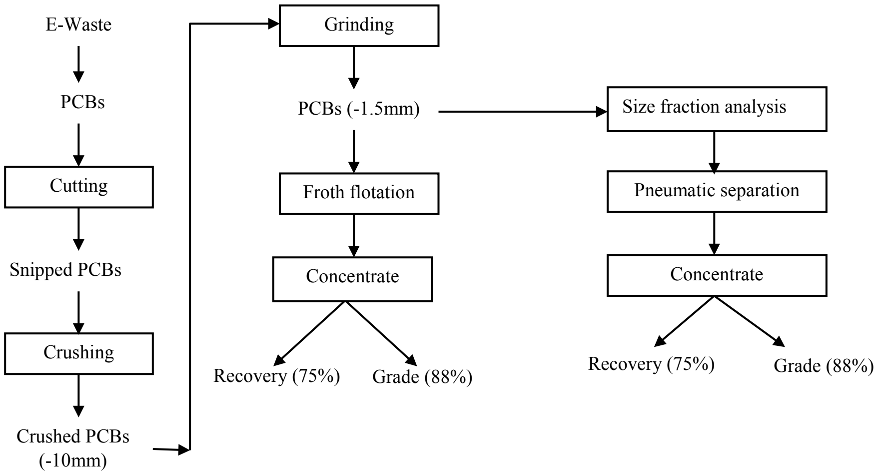

Fig. 1 Mechanical pre-treatment of e-waste to get enriched metallic values [4]

Mechanical Pre-treatment of E-waste

All e-waste contains PCBs, which are made up of various materials and metals. Kumar et al. (2013) developed a mechanical beneficiation route to process the PCBs present in e-waste in eco-friendly manner to get metallic concentrates for further processing (Fig. 1). The separation of material mainly depends on the distribution of metallic and non-metallic fractions and their liberation size due to their physical properties. The experimental data showed the enrichment of metals in coarser particles ($-1000 + 150$ μm) and non-metals in the finer particles <150 μm size following pneumatic separation and froth flotation process. In this case, recovery achieved was 75% with a grade of 88% on applying froth flotation. Simultaneously, lower grade of ~75% with ~65% recovery was obtained using pneumatic separation with <1500 μm powder. Finally, the grade of metals in average obtained was ~88% by controlling the feed charge and rate of air flow during pneumatic separation. The concentration of rare metals presents in the different fractions varying from 1.88% to 4.18% was enriched up to 9% using this beneficiation technique [4]. The developed process contributes to enrichment and the recovery of various metals like Cu, Al, Fe, Zn, Pb, Sn, rare metals, etc. Advantage of this process is the high metal recovery and directed towards the alternative metal resources from e-waste.

Chemical Pre-treatment of E-waste

The mechanical pre-treatment of PCBs is not effective in some cases, due to the lack of feasible milling devices. In order to address such bottle-necks, the feasible milling

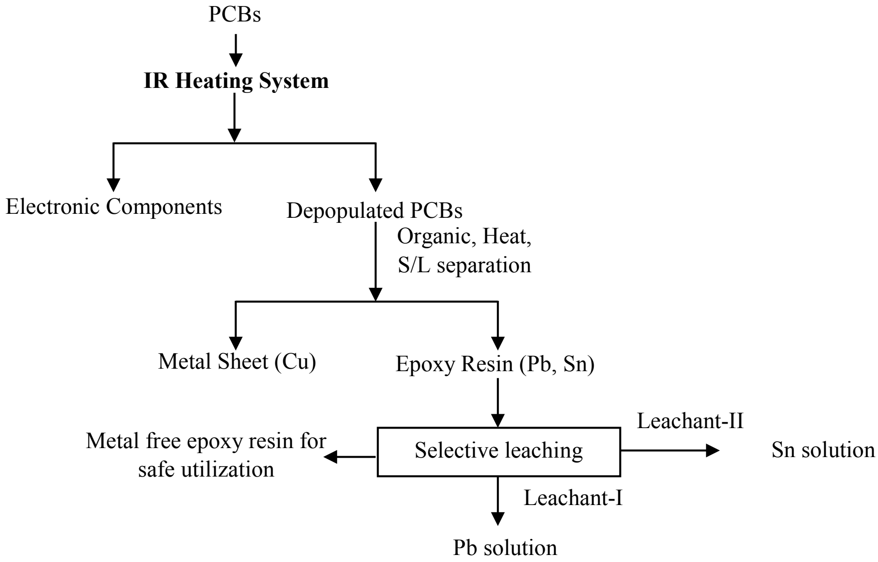

Fig. 2 Process flowsheet to extract metals from the chemically pre-treated e-waste [1]

technique for PCBs was explored. Jha et al. [1] reported a bench-scale laboratory test using an organic to liberate the layer of metals from the PCBs without using any mechanical pre-treatment. Several thin layers of metals from the swelled PCBs were effectively separated leaving solder metals on the surface of the liberated epoxy resin [1]. The samples were processed as per the novel organic-treatment technique developed in our group. In this pre-treatment, the depopulated PCBs were sized into 7 cm × 7 cm and then dipped in a glass container containing the swelling organic. The container having cut PCBs and organic was heated and save for overnight. The outermost layer of PCBs containing soldering metals was removed after separating the swollen material, as presented in Fig. 2, and the thin layer of metal sheets encapsulated by resins was removed one by one. The sheets were dried after washing with hot water to remove the entrapped organic. Sheets were then sized further to ~0.5–0.7 cm and 0.5 mm thick, which contained 74.76% Cu, 0.48% Pb, and 0.52% Sn.

Pyrolysis of E-waste

Pyrolysis is a thermal treatment process, where the organic materials are decomposed to low molecular weight products of liquids or gases that can be used as fuel while the inorganic components containing metals and glass fibers are separated. Kumari et al. [2] and [3] developed processes for pyrolysis of the depopulated PCBs of e-waste in a vacuum pyrolysis device, where the evolved gases were collected and condensed to be reused as a fuel. The pyrolysed PCBs were further beneficiated to separate the metallic content from the burnt epoxies (Fig. 3). The separated metallic content was further screened to get low metal concentrate of size <2 mm size, which was generally lost with the carbon ash. This low metal concentrate (small fraction) is focused here for the recovery of base metals.

The typical chemical analysis of low metal concentrate obtained in our studies showed the presence 34.26% Cu, 2.45% Fe, 0.43% Ni, 1.11% Pb along with negligible amount of several metals and ~45% of burned non-metal carbon. In order to recover metals from the pyrolysed sample, it was physically beneficiated to separate the metallic's from the non-metallic fraction. The sample received was screened and it was observed that the concentrate possessing >2 mm size contained ~65% metals along with polymers/epoxies, while ~45% carbonic ash along with ~38% metallic

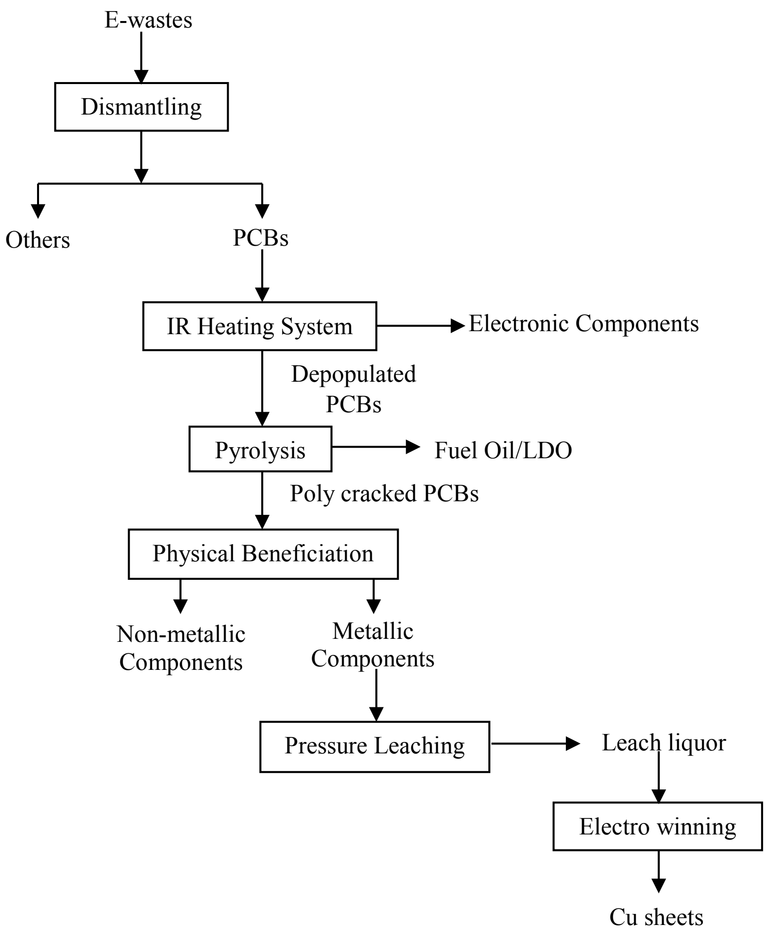

Fig. 3 Process flow-sheet to extract metals from pyrolysed PCBs [2, 3]

content and some plastic parts were separated in <2 mm size. Hydrometallurgical technique was further used to recover/separate metals from the low metal concentrate of pyrolysed PCBs [2, 3].

Hydrometallurgical Processes Developed for the Recovery of Metals from E-waste

Leaching of Pre-treated E-waste

Leaching process is employed for the selective extraction of metals after pre-treatment with application of different leachants viz. acidic, alkaline, and neutral type depending on the nature of the material to be leached, and the presence of other impurities which may affect the leaching process (Fig. 4). Mixed leachants of acidic/alkaline or acidic/salt may also be employed to investigate the leaching behaviour of metals. Jha et al. [5] carried out leaching studies to study the dissolution behaviour of various metals from PCBs with different acids viz. H_2SO_4, HCl, and HNO_3.

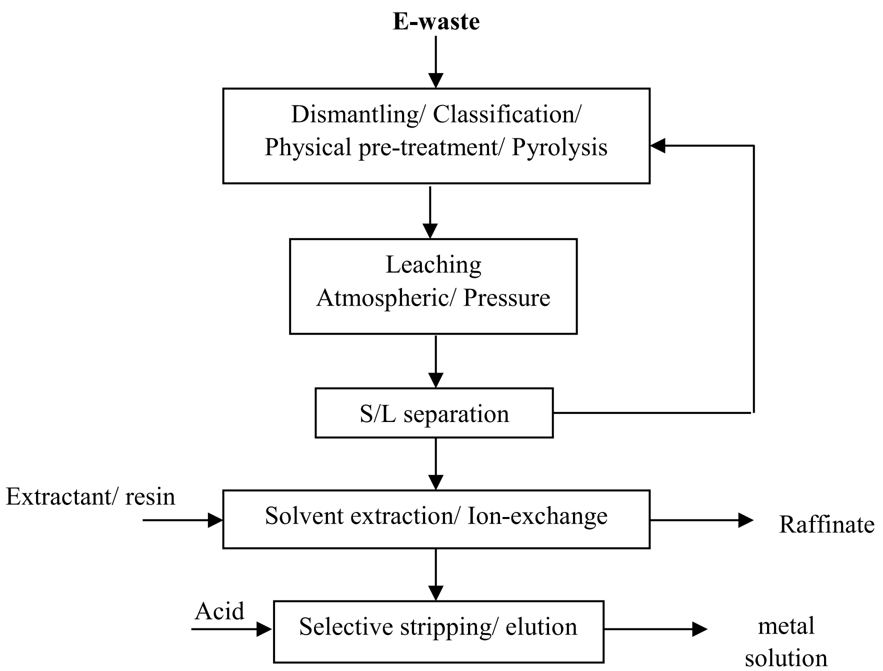

Fig. 4 Hydrometallurgical recovery of metals from e-waste

Sulfuric acid was not found to be a suitable reagent for the leaching of metals from PCBs even at elevated temperature and high concentration. Hydrochloric acid was also not suitable for the dissolution of copper; however, the dissolution of Sn was found to be satisfactory. Nitric acid was found to be a suitable reagent for the dissolution of most of the metals. The Fe and Ni present in the PCBs dissolved easily within 10 min of contact time, whereas 38% Pb leached out in 40 min. The dissolution of Sn was very poor with nitric acid even at high temperature with 6.0 M HNO_3 at S/L ratio 100 g/L and 90 °C. Around 99.99% Cu, Fe, and Ni were found to be leached along with 36.66% Pb. The NOx gas generated during leaching was absorbed in a suitable scrubbing solution. Further leach liquor was purified by solvent extraction, and from the purified solutions, salt/metals were obtained using suitable hydrometallurgical techniques [5].

Another hydrometallurgical recycling process for waste PCBs was also developed, which involved the novel pre-treatment consisting of organic swelling of PCBs to liberate thin layers of metals followed by sulfuric acid leaching of the metals so liberated. Leaching studies were performed for the recovery of Cu from the crushed and organic swelled liberated metals using sulfuric acid in the presence of hydrogen peroxide under atmospheric and pressure conditions [1]. The percentage recovery of copper was found to be 97.01% with addition of 15% (v/v) hydrogen peroxide keeping solid to liquid constant at 30 g/L. Jha et al. [6] and [7] also reported selective leaching of Pb (99.99%) from the liberated epoxy resin of waste PCBs using 0.2 M HNO_3 at 90 °C whereas 97.79% Sn was leached out from swelled and liberated epoxy resin using 4.5 M HCl at 90 °C in 60 min mixing time [6, 7].

Recovery of Metals from Leach Liquor of Metallic Concentrate

The solvent extraction (SX) processes were developed by Jha et al. [19] for the removal/recovery of hazardous metals from the complex leach liquor of electronic scraps following by recovery of valuable metals. As the leach solution of e-scraps contains various metallic constituents such as Fe, Cu, Zn, Cd, and Ni, different organic extractants viz. LIX 84, DEHPA, Ionquest 801, Cyanex 272, Cyanex 923, Cyanex 302, etc. diluted in kerosene have been used for metal separation and recovery. The solvent was modified with isodecanol to improve the phase separation. In order to extract Cu from the sulfate solution in continuous mode in MSU, basic studies have been made for the copper extraction at different pH, extraction isotherms, A/O ratio etc. using 5.0% LIX84 diluted in kerosene. Results were validated in mixer settler unit (MSU—having 620 mL mixing and 860 mL settling capacity) maintaining specific leach solution flow rate and A/O ratio. The results showed almost complete extraction (~97%) of Cu in three stages leaving minor metals Zn, Cd, and Ni in raffinate. The loaded Cu was completely stripped after scrubbing of minor metals using water with diluted sulfuric acid in two stages.

After extracting Cu, the SX study was carried out for the separation of Zn, Cd, and Ni from sulfate solution using different extractants. DEHPA (v/v) was found to be suitable for extraction of metals in comparison to Cyanex 923 and Cyanex 272 and the order of extraction with pH was found to be in the following sequence Zn > Cd > Ni. The kinetics of extraction showed that the equilibrium extraction of both Zn and Cd was attained in 2 min. The results showed the increase in Zn extraction at above 2.5pH. Cd was totally extracted even at lower pH without extracting Ni. The stripping of loaded Zn was carried out with 1.0% sulfuric acid at A/O ratio 1/1 maintaining a contact time of 5 min at room temperature whereas loaded Cd was effectively stripped with 10% hydrochloric acid at A/O ratio 1/1 [8].

Recovery of Metals from LIBs

Mobile phones constitute one of the major fractions of e-waste. These mobile phones consist of lithium ion batteries (LIBs), which are made up of rare and strategic metals such as Co, Li, Mn, Cu, Ni, Al, etc. These LIBs composed of an anode, a cathode, a separator, and an electrolyte. The black cathodic material present in the LIBs contains higher amount of Co (~20 wt% of LIBs) along with Mn, Li, Cu, Al, etc. The presence of ample metals in these discarded batteries has made their recycling very essential to not only cope up with the metals supply but also to comply with the regulations for the disposal of the used batteries. In view of the above, a hydrometallurgical flowsheet has been developed by Jha et al. [9, 10], and Dutta et al. [11] for recycling of spent LIBs to recover rare and strategic metals. Initially, the LIBs were crushed in a scutter crusher followed by physical beneficiation to separate the metallic fractions, plastics, and black cathodic powder [9–11].

Leaching of metals was carried out from the black cathodic material using suitable lixiviant at optimized conditions to dissolve maximum metals. The obtained leach liquor was further purified using precipitation followed by solvent extraction technique. Initially, the pH of the solution was maintained at 1.5 using sodium hypochlorite with constant stirring for 1 h in order to precipitate out Mn. This procedure was repeated thrice for complete removal of Mn. The leach liquor free from Mn was then mixed with 10% LIX 84IC maintaining O/A ratio 1:1 for 5 min to make the solution free from Cu, Fe, and Ni. It was found that ~99% Cu, Ni, and Fe were extracted in two stages at pH 4.5. Further, the loaded LIX 84IC was stripped using 10% H_2SO_4 to get the respective metal solution. Now, the leach liquor containing Co and Li was evaporated to increase the concentration of the metal ions in the solution. Reduced leach liquor containing Co and Li was again treated with 20% Cyanex 272 diluted in kerosene for 10 min maintaining O/A ratio 1:1. It was observed that at pH ~ 5, 98% Co was extracted leaving Li in the raffinate in two stages. The loaded Cyanex 272 was stripped thrice using 10% H_2SO_4 for complete back-extraction of Co from the loaded organic. Thus, 99% pure cobalt solution was obtained at above-described condition which can be further evaporated or electro-won to get Co salt or metal sheet, respectively. The raffinate containing Li was evaporated to get Li salt. The developed process flowsheet for recycling of spent LIBs to recover rare and strategic metals is presented in Fig. 5.

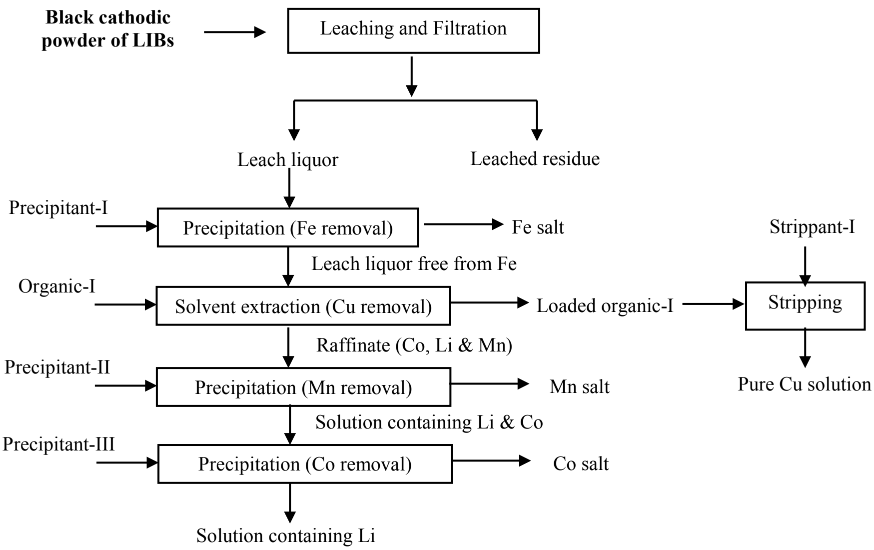

Fig. 5 Process flowsheet to extract metals from the black cathodic material of Li-ion batteries [9–11]

Recovery of Precious Metals from E-waste

A hydrometallurgical process has also been developed by Panda et al. [12] for the extraction of precious metals (Au, Ag, Pd, and Pt) from the e-waste. Initially, the e-waste was dismantled and depopulated to liberate all parts. Further, classification of parts containing precious metals was carried out. The parts containing precious metals were pretreated and physically beneficiated to get enriched metallic concentrate. Leaching of the metallic concentrate was carried out in a suitable lixiviant to get the precious metals into solution. The leach liquor obtained was further processed using standard separation techniques (solvent extraction/ion-exchange, precipitation, etc.) to get purified solutions of individual precious metals [12]. From the purified solutions, value-added marketable products of precious metals could be obtained using the method of evaporation/electrowinning techniques. The flowsheet to extract precious metals from e-waste is presented in Fig. 6.

Recovery of Metals from Scrap LCD Panels

Indium (In) is being widely used as indium tin oxide (ITO) on the glass substrate of the LCD (liquid crystal display) panel [13–15]. About 70–80% In is used in the LCD panel of different electronic goods but due to technological advancement, the lifespan of such electronic goods is decreasing day by day, which has resulted in the generation

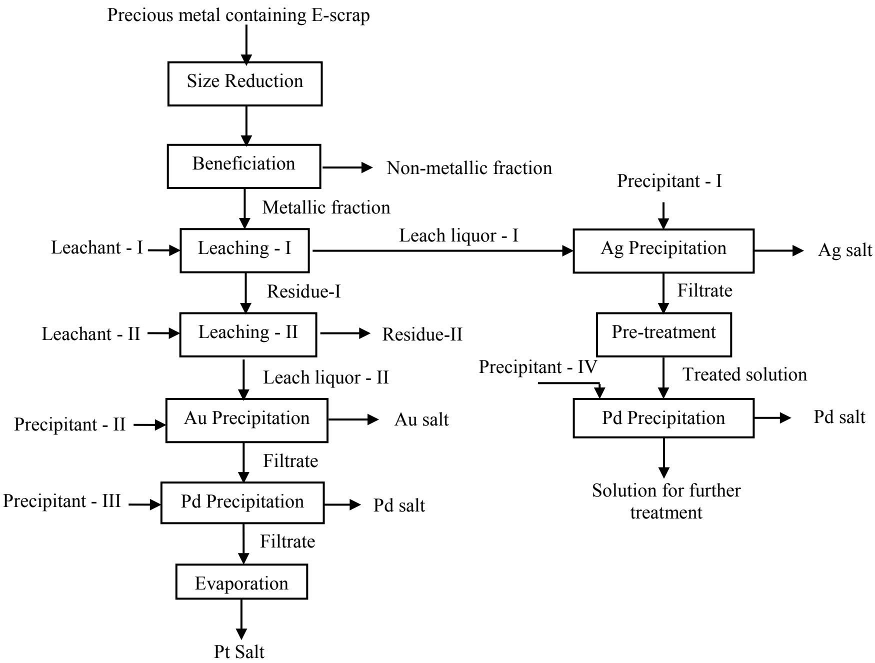

Fig. 6 Process flowsheet to extract precious metals from e-waste [12]

of massive amount of LCD panels [16]. In this regard, a hydrometallurgical flowsheet has been developed by Choubey et al. [17] to recover the indium from discarded LCD panels. Initially, the monitors of personal computers were dismantled to separate the LCD panels. Further, the LCD panels were pulverized and physically beneficiated to get enriched metallic fraction. Selective leaching of In was carried out from the metallic concentrate using different minerals acids [17]. Almost ~94.1, 93.8, and 93.2% In were leached using 1.0 M solution of HCl, H_2SO_4, and HNO_3, respectively at 60 °C in a reaction time of 75 min. Further, ion-exchange studies were carried out to selectively adsorb In from the leach liquor using Indion BSR resin. About 99.2% In got adsorbed onto the resin at pH ~ 1.7 in contact time of 60 min. Elution of the loaded resin was achieved using diluted H_2SO_4 in five consecutive contacts of 10 min each. From the purified solution of In, salt or metal could be produced by evaporation/electrowinning method. The complete process flowsheet is presented in Fig. 7.

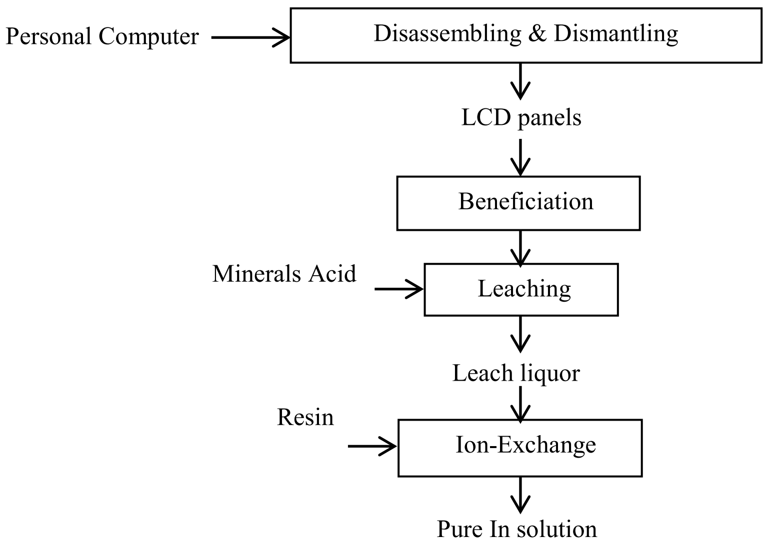

Fig. 7 Process flowsheet for the recovery of In from scrap LCD panels of personal computers [17]

Recovery of Metals from Magnets and Tube Lights

E-waste can serve to be a potential source for REMs along with other valuable metals. About 25–30 wt% of Nd is found to be present in permanent magnets of computer hard disk whereas significant amount of Eu and Y is present in the phosphor powder of tube lights. Hydrometallurgical process has been developed by Kumari et al. [18] for the recycling of scrap magnets to extract Nd, the rare earth metal. Initially, the Nd–Fe–B magnets were demagnetized, crushed, and charged to a chemical leaching reactor. About ~99.99% Nd was leached along with Fe using 1.0 M H_2SO_4 at room temperature in a reaction time of 90 min and 50 g/L pulp density. The leach liquor obtained was subjected to acid extraction using organic extractant TEHA diluted in kerosene for 10 min and O/A ratio 2:1. Precipitation of Nd was carried out from the acid-free leach at pH 1.65 using ammonia solution. The Fe present in the solution was also recovered at pH above 3 [18]. Another flowsheet has also been worked out for the selective separation of Europium (Eu) and Yttrium (Y) from phosphor powder of obsolete tubelights leaving other REMs and impurities in the residue. Phosphor powder obtained from the scrap tubelights was analyzed and found to contain five REMs (2–8% La, 2–10% Ce, 0.5–5% Tb, 0.5–5% Eu, and 10–30% Y) with other metals like Calcium, Aluminum, etc. Depending on the composition of phosphor powder leaching was carried out using suitable lixiviant followed by recovery of REMs from the leach liquor using solvent extraction technique [19].

Conclusion

Varieties of E-wastes are the potential alternative resources to recover rare, rare earth, precious and valuable non-ferrous metals by using the developed hydrometallurgical processes flowsheets, which will conserve the natural resources, save the energy as well as make the environment cleaner and pollution free. Most of these resources can be treated by such approaches while designing treatment steps appropriately to achieve the optimum results with respect to process efficiency with high metal recovery, products in desired forms, and purity.

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