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Business opportunities to reclaim metals by urban mining

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Abstract : In the modern world, changing requirement of advanced and latest features electronic devices in each sectors have created the generations of huge amount of e-wastes. On the other side, depletion of limited metal reserves, illegal recycling and business opportunity by organized sectors compelled the researchers to develop environmental and feasible processes for the recycling of these e-wastes to reclaim different non-ferrous (Cu, Ni, Al, Pb and Sn), precious (Au, Ag, Pt and Pd), rare (Li, Co, In) and rare earth metals (Nd, Ce, La, Y and Eu). Since, last 15 years CSIR-NML, Jamshedpur, India has been actively involved for the development of process Know-how to recycle waste electrical and electronic equipments (WEEEs) to recover metals and materials. At first, the WEEEs were classified, dismantled and pre-treated to isolate plastics, ceramics, rubber, epoxy, iron casing and metallic fractions. Further, the metallic concentrate was treated using hydrometallurgical technique i.e. dissolution of metals by aqueous processing, solvent extraction, adsorption, electro-winning for maximum recovery of metallic values. Various flow-sheets developed for the recycling of WEEEs are discussed for the processing and extraction of metallic values, which strictly complies with environmental rules and regulations.

Keywords: *WEEEs, Recycling, Pre-treatment, Hydrometallurgy, Metals*

1. INTRODUCTION :

At the present time, day to day advancement in electronic equipments and replacement of old devices by newer ones has resulted in the generation of huge quantity of e-wastes. Although worldwide the strict rule and regulations related to e-waste recycling are imposed even more than 80% e-waste are recycled in illegal manner and only 20% e-waste are recycled by organized sectors. It results in the loss of precious as well as valuable metals. Improper collection strategy, recycling through unorganized sectors and unavailability of cost-effective environmental technologies for processing WEEEs, seriously affects the environment. Therefore, effective and cheaper technology with less environmental impact is essentially required for the recovery of metals from WEEEs.

Recycling of e-waste in proper manner is the most efficient and imperative solution and it has become a significant economic activity. Various types of waste electronic devices have been recognized as e-waste/WEEEs viz. spent computers, energy storage devices, mobile phones, fluorescent tubes, magnets, etc. These e-wastes essentially contain printed circuit boards (PCBs) which are made up of metals, epoxies, ceramics and plastics. The PCBs of electronic devices contains rare, rare earth, precious, ferrous and non-ferrous metals; whereas Nd (rare earth) is present in the magnets. In addition, valuable metals like Co, Cu, Li, Ni, etc. are present in the spent lithium-ion batteries (LIBs). Recycling of e-wastes requires pre-treatment (physical/pyrolysis/chemical) followed by further processing using hydrometallurgical separation techniques to recover value added products (salts/metals).

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CSIR-NML, Jamshedpur, India is a pioneer research laboratory in the area of technology development for the recycling of e-waste using feasible and scientifically validated hybrid pyro-, chemical and hydrometallurgical processes to recover rare, rare earth, precious metals and non-ferrous metals from varieties of e-wastes fulfilling zero waste concepts incollaborations with national and international laboratories and industries. Present research paper reports various novel, feasible and scientifically validated hybrid pyro-, chemical and hydrometallurgical processes developed to recover rare, rare earth, precious metals and non-ferrous metals from varieties of e-wastes.

2. DISMANTLING, CLASSIFICATION AND PRE-TREATMENT OF E-WASTE

2.1. Dismantling and classification of WEEEs

To begin with, the collected WEEEs are dismantled and classified to separate different components viz. PCBs, hard disks, DVD slots, wires, cables, steel casings, rubbers, plastics, etc. Among all the components, PCBs are essential part of any electronic devices. PCBs are heterogeneous in nature and composed of plastics, epoxy resins, ceramics and metals. Direct leaching of metals from PCBs coated or encapsulated with plastics and ceramic rarely accomplishes effective recovery of metals, therefore, pre-treatment is essentially required prior to hydrometallurgical processing. Different pre-treatment techniques viz. mechanical, chemical, pyrolysis etc. have been used for pre-treatment of PCBs.

2.2. Pre-treatment of WEEEs

WEEEs are heterogeneous in nature composed of ceramics, plastics, enforced resins and metals. Therefore, pre-treatment is essentially required prior to hydrometallurgical extraction of metals. At first, e-wastes are dissembled, depopulated, pre-treated by mechanical/chemical/thermal means to liberate the encapsulated metals (Figure 1). Leaching of untreated e-waste hardly achieves effective dissolution of metals. Therefore, metallic fractions need to be removed from non-metallic parts before hydrometallurgical treatment. Method of mechanical/chemical/thermal pre-treatment processes i.e. crushing/grinding, organic swelling, low temperature thermal treatment (pyrolysis), etc. were used for pre-treatment of WEEEs, which is described below:

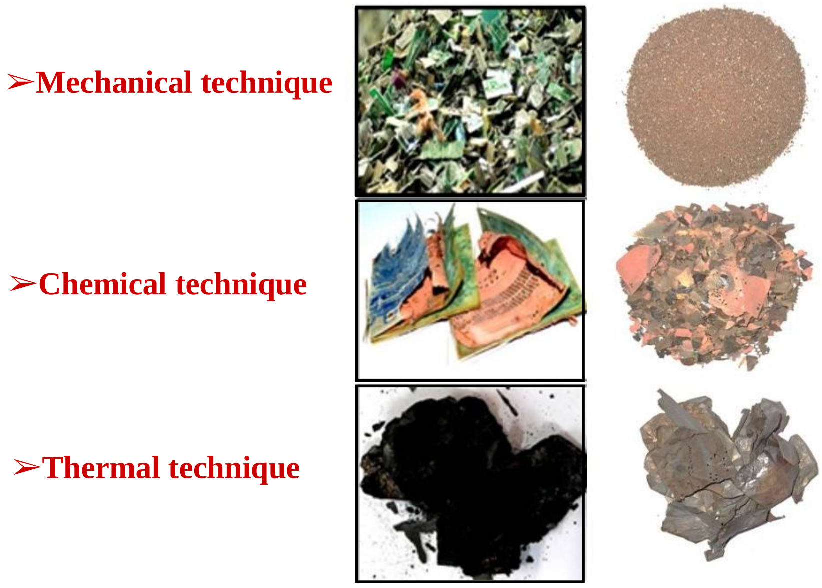

Figure 1. Pre-treatment (mechanical/chemical/thermal) of e-waste to liberate encapsulated metals

2.2.1. Mechanical pre-treatment of WEEEs

The PCBs present in WEEEs are separated and put to various mechanical pre-treatment devices viz. scutter cutter, shredders, mills, pulverizers, etc. to get small fractions, which are further processed using dry/wet gravity separation techniques to separate metallic and non-metallic fractions [1]. Distribution of metallic and non-metallic fractions as well as their liberation size plays important role in the separation of materials.

2.2.2. Chemical pre-treatment of WEEEs

Mechanical pre-treatment of PCBs ineffective due to the lack of viable crushing/milling devices and high energy consumption. To overcome this problem, laboratory scale organic swelling process was carried out to liberate the layer of metals from epoxy resins. PCBs were cut into small pieces and kept in contact with the swelling organic. It was observed that metals were effectively liberated from PCBs of WEEEs at optimized condition [2].The outermost epoxy layer of PCBs containing solder metals was removed and the thin metallic layers encapsulated by resins were removed sequentially. The sheets were dried under very low temperature after washing with hot water to remove the entrapped organic.

2.2.3. Thermal pre-treatment of WEEEs in closed system

Pyrolysis is a process of heat treatment, where the organic materials gets decomposed to low molecular weight products of liquids/gases. The depopulated PCBs were cut into small pieces and pyrolysed in vacuum pyrolysis device, where the evolved gases were collected and condensed as a fuel (low density oil), which can be re-used. The pyrolysed PCBs were beneficiated to separate the metallic content and the burnt epoxies. In order to extract metals from the pyrolysed sample, they are mechanically beneficiated to separate the metallic from the non-metallic fractions [3, 4].

3. HYDROMETALLURGICAL RECOVERY OF METALS FROM WEEEs

3.1. Dissolution of metals from pre-treated WEEEs

Low metallic concentrate obtained from the pyrolysis followed by physical beneficiation technique were utilized for hydrometallurgical extraction of metals. Leaching technique is utilized for the selective dissolution of metal into specific leachants like acidic, alkaline or neutral solution which is mostly dependent on the nature and type of the material, percentage of other impurities present in the material to be leached (Figure 2). Leaching experiments were performed to study dissolution pattern of various material from pyrolysed PCB's with different acids like H_2SO_4, HCl and HNO_3. Specific acid was useful for dissolution of particular metal while not for the other metal even at high temperature and acid concentration (6M). For example, hydrochloric acid was suitable for dissolution of Sn, but not for copper. Nitric acid is suitable leachant for the dissolution of most of the metals like Cu, Fe, Ni in 10 min contact time and Pb in 40 min time but not for Sn. Suitable scrubbing solution was used for the absorption of hazardous NOx gas released during leaching process. Further, this leach liquor was subjected to solvent extraction process at specific pH and organic to get purified metal solution. This purified metal solution was further converted into salt or metal sheet using different hydrometallurgical techniques [5].

Other hydrometallurgical technique for PCB's recycling was also developed in which unique pre-treatment process of organic swelling of PCB's was utilized. It helped to separate outer metal consisting thin layer and then it was subjected to leaching process. Leaching process was standardized for the recovery of copper from organic swelled and liberated metals from PCB's in which sulfuric acid and hydrogen peroxide were used in atmospheric condition. 97.01 % copper was recovered from this leach liquor by using 30g/L of pulp density and 15% (v/v) hydrogen peroxide [2].

3.2. Recovery of metals from leach liquor of metallic concentrate

Leach liquor consist of dissolved metal complex having mixture of hazardous and valuable metals obtained from electronic scarps. Solvent extraction (SX) process was used further to get purified metal solution from the complex mixture consisting metallic concentrate like Cu, Ni, Zn, Cd, etc. Various organic extractants like LIX 84, Cyanex 302, Cyanex 272, Cyanex 923, D2EHPA, etc. were used for the separation of different metals. Isodecanol was used for solvent modification which is helpful in improvement of phase separation. Copper extraction from sulfate medium was standardized by using 5% LIX 84 diluted in kerosene at specific pH. Result indicated that the complete extraction of Cu was achieved in 3 stages maintaining O/A ratio and pH leaving minor concentration like Ni, Zn and Cd in the raffinate. Copper loaded organic was washed with distilled water to remove impurities of entrapped miner then stripped further in 2 stages by using diluted H_2SO_4. Further separation of other minor elements from sulfate solution was done by using different extractants. D2EHPA was found to be efficient extractant as compared to Cyanex 272 and Cyanex 923. Order of extraction found was Zn> Cd> Ni. Result indicated that Zn was extracted above pH 2.5 by using diluted H_2SO_4 at A/O ratio 1/1, contact time of 5 min, while Cd was vigorously extracted using diluted HCl at lower pH maintaining A/O ratio 1/1 [6]. Extraction kinetics indicated extraction of Zn and Cd was attained in 2 min [6].

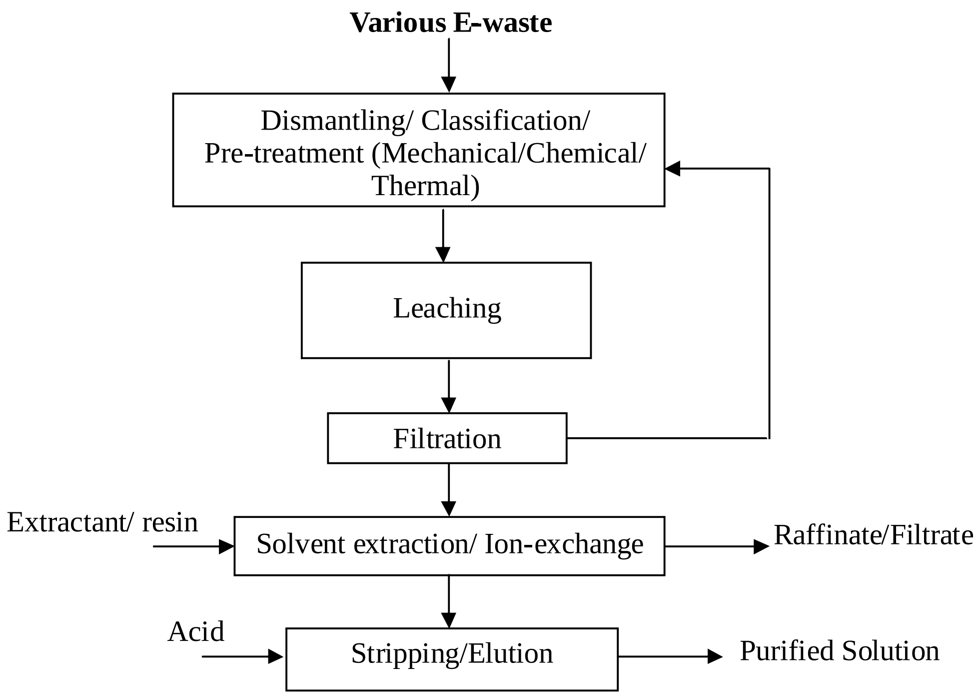

Figure 2. Generalized hydrometallurgical flow-sheet for extraction of metals from e-waste

3.3. Recovery of metals from LIBs

Lithium ion batteries contain rare, rare earth, non-ferrous and valuable metals in majority. These batteries are made up of an anode, a cathode, a separator, and an electrolyte.The black powder present as cathodic material shows presence of Co with Mn, Li, Cu, etc. Due to availability of ample amount of metals, recycling of LIB's is necessary to cope up with metal requirement and government regulations on disposal of these batteries. To overcome this, hydrometallurgical techniques are developed to recycle spent LIBs to recover valuable metals. At start, LIBs were grinded and then physically beneficiated to separate its metallic fractions, plastics and black powder [7].

Black powder obtained from this method was subjected to leaching process to dissolve maximum metals using suitable lixiviant. Obtained leach liquor was further processed through solvent extraction, precipitation technique to get pure metallic content. Mn was separated by maintaining pH 1.5 using sodium hypochlorite with constant stirring for 1h for Mn precipitation. This procedure was repeated three times for complete removal of Mn from the mixture.

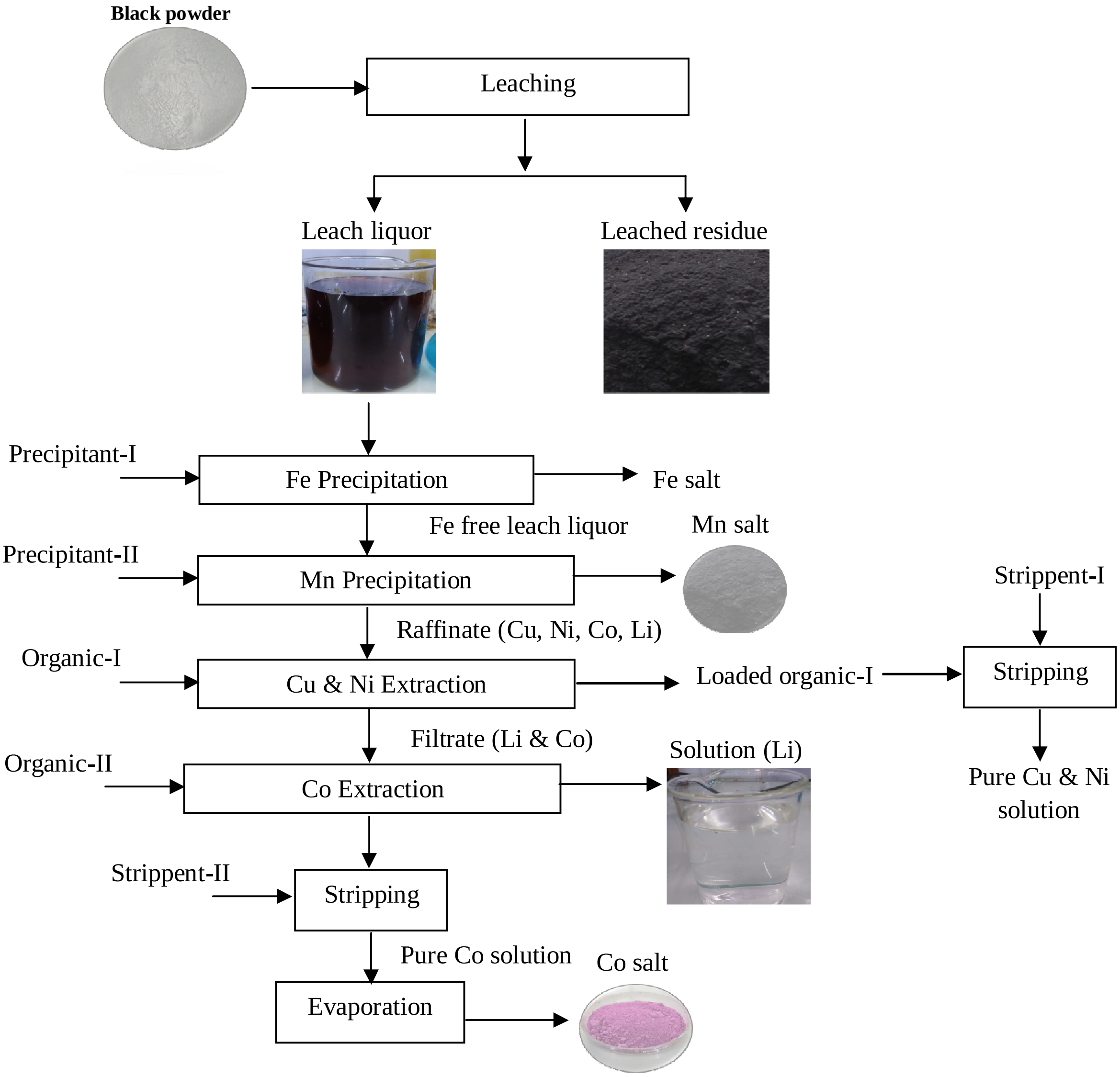

Figure 3. Process flow-sheet to extract metals from the black powder of LIBs

Remaining leach liquor was further mixed with diluted LIX 84IC maintaining O/A ratio 1:1 in 5 min to extract Cu, Ni. Nearly 99% of copper and nickel were extracted in 2 stages at pH 4.5. Further loaded organic was stripped by using 10% H_2SO_4 to get pure metal solution of copper. Remaining copper free leach liquor consist of Co and Li was concentrate first by evaporation technique to increase metal concentration and then subjected to solvent extraction process by using diluted Cyanex 272 maintaining O/A ratio 1:1 in mixing time of 10 min. At pH ~5, 98% of Co was recovered from leach liquor leaving Li in the raffinate in 2 stages. Loaded organic was further stripped using diluted H_2SO_4 for complete removal of Co from the leach liquor. Hence, 99% pure Co solution was obtained by this method. Further purified solution was subjected to evaporation/electro-winning technique to get Co salt/sheet. Raffinate left contained Li was further evaporated to get Li as salt (Figure 3).

3.4. Recovery of precious metals from WEEEs

Precious metals like Au, Ag, Pd and Pt from WEEEs have been separated by using hydrometallurgical techniques through developed process. At start, the e-waste was dismantled and then depopulated to get small mounted components having precious metals. These were classified and separated further depending on the availability of the specific metal in particular component of e-waste. These components were pre-treated and physically beneficiated to get enriched metallic concentrate.

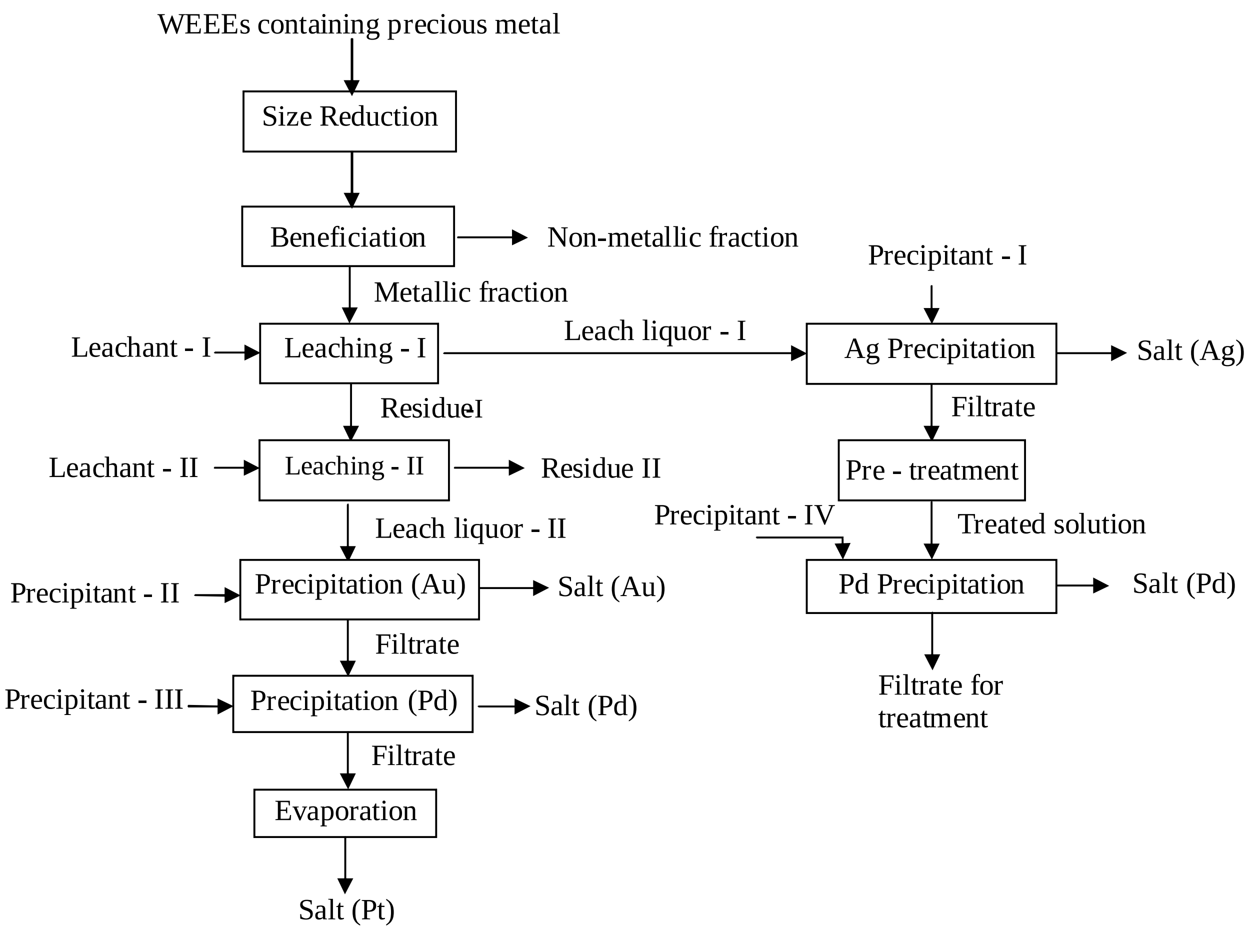

Figure 4. Flow-sheet for extraction of precious metals from WEEEs

These were further subjected to leaching technique for maximum dissolution of precious metals using suitable leachant. Leach liquor was processed further through advanced hydrometallurgical techniques like solvent extraction, ion- exchange, precipitation, etc. to get purified solution of specific precious metal [8]. The pure metallic solution was evaporated or electrowon to get value added products of precious metals. Figure 4 presents the processed flow sheet for precious metal extraction.

3.5. Metals recovery from scrap LCD panels

Indium (In) is a rare element mostly used as indium tin oxide (ITO) in LCD panels [9-11]. 70-80% of In was utilized in LCD panels of different electronic equipments. Due to frequent updation of electronic goods, life span of these equipments have been reduced resulted in the generation of substantial amount of used LCD panels [12]. This rich source of Indium metal has been recovered from LCD panels by developing process flow sheet using hydrometallurgical route. Initially, LCD panels were crushed, pulverized and physically beneficiated to get enriched metal fraction from it.

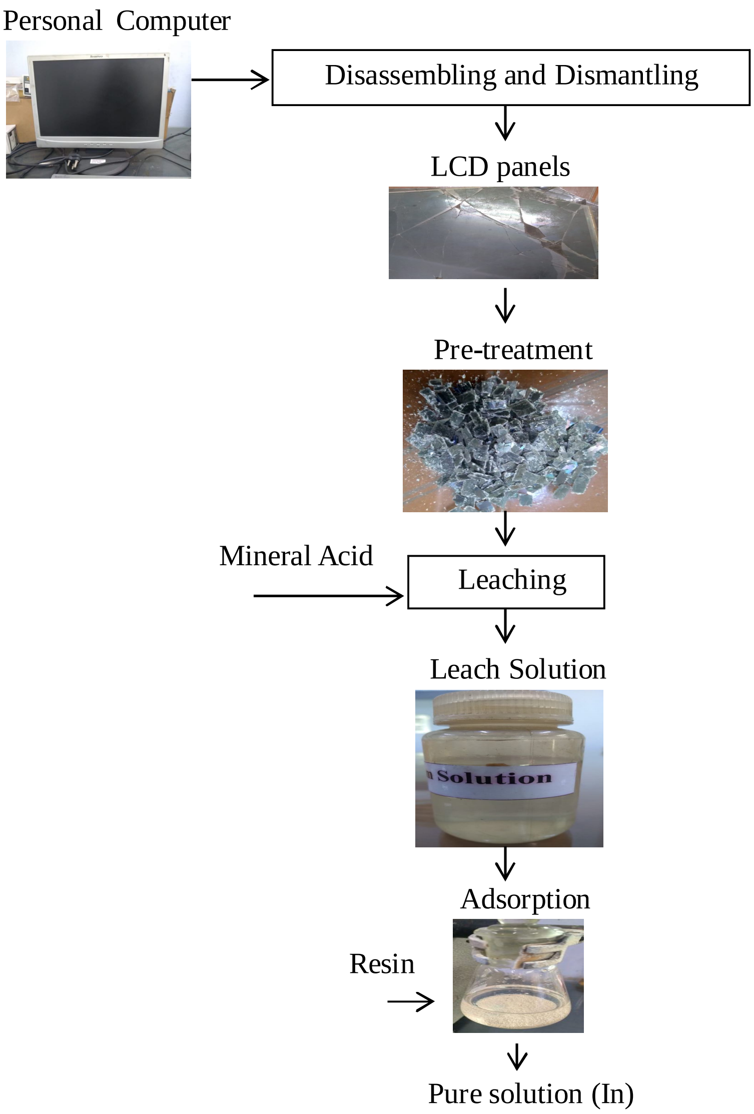

Figure 5. Recovery of In from scrap LCD panels of personal computers

Selective dissolution of In was done by various leaching technique mineral acid using. 1 M of HCl, H_2SO_4 and HNO_3 were used for the extraction of ~94.1%, 93.8%, and 93.2% In, respectively at 60 C with constant stirring for 75 min. This indium containing leach liquor was further processed through the ion-exchange technique for selective In adsorption using Indion BSR resin. Experimental conditions were optimized for 99.2% In adsorption on Indion BSR resin in contact time of 60 min at pH 1.7. This adsorbed Indium was further eluted by using dilute H_2SO_4 in five consecutive contacts. Obtained pure and enriched Indium solution was further processed through evaporation/ electro-winning method to get pure metal salt/ sheet. Complete flow sheet for Indium recovery from LCD panels is presented in Figure 5.

3.6. Recovery of REMs from magnets and tubelights

Electronic waste is also a potential source of rare earth metals (REMs). It is found that 25-30 wt.% of Neodymium is present in magnets of computer hard disk, while Europium (Eu) and Yttrium (Y) are present in phosphor powder of tubelights. Different hydrometallurgical techniques were developed to extract Nd from the scrap magnets from computer hard disks. At start, these Nd-Fe-B magnets were demagnetized and then crushed and charged for the chemical leaching process. Leaching conditions were optimized for ~99.99% Nd dissolution i.e. 50 g/L Pulp density 1 M H_2SO_4. and mixing time 90 min at room temperature. Further, for acid extraction, solvent extraction technique was employed using diluted TEHA (organic extractant) in mixing time of 10 min and O/A ratio 2:1. Precipitation of Nd was carried out from the acid free leach solution at pH 1.65. In addition, Fe present in remaining solution was recovered at pH 3 [13]. One more process has been developed for the selective separation of Eu and Y from the phosphor powder present in the tubelights. Phosphor powder contains several REMs (2-8% La, 2-10% Ce, 0.5-5% Tb, 0.5 -5% Eu and 10-30% Y) with various other metals i.e. Ca, Al, etc. Depending on the composition of phosphor powder, suitable hydrometallurgical process was developed for the recovery of individual REMs [14].

4. CONCLUSIONS

Based on the above discussion, the following conclusions have been drawn:

- WEEEs/e-wastes are the potential secondary resources of rare, rare earth, precious and valuable non-ferrous metals.
- Pre-treatment (mechanical/chemical/thermal) is necessary requirement before hydrometallurgical processing of e-wastes/WEEEs.
- Developed hydrometallurgical processes flow-sheets for the recovery of metallic values will not only conserve the natural resources and save the energy but also make the environment clean and pollution free.

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