

## Chapter 10

# Hydrometallurgical Recovery of Metals From E-waste

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## 1 Introduction

E-waste recycling comprises collection, preprocessing, and end processing. The metal fractions are refined and recovered in the preprocessing stage using hydrometallurgy, pyrometallurgy, electrometallurgical, and biometallurgical processes, sometimes with a combination of processes (Khaliq et al., 2014; Meskers et al., 2015). Increased usage of electronic equipment as technology has advanced has created complexities for the separation process of constituent materials. Most of these discarded wastes have a significant economic worth. The metallurgical processing of E-waste involves smelting the components using heat, known as pyrometallurgical processing, or dissolving in the appropriate solvent or liquid, known as hydrometallurgical processing, and then further refining the target metal using its chemical properties, either through currents and voltage, i.e., electrolytic cells, or simply through precipitation (Kaya, 2016).

Pyrometallurgical methods are high in energy consumption and costs. Although it is the most extensive method being applied for E-waste management, metal recovery of individual species is limited. However, the enormous amount of slag that is created by pyrometallurgical processes contains several heavy metals that cannot be recovered and hence this is not conducive to the reutilization of resources and sustainability (Cui and Zhang, 2008; Kaya, 2016). These processes include incineration, the use of arc furnaces, high temperature roasting in the presence of a selective gas, and can be used for both metallic and nonmetallic waste (Kaya, 2016; Kaya and Sozeri, 2009). The release of halogenated and chlorinated compounds such as dioxin from burning the nonmetallic parts of the E-waste (Tsydenova and Bengtsson, 2011) has resulted in the search for alternative recovery methods.

Hydrometallurgy is the first step that needs to be investigated for metal recovery: extracting the valuable metals into solutions through leaching in acidic or alkaline medium, and then extracting the targeted metal from the solution using precipitation, absorption, ion exchange, electrowinning, or solvent extraction. These methods are all environmentally-friendly approaches and can be undertaken in controlled and moderate conditions (Birloaga et al., 2014)—all of which is discussed later in the chapter.

### 1.1 WEEE: Materials and Contents

E-waste is made up of a diverse range of materials which makes it difficult to generalize the composition. Nevertheless, it can be categorized into five main components: ferrous metals, non ferrous metals, plastics, glass, plastics and other materials (Ongondo et al., 2011).

### 1.2 Recovery and Recycling Technologies

The recycling process is initiated with three major steps: dismantling, upgrading, and refining. Dismantling involves human labor and is the first crucial step for all types of electronic waste aimed at separating hazardous or valuable constituents. This is mostly done using hammers, screwdrivers, and conveyer beds for disassembling the components into various categories for their recovery. The next step is the shredding of the materials mechanically through crushers and grinders to then go through electrical and magnetic separators to separate the electrical nonmetallic components. Finally, after these physical or mechanical recycling techniques, the hydrometallurgical, pyrometallurgical, electro-metallurgical, biometallurgical processes and/or a combination is employed to the metal items for their further enhancement and recovery.

### 1.3 Hydrometallurgical Processing

Traditionally, the hydrometallurgical process has been implemented for precious metal extraction from mineral ores. These processes have been utilized for the recovery of metals from E-waste using acid or caustic leaching of selective dissolutions of the targeted metals from the solid E-waste. Then the solution with the targeted metal and a few impurities is refined further for concentrating the metal via solvent extraction, adsorption, or ion exchange processes (Cui and Zhang, 2008; Khaliq et al., 2014; Ritcey, 2006). Finally, the metal is fully recovered through electrorefining or through electrochemical reduction reactions to regain the solid metals from the E-waste. Fig. 1 shows how the trace metals found in E-waste can go from percolating in the landfill sites that seeps into the groundwater, to percolating into the appropriate amounts of solution to capture the metal for further recovery via hydrometallurgy.

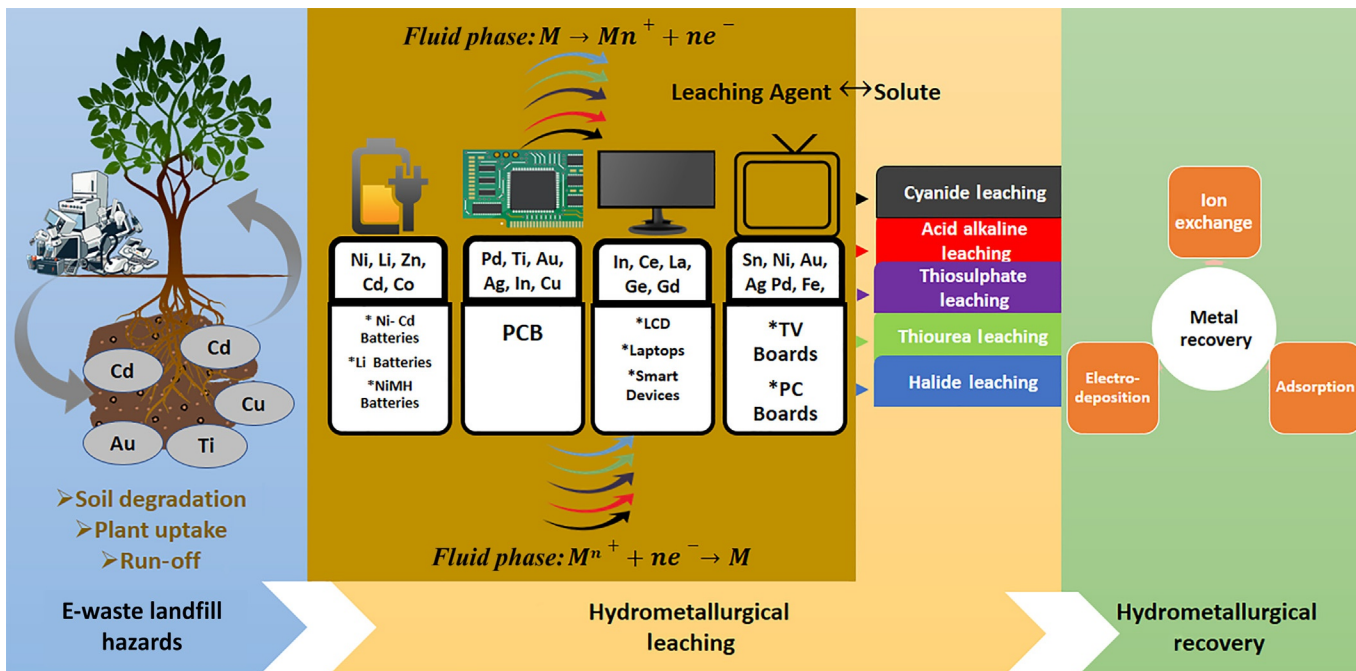


FIG. 1 E-waste from landfills to resource recovery.

In the past decade, hydrometallurgical processing has been considered as an alternative to pyrometallurgy due to the high energy demands the latter requires. It is the most efficient method of recovering metals as it can control the different levels of impurities at their different stages and it is the most environmentally suitable and economically-viable process to use with the chemicals for refinement at different stages (Sadegh Safarzadeh et al., 2007). This chapter opens up different hydrometallurgical routes to recover target metals from the E-waste mentioned above and then goes on to further explain the future state-of-the-art processes.

## 2 Hydrometallurgical Techniques

The targeted metals are made to leach into solutions of desired concentration consisting of mostly acids, i.e., strong sulfuric acid, hydrochloric acid, nitric acids, aqua regia, and a few alkalis. The metal that needs to be recovered from the solution goes through electrorefining, precipitation, cementation, adsorption, solvent extraction, and/or ion exchange (Abdelbasir et al., 2018; Tsydenova and Bengtsson, 2011). This technique is easier to control when it comes to being selective regarding concentrating a certain metal with the correct amount and the correct acid and acid concentration (Ghosh et al., 2015).

### 2.1 Leaching Methods

Chemical leaching is a method involving the reaction of a solid when exposed to a liquid. Leaching is the process of using chemicals and titration techniques of metal complex formations to target the valuable metal using acids, ligands attached to the metals, several leaching agents such as thiosulfate, alkali (Guo et al., 2015), cyanide (Awasthi and Li, 2017; Bas et al., 2015; Raphulu and Scurrell, 2015), and many acids such as hydrochloric acid (Jha et al., 2012; Kim et al., 2011a, 2011b), sulfuric acid (Rocchetti et al., 2013), and nitric acid (Bas et al., 2014; Petter et al., 2014). Metallurgical studies started with the simple recovery of copper or iron from various ores and other sources using hydrochloric acid. This has proven to be promising for the simple recovery of gold (99.2% recovered) with a combination of hydrochloric acid and nitric acid. The process of leaching involves percolation of leaching solutions in a large group of ores and then the concentrated solution containing the target element is enriched in the solution and settled by gravity into the liner, and hence accumulates for further processing and recovery of the metals (Jergensen, 1999; Veit et al., 2015). These are the processes normally employed for extraction of precious elements from ores. Similar procedures are often employed for electronic waste. Leaching parameters are influenced by the mineralogical studies involved—in terms of E-waste these are factors such as particle sizes, the concentrations of the solvents used, temperature, and the contact time between the solid and the liquid (Richardson and Coulson, 2002). Most valuable metals exist as complexes with other metals, which becomes challenging for separation

and extraction. However, chemical leaching has proven to be advantageous compared to pyrometallurgical processes as it does not emit harmful gaseous compounds, nor does it generate particulate matters, and consumes very little energy as it only uses solvents and acids. Additionally, there are much higher recovery rates and it can be very easily undertaken. The principle involves the dissolution of ions and the subsequent exchange with the so-formed “pregnant solutions” in aqueous forms (hence the term “hydro”) and then a resultant ion exchange (“electrometallurgical”) (Veit et al., 2015). The process utilizes chemicals that have been described in detail and brief conditions on the leaching procedure are summarized in Table 1.

**TABLE 1** Leaching of WEEE From Sources and the Recovery Statistics

| Leaching Type        | Conditions Applied to the Normally Found E-wastes With Their Leaching Agents  | Recovery           | References               |
|----------------------|---|--------------------|--------------------------|
| Halogenated leaching | Solid/liquid ratio is 1:10, contact time 4 h, pH 7; 1.1% iodine concentration   | 97.5% Au           | Liang and Manhong (2009) |
|                      | SAHPI leaching (sulfuric acid, hydrogen peroxide and iodine)  | 95.27% Cu          | Yin et al. (2014)        |
|                      | Iron (III)/(II) in acidic sulfate medium at increasing temperatures and increased chloride ferric ratio, increases the leaching rates | 98% Au             | Liu and Nicol (2002)     |
| Thiourea leaching    | Thiourea at 20 g/L, oxidizing agent ferric (III) 6 g/L in 10 g/L sulfuric acid at 600 rpm for 3.5 h                                   | 82% Au             | Zhang et al. (2012)      |
| Thiosulfate leaching | 0.12 M thiosulfate, 0.2 M ammonia and 20 mM copper as oxidizing agent   | 98% Au             | Ha et al. (2010)         |
|                      | Ammonium Thiosulfate 0.2 M, copper sulfate 0.02M, ammonium hydroxide (0.4M) at 40°C, 48 h for Au and 24 h Ag                          | 100% Ag, Au > 95%  | Oh et al. (2003b)        |
| Acidic leaching      | S/L ratio maintained up to 1:50 by volume, 80°C and 3 M HCl and 90 min  | 99.4% Li           | Guo et al. (2016)        |
|                      | 1.25 M ascorbic acid, 70°C, S/L ratio maintained at 25gL <sup>-1</sup> , 20 min   | 94.8% Co, 98.5% Li | Li et al. (2012)         |
|                      | HCl/NaCl with HNO <sub>3</sub> /H <sub>2</sub> O <sub>2</sub> leaching  | 93%–95% Pd         | Quinet et al. (2005)     |

*Continued*

**TABLE 1** Leaching of WEEE From Sources and the Recovery Statistics—cont'd

| Leaching Type      | Conditions Applied to the Normally Found E-wastes With Their Leaching Agents   | Recovery | References                  |
|--------------------|--|----------|-----------------------------|
| Solvent extraction | Countercurrent extraction of Co/Li separation in acidic media. Extractant: 2-ethylhexyl-2-ethylhexyl-phosphonic acid | Co/Ni    | Shtllington and Tait (1991) |
|                    | Basic media removal of silver and gold. Extractant: 1,3-bis(2-ethylehexyl) guanidine                                 | Au, Ag   | Chagnes and Pospiech (2013) |

## 2.2 Cyanide Leaching

Despite the toxicity issues in handling cyanide-based solvents, industrial processes for the recovery of gold from the electronic scraps have shown promising concentrates by using alkaline solutions or alkaline-based metal-cyanide solutions to dissolve the gold at aerated conditions (Bisceglie et al., 2017; Marsden and House, 2009). These cyanide-containing compounds are used in electroplating processes as well. The important factors to be considered for gold leaching using cyanide are the air/oxygen presence, pH, temperature, the cyanide concentration employed, presence of anions/cations in the solid-liquid interface, the stirring rate, and the contact surface. Potassium cyanide (KCN) and 3-nitrobenzene sulfonic acid sodium salts are used primarily for the dissolution of gold on a large scale. When reacted with KCN, a water-soluble dicyanoaurate gold complex is obtained and the reaction proceeds at a very slow pace lasting for days and in the presence of air. Thus, on a large scale, KCN and 3-nitrobenzene sulfonic acid sodium salt is added together to increase the dissolution rate and thereby forming complexes at stoichiometric levels (Bisceglie et al., 2017).

Copper readily dissolves in cyanide solutions. Copper is present in considerable amounts in printed circuit boards. Research has shown that the use of a simple acid sulfate is most successful pathway for copper recovery at the first stage and then cyanide treatment for complex formation in the pregnant solution is the next phase (Kamberovic et al., 2011; Oh et al., 2003b; Quinet et al., 2005).

## 2.3 Acid and Alkaline Leaching

Dissolution of precious metals from solid electronic waste in an alkaline or acidic medium is the foundation for most parts of the hydrometallurgical

processing. Several studies are ongoing investigating the use of nitric acids, sulfuric acids, and hydrochloric acids as the prominent mineral acid for recovering these targeted metals (Madenoglu, 2005; Mecucci and Scott, 2002; Oh et al., 2003a). A few organic acids such as ascorbic acids, citric acids, and sometimes acetic acids are used to remove some of the light metals, especially from spent batteries and mobile devices. In general, printed circuit boards contain an inert chemical coating that does not allow any lixivants to interfere chemically. This is first removed by applying sodium hydroxide (Adhapure et al., 2014; Jadhav and Hocheng, 2015). Cobalt and lithium, found extensively in lithium-ion batteries (LIBs), are removed by this method. Additionally, LIBs may contain traces of nickel and aluminum in their electrode plates (Chagnes and Pospiech, 2013; Guo et al., 2016). Complete recovery of Li was obtained by treatment with citric acids and hydrogen peroxides as reducing agents from spent LIBs, resulting in 90% of cobalt being recovered (Li et al., 2010). Similar studies were conducted to leach out complete Li from spent batteries using hydrochloric acid as the leachant and hydrogen peroxide as a reducing agent (Guo et al., 2016). The increase or decrease in the amount of the reducing agent did not affect the leaching rates, however, in that study it was concluded that with the increase in the concentration of hydrochloric acid and temperature, the leaching efficiency increased up to a point, and then decreased. Additionally, an increase in the contact/leaching time and a decrease in the S/L ratio had a positive effect on the leaching efficiency (as in conditions shown in Table 1) (Guo et al., 2016). For the most part of the acid leaching from electronic waste, hydrogen peroxide is commonly used and is combined with acids to improve the leaching performance.

## 2.4 Thiosulphate Leaching

The use of cyanide-leaching agents for the recovery of precious metals have resulted in environmental concerns. Consequently there was considerable need for an alternative leachant, especially for the recovery of gold and silver that are present mainly in cell phones in considerable amounts, amongst other precious metals (Abbruzzese et al., 1994). A major advantage of using thiosulfate for the recovery of precious metals is less interference with the other cationic species and the solubilizing effect to convert it into recoverable complexes (Abbruzzese et al., 1995). Reagents such as ammonium thiosulfate solution solubilize gold, silver, platinum, and other precious metals in the form of anionic stable complexes for a wide range of pH; the presence of ammonia in the so-formed pregnant solution stabilizes the complex without forming further oxides (gold to gold (I)) (Abbruzzese et al., 1995; Ubaldini et al., 2000). For gold recovery from waste, two types of thiosulfates are being employed: sodium thiosulfate and ammonia thiosulfate. They are mildly stable in alkaline media, nontoxic and noncorrosive, however, its requirements are comparatively higher than the other lixivants as it requires large quantities. As seen from Table 1, the leaching

behavior of the scraps and electronic waste was significantly different when the concentrations of thiosulfate, ammonia, and the oxidizing agents were changed (Ha et al., 2010). In a matter of 2 h, 98% of gold was leached out of the scraps in the environment described.

Thiosulfate requires an oxidizing agent such as copper (II) or iron (III) along with the solid-surface contact and a leaching agent such as ammonia or thiourea. The mechanism explained in Abbruzzese et al. (1995) indicates the complex formed by the reaction of gold with ammoniacal thiosulfate results in a higher solubility and stability, thereby not producing any harm to the environment, unlike the cyanide-forming compounds. They solubilize gold in an anionic (Au) complex that is stable over a range of aqueous environments with different potential values. They consume fewer oxidizing agents as copper ions for the dissolution, oxidation, and complexation to occur. In order to assist the solubility of the ammoniacal solutions formed to obtain the complex, additives are used to stabilize the oxidizing agents, such as ethylenediaminetetraacetic acid (EDTA) (Feng and van Deventer, 2010; Puente-Siller et al., 2013) and monoethanolamine acid (MEA) (Cho et al., 2014; Ko and Lee, 2010; Puente-Siller et al., 2017).

## 2.5 Thiourea Leaching

Thiourea is a complexing agent, a sulfur-based organic agent, that forms a cationic soluble complex with the target metal, unlike other anionic complexes. The leaching rates are up to 99% for this complex. As thiourea is not stable and decomposes easily in alkaline environment, the reaction requires an acidic media. In printed circuit boards, the gold and silver selectively forms a metal- $\text{CS}(\text{NH}_2)_2)_2^+$  complex. Jing-ying et al. (2012) showed a linear increase of leaching rates when the thiourea mass concentration was increased, however, it declined after a certain addition because of the oxidizing presence of ferric ion in the acidic media; which does not happen for complexes without ferric ions as the oxidizing agent. Thus, a threshold mass of thiourea concentrations were studied. The effect of reaction temperature, initial feed concentrations, contact time, and the solid interface influences the leaching rates of the target metal ions from the electronic solid wastes (Veit et al., 2015; Xu and Li, 2011). Thiourea gives quick rates of leaching, less interference of ions, is environmentally friendly, and has a low cost. All of these factors influence more researchers in the field to investigate its use for the recovery of gold and silver from various PCBs and waste cell phones that contain these targeted materials (Jing-ying et al., 2012).

## 2.6 Halide Leaching

The gold obtained from the PCB waste is recovered mostly through the use of chloride, bromide, and iodide. Leaching rates are found to be high on in



halogen-based environments. They have been employed as a replacement for cyanide leaching in most of the hydrometallurgical processes due to the environmental implications that cyanidic compounds possess (Seisko et al., 2018). High solubility, improved redox potentials, and high rates have been achieved from leaching of gold from halide media (Liddicoat and Dreisinger, 2007). Ideal lixivants must be economically viable or least recyclable, selective to the target, compatible, and does not affect the downstream processes; these criteria are met by halogenate leaching agents. Tri-iodide ions act as oxidants for a number of elements such as gold to form the gold-iodide complex from the different sources of waste containing gold, such as PCBs. These tri-iodide ions are formed by providing iodine to iodide with the other conditions applied as summarized in Table 1. Gold is mostly found in its monovalent aurous form ( $\text{Au}^+$ ) or in trivalent auric form ( $\text{Au}^{3+}$ ). The procedure takes place normally in two dissolutions: the anodic reactions take place at the liquid-solid interface which forms unstable intermediate  $\text{AuCl}_2^-$  which further reacts with excess chloride to precipitate out the silver (Diaz et al., 1993; Seisko et al., 2018). In Liu and Nicol (2002), further treatment of the complex formed with ferric chloride lead to  $\text{AuCl}_4^-$  and the ferrous ions formed were regenerated back to ferric ions through appropriate purging of oxygen gas in the dissolution environment.

### 3 Recovery of Metals

The targeted removal of metals from leach solutions is achieved by a variety of methods such as solvent extraction, ion exchange, adsorption, precipitation, and cementation (Cui and Zhang, 2008). Selective recovery is possible for most processes. Developing an optimum flowchart for the separation and purification of metals depends on the composition of the electronic scrap.

#### 3.1 Solvent Extraction

Separation of the constituent target element by contact of a liquid solution with an insoluble liquid, mostly an organic solution, is the process of liquid-liquid extraction or solvent extraction. The transferring of solute from the “pregnant” solution obtained from leaching known as the “raffinate” in to the organic solvent (Theodore and Ricci, 2011) is the mechanism involved in extraction. The principle involved in extraction is the solubility of both the solution and the solute; at some level all of the components are significantly soluble in each other, however, the separation becomes feasible if the solubility is sufficiently different from each other and thus will form a two-phase system (Veit et al., 2015; Wenzel et al., 1980).

Depending on the ions present in the acidic solutions, different extractants are employed such as anionic, cationic, or solvating-type extractants. The anionic type is mostly amides or amines used for the extraction of vanadium, gold, iridium, and sometimes rhodium and tungsten. They already exist in

commercial practices (Jha et al., 2012). Methyl-iso-butyl ketone is used as an extractant for gold, amide extractant for the iridium found in electronic waste through chloride leaching, postleaching, using acid treatments. Diamine extracts platinum and palladium at high levels which has been found to be efficient after the leaching processes (Shtllington and Tait, 1991). Using di-2-ethylhexyl phosphoric acid (DEHPA) as an extractant for recovering zinc and cadmium found in the waste is promising and has been used predominantly. Apart from the anionic and the cationic presence as mentioned earlier, the solution composition, pH, extractant concentration type, and the aqueous-to-organic volume ratio are the other factors involved in the solvent extraction. The major advantage of using extractant processes is high purity and the selectivity of the target element, with large quantities able to be processed at a single time (Chagnes and Pospiech, 2013).

### 3.2 Electrodeposition

Generally, electrodeposition is used to recover base metals from electronic scrap, which precedes the recovery of precious metals. Electrodeposition, when optimized, offers the advantages of high efficiency, less use of auxiliary materials, low environmental impact, and cost-effectiveness (Fogarasi et al., 2014).

Lead, tin, and copper from PCBs can be recovered by leaching followed by electrodeposition. Conventional electrodeposition is not an efficient way of recovering copper and lead. A rotating cylinder electrode reactor (RCER) was therefore used to deposit lead dioxide at the anode and copper at the cathode simultaneously, achieving better recovery efficiencies (Mecucci and Scott, 2002). Electrodeposition as the solitary end process to recover copper from PCBs requires experimental work to determine optimum conditions. For high percentages of copper in PCBs, electrodeposition is a feasible way of recovery, allowing almost 92.8% recovery (Kasper et al., 2011).

Direct and mediated electrochemical oxidation for recovering copper has been developed by Fogarasi et al. These processes dissolve metals from PCBs into leaching solutions and achieve simultaneous cathodic electrodeposition of copper from the leaching solution. Use of the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  redox couple in acid electrolytes allow good copper recoveries along with gold enrichment in the residue (Fogarasi et al., 2014). The deposition of copper at the cathode and the current efficiency are functions of the system flow rate. Further optimization of this process by using ceramic separators and establishing an optimum flow rate gave a 99.953% copper content at the cathode along with gold and silver enrichment in the residue. This system has a low environmental impact, does not require mechanical pretreatment of PCBs, and does not involve the use of harmful reagents (Fogarasi et al., 2015).

Electrodeposition finds applications in recovering metals from copper indium gallium diselenide (CIGS) solar cells. After leaching and solvent extraction, indium is recovered by electrodeposition (Tunsu and Retegan, 2016).

Another method of metal recovery from CIGS is the separation of selenium followed by dissolution with mineral acids. Gallium, indium, and copper can easily be recovered by electrodeposition from this leachate due to the difference in their reduction potentials (Gustafsson et al., 2014).

### 3.3 Ion Exchange

The first hydrometallurgical application of ion exchange resins was for uranium recovery. However, their use became widespread with the development of chelating and impregnated ion exchange resins. Chelating resins use functional groups to form complexes with metals, and thus can be used for selective recovery of the desired ion or complex; impregnated resins are developed by adsorbing solvent extraction reagents onto polymer beads (Tavlarides et al., 1987).

The effectiveness of an ion exchange resin is generally expressed as exchange capacity or equilibrium loading capacity. Other characteristics of resins are their selectivity ratio, matrix geometry and cross-linking, porosity, and functional groups. Some advantages of using ion exchange resins for recovery of metals are their ease of operation, no reagent losses, no disengagement of phases, economic feasibility for use in low concentrations of metal ions and environmental safety (Nikoloski and Ang, 2014; Tavlarides et al., 1987). Ion exchange can successfully be used for selective recovery of metal ions by changing the properties of the resin, specifically its functional groups.

Ion exchange resins have been used to recover a variety of metals from aqueous solutions. The recovery of palladium group metals (PGMs) in hydrochloric acid using ion exchange resins has been extensively studied (Bernardis et al., 2005; Hubicki et al., 2008; Nikoloski and Ang, 2014). In such a system, the speciation of PGMs and the formation of PGM chloro-complexes are important factors determining the removal efficiency.

In aqueous solutions, the cation exchange resin KB-2 and the anion exchange resin AN-108, synthesized with long-chain cross-linking agents (LCAs), were shown to completely remove Mn (II) and Cr (VI) respectively. Using LCAs in the resins was shown to have significantly better results than using divinylbenzene (DVB) and divinylsulfide (DVS), which are widely used for synthesizing resins (Kononova et al., 2013). Table 2 gives the conditions and the recovered precious metals with their functional groups.

Ion exchange resins have found a wide application in recovering gold from cyanide and thiosulfate leach solutions. Recovery of gold from thiosulfate leach pulp, in particular, is viable only by ion exchange resins. Although many resins have been studied for this purpose, adsorption of unwanted complexes on the resins and commercial unfeasibility hampers its utility. Rather than electrostatic interactions, using steric factors for selective gold recovery would be beneficial (Grosse et al., 2003).

Other metals recovered by ion exchange are silver from thiosulfate solutions (Grosse et al., 2003) and metal chloride solutions (Virolainen et al., 2015);

**TABLE 2** Ion Exchange Resins Used to Recover Metals (Tunsu and Retegan, 2016; Virolainen, 2013)

| Type                              | Name                                | Structure/Functional Group | Applications  | References   |
|-----------------------------------|-------------------------------------|----------------------------|---|--|
| Chelating resins                  | Lewatit TP214                       | Thiourea                   | Pd, Hg (II)   | Hubicki and Wołowicz (2009)                              |
|                                   | Purolite S920                       | Isothiourea                | Hg (II), Au, Pt, Pd   |  |
|                                   | Aurix                               | Guanidine                  | Au from cyanide solutions   | Grosse et al. (2003)                                     |
|                                   | Minix/Dow XZ-91419.00/Purolite A194 | Tributylammonium groups    | Au from cyanide solutions   |  |
|                                   | Lewatit TP-260                      | Aminomethylphosphonic acid | Cu/Co, Zn/Co, U, Ti   |  |
|                                   | Chelex 100                          | Iminodiacetate             | Cu, Fe, rare earth elements   |  |
| Strong base anion exchange resins | Amberlite IRA-458                   | Quaternary ammonium        | Ag(I) from thiosulfate liquor   | Grosse et al. (2003)                                     |
|                                   | Amberlite IRA-410                   | Quaternary ammonium        | Au from thiosulfate solutions, recovery of precious metals, water treatment | Tunsu and Retegan (2016) and Zhang and Dreisinger (2004) |
|                                   | Dowex 21K                           | Quaternary ammonium        | Au from thiosulfate solutions   | Zhang and Dreisinger (2002, 2004)                        |
|                                   | Amberjet 4200                       | Quaternary ammonium        | Au from ammoniacal thiosulfate liquors                                      | Grosse et al. (2003)                                     |
|                                   | Amberjet 4400                       | Quaternary ammonium        | Au from cyanide solutions   | Kwak et al. (2010)                                       |
|                                   | Lewatit MP500                       | Type I quaternary amine    | Cu-cyanide complexes from gold ore wastes                                   | Bachiller et al. (2004)                                  |

**TABLE 2** Ion Exchange Resins Used to Recover Metals (Tunsu and Retegan, 2016; Virolainen, 2013)—cont'd

| Type                              | Name             | Structure/Functional Group       | Applications                                     | References   |
|-----------------------------------|------------------|----------------------------------|--|--|
| Weak base anion exchange resins   | Lewatit MP64     | Tertiary and quaternary ammonium | Au from hydrochloric acid solutions              | Alguacil et al. (2005) and Bachiller et al. (2004) |
|                                   | Amberlite IRA 67 | Tertiary amines                  | Water treatment                                  |  |
| Strong acid cation exchange resin | Dowex 50         | Sulfonic acid                    | Water treatment, recovery of rare earth elements |  |
| Weak acid cation exchange resin   | Purolite C-104   | Carboxylic acid                  | Water treatment, transition metals               |  |

copper in cyanide leach solutions (Dai et al., 2010); nickel from ferrous solutions (Abbasi et al., 2018); lead, cadmium, chromium, and zinc (Dąbrowski et al., 2004).

Ion exchange resins find important applications in the separation and recovery of valuable metals as an end process in WEEE. The recovery of palladium, copper, silver, and gold from printed circuit boards in cell phones was investigated by Quinet et al. (2005). Removal efficiencies of these metals using the anionic resins Amberlite IRA400 and Amberlite IRA68 showed excellent recovery yields for palladium (99.05%) and gold (97.25%). In the case of gold, however, the recovery yields were offset by the poor elution yields (27.33%).

For selectively recovering gold from cell phone PCBs, ion exchange is incorporated into the process flow after two-stage leaching by electro-generated  $\text{Cl}_2$ . The resins used were Amberlite XAD-7HP, Bonlite BA304, and Purolite A-500, with the former being a nonionic resin and the latter two being strong-base resins. All three resins showed almost equal removal efficiencies for copper (95%–97.70%) but low selectivity for gold (7%–8%). Therefore, after concentrating the gold with second-stage leaching, ion exchange with Amberlite XAD-7HP gave 95% recovery of gold. Copper and gold were eluted separately, copper with 0.1 mol/L HCl and gold with 1.0 mol/L HCl in acetone (Kim et al., 2011a, b).

Indium from LCD panels can be recovered by chelating resins with imino-diacetic acid, or impregnated resins selective to indium. Lanthanum, gadolinium, and germanium, used in magnetic refrigeration, are also metals that can be removed by ion exchange resins (Tunsu and Retegan, 2016).

### 3.4 Adsorption

Adsorption of single-component metal systems is commonly characterized by the Freundlich and Langmuir isotherms. Multicomponent isotherms used for modeling adsorption are: (1) the empirical equation proposed by Fritz and Schluender to calculate adsorption equilibria of organic solutes in aqueous solutions; (2) a Freundlich-type multicomponent isotherm; and (3) the ideal adsorbed solution (IAS) theory (Cui and Zhang, 2008; van Deventer, 1986; Sheindorf et al., 1981).

Adsorption of metals on activated carbon for recovery from a variety of streams is being actively studied. Perhaps the most studied adsorption mechanisms are of gold complexes with activated carbon. The adsorption of gold on activated carbon from cyanide solutions using either carbon-in-pulp (CIP) or carbon-in-leach (CIL) technologies are being widely used commercially due to its efficiency and cost-effectiveness (Cui and Zhang, 2008). Adsorption of gold-thiourea complex ( $\text{Au}(\text{tu})_2^+$ ) on activated carbon has also been extensively studied. For thiourea leach systems, copper ions are observed to have a notably detrimental effect on equilibrium gold loading due to competition for adsorption sites (Zhang et al., 2004). Aurothiosulfate complexes have demonstrated low adsorption on activated carbon (Grosse et al., 2003).

Adsorption is used in the process flowchart of metal recovery from PCBs by Quinet et al. The effectiveness of activated carbon to recover Pt, Au, Ag, and Cu from the chloride leach solution described earlier did not show favorable results; palladium, silver, gold, and copper yields were 74.39%, 46.43%, >60%, and 18.18% respectively. However, in this same study, the activated carbon process was shown to be highly effective for recovering these metals from a cyanide leach solution. At a concentration of 8.3 g/L activated carbon, 99% gold, 95% silver, and 100% palladium were recovered.

A sustainable way of recycling waste PCBs is the transformation of the non-metallic fraction (NMF) into an adsorbent. This chemically activated NMF-adsorbent had a higher adsorption capacity for metals such as Cu, Co, Pb, and Ni than commercial resins. Its efficiency was constant in both single and multicomponent systems. Such an adsorbent/ion exchange resin is a promising development, not only for metal recovery, but also for tackling the large portion of nonmetallic waste (Hadi et al., 2015).

Adsorption by biosorbents: Tannin has been extensively studied as a biosorbent for precious metals. This remarkable affinity for precious metals, ease of recovering adsorbed metals, cost-effectiveness and environmental sustainability make it an attractive option for recovering Au, Ag, Pd, and Pt from electronic waste.

A study focused on an optimized and sustainable way to recovery of gold and silver from PCBs of cell phones used crosslinked persimmon tannin gel (CPT) for adsorption of gold-thiourea and silver-thiourea complexes. Along with there being an almost quantitative recovery of both metals, the cationic gold and silver complexes were reduced to their elemental forms. For gold, this reduction is postulated to be due to the reaction with the phenolic functional groups of the CPT. A comparison of activated carbon and CPT showed similar recovery rates for gold, but a higher recovery rate of silver for CPT (Gurung et al., 2013b).

Recovery of gold and palladium from PCBs using an ethylenediamine-modified persimmon tannin resin (EPPFR) showed favorable recoveries for both metals. The adsorption mechanism onto this resin was hypothesized to be reduction for gold and chelation for palladium (Yi et al., 2016). Tetraethylenepentamine-modified persimmon tannin gel (TEPA-PT) and *N*-aminoguanidine-modified persimmon tannin (AG-PT) had some of the highest maximum adsorption capacities for Au(III) among all adsorbents at 5.93 mol kg<sup>-1</sup> and 8.90 mol kg<sup>-1</sup> respectively (Gurung et al., 2013a, c). In general, the superior adsorption of gold onto tannin has been postulated by the authors to be related to the capacity of tannin to reduce gold to an elemental form (Gurung et al., 2013a)

Various other studies detail the mechanism and kinetics of Au, Ag, Pd, and Pt adsorption on tannin or tannin-modified adsorbents (Ogata and Nakano, 2005; Wang et al., 2017; Yurtsever and Şengil, 2009). Other biosorbents used for precious metal recovery are chitosan derivatives, algae, fungi, and bacteria (Das, 2010).

#### 4 Proposed Flow for the Recovery of Metals From E-waste

See Fig. 2.

#### 5 Concluding Remarks

E-waste is a treasure of high economic worth. Hence, proper recovery should be initiated for resource utilization that does not affect the environment nor cause any adverse health effects. Hydrometallurgy is a promising process for the recovery of metals from WEEE ranging across all concentrations. The complete route as shown in Fig. 2 that goes through a leaching step followed by solvent extraction, ion exchange, adsorption, and then electrodeposition. Combinations of these processes are often followed in practical applications. For the most part, the leaching and solvent extractions utilize high amounts of solvents where the process controls must be taken into account while ensuring the correct concentrations and the solid-to-liquid ratios. Electrochemical routes have proven much more effective than chemical leaching as it does not produce unwanted byproducts. Biotechnology

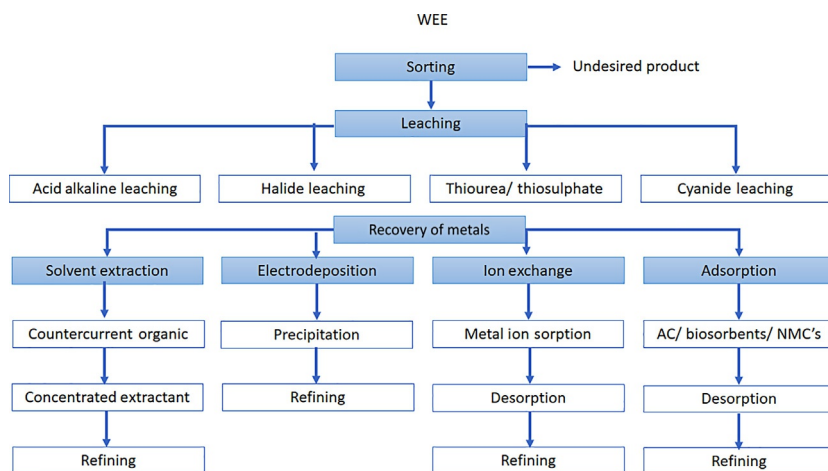


FIG. 2 Brief block flow for hydrometallurgical recovery of E-waste.

has given rise more promising outcomes for resource recovery. Biosorption of precious metals from aqueous environments has received a great deal of attention because of its low operating costs, minimal usage of chemicals, and detoxifying sludge that is easily to handle (Cui and Forsberg, 2003). Hence, further research should be conducted on how to make use of this biomass for a high uptake of precious metals from electronic wastes. There have also been studies with the use of polymer-polymeric chains of aniline as a candidate for acid leaching of precious metals. Wu et al. (2017) studied the various inter-conversion between the oxidative and the protonated states of polyaniline (PANi) coupled with metal reduction to its pure elemental state both sustainably and at controlled levels. These chemicals coupled with leaching gives options for the use of hydrometallurgy.

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## Further Reading

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