

# Urban mining of E-waste: treasure hunting for precious nanometals

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## 2.1 Introduction

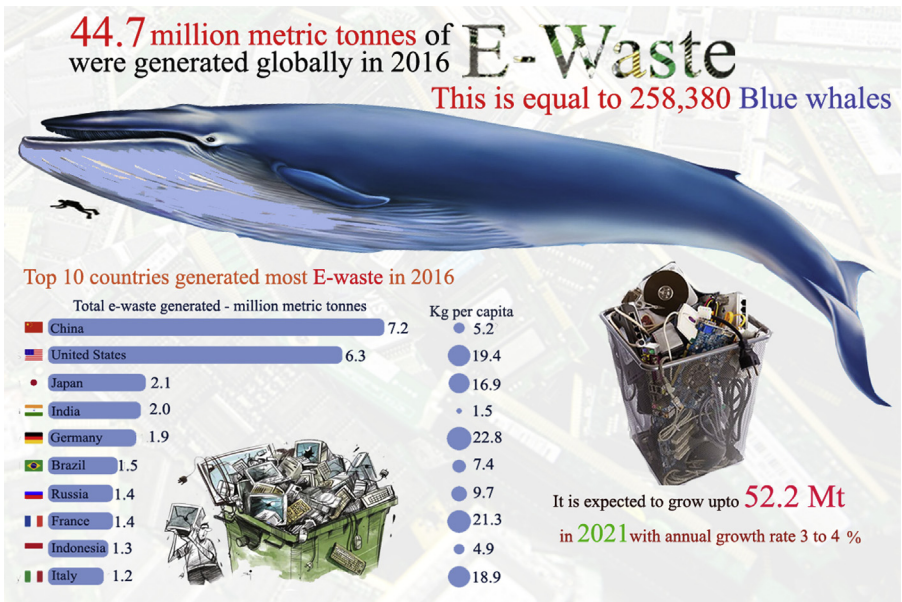
With the technological advancement, many types of electrical and electronic equipment (EEE) products are now in the market and due to traditional linear economic system (make-use-dispose) waste EEE has already become a massive issue in the world. Because of the complexity and rapid advancement of technology, it is difficult to group them into sensible and practically useful categories. Electronic waste, or E-waste, is a generic term which refers to the waste generated from all EEE and their parts without the intent of reuse. Moreover, E-waste is also referred to as WEEE—waste electrical and electronic equipment. E-waste includes a wide range of products—almost any household or business item with circuitry or electrical components with power or battery supply (Baldé et al., 2017). Six categories have been listed to be considered as WEEE, and those categories are (1) temperature exchange equipment; (2) screens and monitors; (3) lamps; (4) large equipment; (5) small equipment; and (6) small IT and telecommunication equipment (Perkins et al., 2014). Further descriptions for the categories are as follows.

1. *Temperature exchange equipment*: Those are in general referred to as cooling and freezing equipment such as refrigerators, freezers, air conditioners, and heat pumps.
2. *Screens and monitors*: Those include televisions, monitors, laptops, notebooks, and tablets.
3. *Lamps*: Fluorescent lamps, tungsten bulbs, compact fluorescent lamps, high-intensity discharge lamps, and LED lamps.
4. *Large equipment*: Commonly referred to washing machines, clothes dryers, dish-washing machines, electric stoves, large printing machines, copying equipment, and photovoltaic panels.
5. *Small equipment*: Those equipment include vacuum cleaners, microwaves, ventilation equipment, toasters, electric kettles, electric shavers, scales, calculators, radio sets, video cameras, electrical and electronic toys, small electrical and electronic tools, small medical devices, and small monitoring and control instruments.
6. *Small IT and telecommunication equipment*: Mobile phones, global positioning systems (GPS), pocket calculators, routers, personal computers, printers, telephones, and e-book reader.

It has been observed that WEEE disposal has been doubled between 2009 and 2014 to 41.8 million tons per year globally, and in 2016, it reached 44.7 million tons per year (Fig. 2.1). Projections have been made and reported that the total amount of WEEE disposal per year could exceed 50 million tons by 2021 (Hsu et al., 2019). The projected data shows that by 2030, the obsolete computer waste will reach 1000 million tons (Tiwary et al., 2017). Fig. 2.1 further illustrates that the global annual E-waste generation per inhabitant had been 6.1 kg, whereas it has been projected to be 6.8 kg in 2021. However, the estimates report that only 8.9 million tons of E-waste is collected and recycled, which resembles 20% of all the annual E-waste generated (Baldé et al., 2017).

### 2.1.1 Driving factors for E-waste

The global information society is growing at a pronounced speed due to the advancement in technology. Availability of Internet, mobile networks, new applications, and services supplied at increasingly high speeds and techniques for handling big data have provided new opportunities to the public for health, education, government, entertainment, and commerce. At the same time, a throw-away society characterized by the consumerism, high income, urbanization, and industrialization are some of the factors for experiencing leading to growing amounts of EEEs, and consequently E-waste. Simultaneously, technologies that became obsolete because the technology is old and replaced by new technology drive the production of E-waste. As an example, the most significant declines in sales were found for



**Figure 2.1** Schematic diagram representing global E-waste production.

portable audio, portable video, the bulky cathode ray tube (CRT) monitors and televisions with the advancement of technology. Furthermore, devices with single functionality are being replaced by items with multiple functionalities is another driving force for E-waste generation. Multiple device ownership, the tendency to electrify nonelectrical equipment such as wristwatches with shorter replacement cycles, growth in cloud computing services, a rising number of data centers, and unavailability of universal power adapters promote E-waste generation.

Most recent assessments reported that the amount of E-waste generated from Asia was 18.2 million tons and reached as the largest, followed by Europe (12.3 million tons), the Americas (11.3 million tons), Africa (2.2 million tons), and Oceania (0.7 million tons). Although Oceania generated the smallest amount, the E-waste generation density is 17.3 kg/inh. Based on the E-waste generation per inhabitant, Europe is the second largest with an average of 16.6 kg/inh whereas Americas generate 11.6 kg/inh. The E-waste collection in Europe has been the highest of 35% where the Americas collect only 17% and 15% in Asia. An alarming situation is noted from India where the generation of E-waste was around 470,000 million tons as on 2011, out of which the annual generation from each big cities, Mumbai generates around 11,000 million tons, Delhi 9000 million tons, Bengaluru 8000 million tons, and Chennai 5000–6000 million tons (Vidyadhar, 2016).

Nanotechnology has become an exciting route to chemical innovation basically in every field as diverse as medicine, water treatment, and energy storage to improve technologies related to human health, communications, and transportation. It is well known that WEEE is a complex mixture of metals, plastics, glass components, and more. Among the mixture, precious metals such as gold, silver, and palladium, in E-waste continues to drive recycling although they are not trivial to recover in an economic sense. Therefore recovery of high added-value products from the metals, for example, nanoparticles from WEEE has recently become a trending research direction. Few attempts have been made to convert WEEE to nanodust, nanoparticles, and extract nanometal elements for other benefits using different resource recovery techniques. Nanoscale materials in electronics are able to transform, release heavy metals, and potentially toxic elements (PTEs).

Consequently, E-waste could be an unintended exposure source to PTEs which may pose a significant risk to human health and the environment. Hence, extracting nanomaterials from E-waste can be considered as a dual benefit in terms of the economy and ecological and human health risk. This chapter summarizes the resource recovery techniques and pathways of nanoparticles extraction from E-waste.

### ***2.1.2 Raw materials in electrical and electronic equipment and their waste***

E-waste is a combination of heterogeneous materials, where the mass fraction is bulk metals (aluminum, copper, and ferrous), plastics, and glass. Each EEE contains as many as 60 elements, for example, the thin, conductive layer of indium tin oxide

on a screen to the lithium in the batteries of a smartphone; many precious metals are used. Furthermore, trace amounts of economically important critical materials such as rare earth metals, indium, and platinum group metals are present in high concentrations in WEEE than their respective ores indicate the potential of WEEE as a secondary resource (Li et al., 2007). Microelectrical components of EEE's wiring mainly comprise copper, gold, and silver, while tantalum is used in microcapacitors. In microphones, speakers, and vibration units, neodymium–iron–boron magnets are commonly used. Some of the precious metals used in EEEs are hard to replace with substitution, and the best example is Tantalum metal used in phones (Davies, 2017). Manufacturing of EEE consumes considerable fractions of the gold (Au), silver (Ag), and palladium (Pd) mined annually worldwide for phones and computers (Hadi et al., 2015). The third largest consumer of Au is the electronic industry. It has been estimated that more than one million people in 26 countries across Africa, Asia, and South America work in Au mining mostly in illegal conditions due to its demand for EEEs (Işıldar et al., 2018).

It has been estimated that the total value of all raw materials present in E-waste is approximately 55 Billion Euros in 2016 (Baldé et al., 2017). Linear economic practices will lead the raw materials in E-waste to end up in landfills and contaminate the environment as there is no closing loop of material flow. The rate at which EEE is discarded and replaced will contribute to global resource depletion due to high resource consumption (Li et al., 2015). Table 2.1 reports the precious metals that are being used as raw materials in different EEEs and E-waste streams, which will gain future attention as secondary raw materials.

Among the major metals present in E-waste, the iron amount exist is considered has no real economic value. However, E-waste contains around 20% copper and the main metallic constituent (Ilankoon et al., 2018). It is evident that the chemical composition of WEEE varies with its type, age, origin, and manufacturer, however,

**Table 2.1** Precious metals in various EEEs and their waste streams.

Electrical and electronic equipment	Precious metals
Photovoltaic panels Liquid crystal displays (LCDs), Cathode ray tubes (CRTs) and light emitting diode (LED)	Cadmium, tellurium, indium, and gallium Indium, gallium, and germanium
Printed circuit boards (PCBs)	Gold, silver and platinum, copper, aluminum, iron, antimony, arsenic, mercury, and lead
Notebooks and tablets Hard drives	Gold, silver, palladium, and copper Neodymium (Nd), praseodymium (Pr), dysprosium (Dy), aluminum, iron, copper, tin, nickel, silver, gold, and palladium
Cell phones and smartphones	Copper, silver, gold, palladium, lithium, aluminum, cobalt, lead, nickel, and zinc

estimates denote the gold content in E-waste is in the range 80–250 g/tons in general (Cui and Zhang, 2008). Both gold and copper seem to be present in WEEE at higher concentrations than their respective ores. The quantity of precious metals in WEEE is crucial to the economics of recycling and recovery processes. It is known that as much as 75% of the intrinsic value of E-waste is in the gold, copper, and palladium content (Cucchiella et al., 2015); for example, recycling and recovery of one million mobile phones would generate 24 kg of gold, 250 kg of silver, 9 kg of palladium, and 9000 kg of copper as per the Electronics Take Back Coalition, 2014. Moreover, it has been estimated that the entire global gold quantity of WEEE inventory as 300 tons in 2014, which is valued at 10.4 billion euros (Bigum et al., 2017).

### **2.1.3 E-waste resource recovery**

Different driving forces act upon the resource recovery through recycling of WEEE; major is the value of the precious metals, whereas environmental pollution has also been a reason. Up until recent times, the E-waste recycling was done primarily to separate and recover individual precious metals, predominantly copper and gold due to their high grade and economic value. Feasibility and cost-effectiveness of the recovery processes were given the priority for the extraction of other metals. Visibly, the nonmetallic is considered as the most significant proportion of E-waste compared to metallic fraction, were in general treated by incineration or landfilling. E-waste contains potentially toxic metals, such as lead, mercury, and cadmium, hazardous chemicals, such as flame retardants, PAHs (polycyclic aromatic hydrocarbons), and plastics (Lecler et al., 2018). As an example, the CRT screen in old television used to contain 2–3 kg of lead (Cui and Forsberg, 2011). Whereas the flat screens contain less lead, which is no more than 1 kg (Bigum et al., 2017). End of the life of CRT screens, large Pb concentrations are observed entering the waste inventory. Therefore resource recovery may play a significant role in recycling the precious metals rather their contribution to environmental pollution.

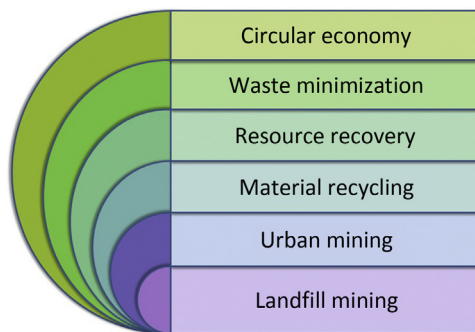
Different metals in WEEE can be clustered into five major categories: precious metals (Au and Ag); platinum group metals (Pd, Pt, Rh, Ir, and Ru); base metals (Cu, Al, Ni, Sn, Zn, and Fe); metals of concern (Hg, Be, In, Pb, Cd, As, and Sb); and scarce elements (Te, Ga, Se, Ta, and Ge) (Tefaye et al., 2017). Resource recovery is based on the extraction of precious metals, platinum group metals, and base metals from E-waste. Printed circuit boards (PCBs) have received the attention of the recyclers as the most treasurable part in E-waste streams. PCBs are found in all EEEs such as TVs, computers, and mobile phones. Precious metals can be found in the components such as PCBs, connectors as well as in the solders; for example, PCB from an LCD TV contains 575 mg of Ag, 138 mg of Au, and 44 mg of Pd (Tefaye et al., 2017). It has been reported that the precious metals in PCB are worth more than 80% of the total intrinsic value, although their composition is <1 wt.% in E-waste (Park and Fray, 2009).

Several different technical and nontechnical tools have been applied to recover resources from WEEE in a sustainable manner (Ravi Naidu, 2013). WEEE is rich in a complex mixture of metals, alloys, and polymetallic compounds and hence is considered as a better source than primary ores (Ongondo et al., 2015). Resource recovery encounters sustainable use of the natural resources by breaking the closed loop of traditional linear use of resources to a cyclical utilization that allows maximum recovery of resources from waste (Cossu, 2013). Advancement of technology relies on a great number of elements, and therefore the complexity of WEEE increased. As modern devices consist of up to 60 elements in various mixtures of metals, the resource recovery becomes difficult since complex alloys pose a challenge for efficient metal recovery technologies (Bloodworth, 2014).

## 2.2 Urban mining E-waste for metals

Urban mining is a concept linked to resource efficiency which extends landfill mining to the process of resource recovery from anthroposphere that represents a significant source of resources, with concentrations of elements often comparable to or exceeding natural stocks (Cossu and Williams, 2015). About the critical raw materials, WEEE is considered as the backbone stream in urban mining. Urban mining activities involve systematic management of anthropogenic resource stocks and waste in order to protect the environment, conserve resources, and derive economic benefits (Baccini and Brunner, 2012). Although urban mining is a pleasing concept from an environmental perspective, it is still in the kindergarten level from the resource recovery perspective as a lot of valuable materials are ending up in a landfill. Therefore resource recovery in urban mines requires a paradigm shift (Baccini and Brunner, 2012).

Urban mining is a collection of processes. The first phase in the urban mining chain is the collection and consolidation of E-waste (Fig. 2.2). Efficient E-waste collection is lacking in many countries where it requires a high awareness level of



**Figure 2.2** Schematic diagram for urban mining in an ideal circular economy model which leads to sustainable production and consumption.

consumers as well as collectors. Usually, the collection happens in different scenarios: stationary and mobile methods. Cost minimization has been the primary concern in the E-waste collection (Nowakowski, 2017). Source separation is a must, which will benefit in many ways in order to reduce labor involvement and time. The fixed collection points can easily be established in places where municipal waste is being collected, service shops, and community centers.

Ensure consumer participation may lead to achieving good collection rates of E-waste. Awareness plays a major role to improve WEEE collections and recycling. Economic incentives such as providing free collection services, including transportation of EEE to collection or recycling centers may improve the WEEE collection. It has been observed that only 9% of respondents claimed to have delivered their used mobile phones to a proper recycling system in 2011 (Nowakowski, 2017). Though, in general, a large proportion of mobile phones in the developing countries specifically are stored by the consumers over more extended periods. Also, since it is easy for the small-sized devices to be thrown away with the municipal solid waste plays a role in the improper disposal and end up in landfills or dump sites.

With the objective of the highest recovery of precious metals, E-waste recycling includes three stages: pretreatment, size reduction, and separation including comminution and separation of materials using mechanical/physical processing, and metallurgical/chemical refining/purification through pyro/hydro/electro/biohydro metallurgical processes (Hsu et al., 2019; Kaya, 2016; Lu and Xu, 2016).

## **2.2.1 Physical techniques**

Physical separation techniques are conducted to separate metallic and nonmetallic fraction without any loss of valuable metals. The physical properties such as size and shape of WEEE influence the efficiency of physical recycling. Three different physical separation techniques are being practiced: density separation or particle shape-based separation, electrostatic separation mostly eddy current separation, and magnetic separation (Hsu et al., 2019). Process of physical recycling is well demonstrated by Kaya (Kaya, 2016). When the collected WEEE reaches the recycling facility, it may undergo various processes before actual recycling to take place. During the pretreatment operation, size reduction and separation are conducted. The WEEE is ended up with physical separation techniques for further processing through recycling techniques (Hsu et al., 2019).

### **2.2.1.1 Dismantling**

Dismantling or disassembly is mainly conducted to remove hazardous components in order to minimize the toxic materials into the recycling stream and to separate reusable parts (Lu and Xu, 2016). Dismantling can also be performed manually or mechanically where mechanical disassembly further classified semiautomatic or automatic dismantling. Desoldering is done via heating the solder above the melting point and separate reusable items for reselling. Removal of components, parts and/or a group of parts attached through fastening by screws, clinks, and rivets,

inserting, welding, binding, wrapping, coating, and plating in a systematic manner from E-waste is called as dismantling. Disassembly is a manual or mechanical process based on the economy of the country and not energy intensive. Two basic forms of dismantling are selective and simultaneous disassembly. In selective dismantling, look and pick specific components and removed. Simultaneous dismantling is an efficient process; however, there is a risk for the components to be damaged and, also requires an additional sorting that increases the time and cost. In simultaneous disassembly, desoldering is done by heating the whole unit in a tin furnace. Geometrical and physical criterions are used in identifying and sorting which is called as “evacuate and sort.”

### *2.2.1.2 Crushing, shredding, and milling*

After physical dismantling, the remaining WEEE undergoes crushing, shredding, and grinding to pulverize the waste to powder. Shredding/crushing is conducted to strip metals from WEEE (Tesfaye et al., 2017). Further reduction of the dimensions of WEEE is made through shredding. Double shaft shredder is widely used E-waste recycling (Tesfaye et al., 2017). After shredding, crushing/pulverizing is done with dust collection systems. Subsequently, density separation isolates the nonmetals and metals. Crushing consumes energy and useful in selective efficiency. Comminution of WEEE and effective detachment of metals from nonmetals is the prerequisite. Low-speed high torque shear shredders are considered as the best for the primary crushing (Lu and Xu, 2016). Crushing in two steps has proved efficient shearing actions which generated by the rotor, stator cutters, and crude crusher and afterward further crushing in a hammer grinder are explicitly used for printed circuit boards. It has been described that shredding or grinding may lead to a 40% loss of precious metals (Jiang et al., 2012). Crushing can generate hazardous dust due to the strength and tenacity of the WEEE; hence, an efficient dust collection system is a must. Grinding process makes metals to be turned into a spherical shape due to their malleability and ductility, whereas nonmetals (plastics and glass fibers) remain non-spherical in shape, usually as rods or strands, due to stress (Hsu et al., 2019). After crushing process, pulverizing of WEEE is done using ball and disc milling (Ghosh et al., 2015). Various types of mills have been described for the finer comminution where swing hammer types appearing to be the standard.

### *2.2.1.3 Sieving and separation*

Sieving is carried out in the physical recycling process to classify the different sized particles based on the various sizes of sieve apertures to the desired particulate size for separation. Sieving is not only been utilized to prepare a uniformly sized feed but also to upgrade metal contents (Kaya, 2016). The screening is essential as the particle size and shape of metals are different from that of plastics and ceramics. Rotating screen is used mainly for metal recovery in WEEE recycling process.

Based on the variation in shape, density, and electric conductivity of metallic and nonmetallic materials in WEEE electrostatic separation are considered as a



promising way to recover metals from pulverized WPCBs. Recycling industry basically used shape separation by tilted plate and sieves. Copper recovery is promising by an inclined conveyor with a vibrating plate from electric cable waste, printed circuit board scrap, and waste television and personal computers in Japan (Cui and Forssberg, 2003).

Magnetic, electrostatic, and density separation are mechanical separation techniques that have been widely used in urban mining of WEEE. Low-intensity drum separators are the standard method of magnetic separation for the recovery of ferromagnetic metals from nonferrous metals and other nonmagnetic wastes (Hsu et al., 2019). Magnetic separation is in general performed first, followed by shredding or grinding to fine particle size, and after that electrostatic separation is applied. High-intensity separators are used for possible separation of copper alloys from the waste matrix (Veit et al., 2005). Through an intense magnetic field, copper alloys with relatively high mass susceptibility (Al multicomponent bronze), copper alloys with medium mass susceptibility (Mn multicomponent bronze, special brass) and copper alloys with low mass susceptibility and/or diamagnetic material behavior (Sn and Sn multicomponent bronze, Pb and Pb multicomponent bronze, and brass with low Fe content) can be separated (Cui and Forssberg, 2003).

Electrostatic separation is considered as advantageous compared to the other physical techniques as it is smooth operation, less hazardous, and requires less energy (Lu and Xu, 2016). Electrostatic separation is based upon electrical conductivity and separates the nonconductive materials from the conductive ones. Although the electrostatic separators were initially recovered nonferrous metals from automobile scrap or municipal solid waste, now widely used for WEEE utilized explicitly for the recovery of copper or aluminum from chopped electric wires and cables and recovery of copper and precious metals from printed circuit board scrap (Lu and Xu, 2016). It has been observed that the multistage process is needed to separate conductors from nonconductors (Hsu et al., 2019). Both corona discharging and eddy current-based electrostatic separation have received significant attention in the separation of ferrous and nonferrous metals and the separation of plastics from the plastic and metal mixture. Particle size has become a limiting factor, along with the sticking effect of larger particles in terms of corona separation, whereas eddy current-based electrostatic separation depends on the flow of the particles (Cui and Forssberg, 2003).

Gravity separation is considered as the best physical separation option for non-metals from the metals by different specific gravities. Density separation is dependent on the density and the size of the components. Viscous liquids such as tetrabromoethane can serve as the separation medium where the metals can be separated from the plastics or ceramics. Conventional gravity separators that are used in E-waste recycling are water or airflow tables, dense media separation, and sifting. Density separation techniques that have extensively been used in the mineral processing industry are now applied into E-waste recycling as WEEE consists of many plastics, with a density less than  $2.0 \text{ g/cm}^3$ ; light metal, primarily Al and glass, with a density of  $2.7 \text{ g/cm}^3$ ; and heavy metals, predominantly Cu and ferromagnetic, with a density more than  $7 \text{ g/cm}^3$  (Kaya, 2016). The enriched fractions are treated

by chemical techniques: pyrometallurgical and hydrometallurgical processes after mechanical/physical treatments in order to extract precious metals.

## 2.2.2 Chemical techniques

Chemical processes that are used in resource recovery of WEEE include pyrolysis and pyrometallurgical processes for the nonmetallic fractions, whereas various metallurgical processes are used for the separation of the metallic fraction of E-waste. Most common chemical techniques for precious metal recovery from WEEE are pyrometallurgy and hydrometallurgy. Pyrometallurgy is the most traditional and standard treatment process where hydrometallurgy is a recent advancement (Khaliq et al., 2014). For the resultant, electrometallurgical/electrochemical processes and biometallurgy can be applied for further separation.

### 2.2.2.1 Pyrometallurgy

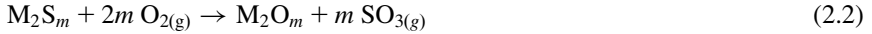
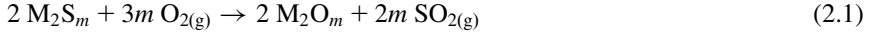
Pyrometallurgy involves incineration, smelting in plasma arc or blast furnaces, drossing, sintering, melting, and gas-phase reactions at high temperatures (Hsu et al., 2019). Presently, WEEE recycling is dominated by pyrometallurgical routes (Khaliq et al., 2014). Pyrometallurgical routes are similar to mechanical or hydrometallurgical processes with the steps of liberation, separation/upgrading, and purification. More than 70% of WEEE is treated in smelters instead of mechanical processing (Cui and Zhang, 2008). After the reduction of size via physical techniques, WEEE essentially transferred into smelters for separation and recovery of copper and other precious metals. In the pyrometallurgical process, the liberation of valuable metals is achieved by smelting in furnaces at high temperatures. In these processes, metals are sorted by exploiting their chemical and metallurgical properties. “Bath” or “flash” smelting are known as the copper smelting processes. Bath smelting is a molten liquid bath where the smelting and converting occurs, and the concentrate is in contact with the liquid slag and matte. Injection of air into the bath or on top of the bath converts the matte. In the case of flash smelting, the converting happens in the air stream. Physical techniques result in preprocessed E-waste which is composed of Fe, Al, Cu, and Pb in high amounts and precious metals in low concentrations. Typical E-waste is rich in Fe and Al followed by Cu and Pb. Therefore WEEE may undergo Pb smelting and Cu smelting routes in order to separate Pb, Cu, and precious metals. Recent techno-economic analysis of pyrometallurgy has revealed that the E-waste recycling process embedded in copper smelting has potential value and is economically feasible with a minimum plant capacity of 30,000 tons of E-waste/year (Khaliq et al., 2014).

*Incineration:* The incineration process can be done at a high temperature where a tremendous amount of mass losses (70%) and E-waste scraps converted into liquid matte and slag. The organic matter presents in WEEE facilitates burning and turns it into solid char, gases, and oil.

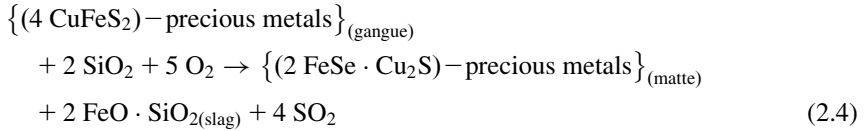
*Smelting:* In the process of smelting, physical and chemical changes occur in the furnace at a temperature between 1000 °C and 1300 °C. There have been several

processes employed during the smelting process, including flash and bath smelting. Various metallurgical processes such as oxidation, reduction, vulcanization, melting, matte forming, slag forming, and fumes of nonferrous metal compounds can occur during the smelting process (Ma, 2019).

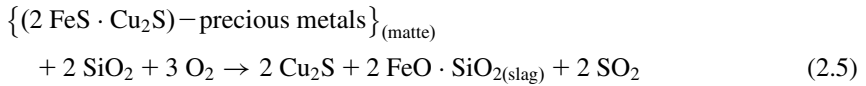
The metal sulfides impurities such as Pb, Zn, and Fe, oxidized to metal oxides in the presence of oxidizing environment and moved to the slag while recovering metals such as Cu and precious metals (Ag, Pt, Pd, and Au) formed liquid matte (Namias, 2013). The typical reactions took place during the oxidation as given in chemical Eqs. (2.1)–(2.3):



For an example, In Cu recovery from WEEE, during the smelting process, Cu with precious metals and iron sulfide formed liquid matte whereas some other metal sulfides like Fe and Zn, oxidized to metal oxide and produced slag. This process illustrated by the following chemical Eq. (2.4):



The above-mentioned process continued by the conversion process where the matte is oxidized further in the presence of an oxidizing atmosphere and produced impure copper blister liquid, whereas chemical Eqs. (2.5) and (2.6) illustrates:



Finally, the copper blister liquid treated with anode furnace to separate the pure copper from the blister. About 99% of copper from the blister can be separated, and the remaining can be recovered during the electrorefining process (at the cathode terminal). Using the electrorefining cell, 99.99% of copper was recovered from the WEEE and precipitated the precious metals such as Au, Ag, Pt, and Pd. The further recovering process needs to be carried out to recover the precious metals from the final residue (Dennis, 2018; Ding et al., 2019; Ma, 2019).

Although the pyrometallurgy is traditional and commonly used in metal recovery in the past two centuries, it has borne some merits and demerits. The ability to

accept any form of WEEE scrap since the organic matters in WEEE has been used as fuel during the incineration process is one of the main merits (Kaya, 2016). However, there are some demerits of pyrometallurgy process have been reported as follows (Namias, 2013; Ma, 2019):

- Pyrometallurgy process cannot recover metals like Al and Fe since these are oxidized to metal oxides and shifted into the slag.
- It produces a large quantity of slag.
- It is impossible to recover some certain products such as plastic, ceramic, and glass since these are provided thermal energy to the burning process.
- The combustion of plastics generated environmentally toxic fumes such as furans, poly-brominated diphenyl ethers and dioxins and individual attention needed to be controlled this harmful emission.
- This process emits fumes along with heavy metals which have low melting points such as Pb, Hg, and Cd.
- Uncontrolled combustion of WEEE during the incineration process.
- Lengthy process: at the end of the process the precious metals such as Au, Ag, and Pt residue obtained and it is very challenging tasked to recover the precious metals from the residue.

### 2.2.2.2 Hydrometallurgy

Compared to pyrometallurgy, hydrometallurgy is considered to be better as the technique can be conducted in controllable, more exact, predictable conditions through an environmental friendly manner. The hydrometallurgical process involves a series of acid or caustic leaches of WEEE followed by separation and purification techniques, such as cementation, solvent extraction, ion exchange, and activated carbon adsorption, to isolate and concentrate the metals from the leached solutions (Hsu et al., 2019). Chemical leaching processes have gained traction, and a plethora of research on leaching has been done in recent years. Similar technology of acid or caustic leaching is employed in traditional hydrometallurgical processes for metal extractions from the particular primary ores are applied for WEEE. The separation of metal of interest is conducted through solvent extraction, adsorption, and ion exchange enrichment processes (Khaliq et al., 2014). Four methods are used commonly for chemical leaching, based upon the extraction chemistry: acid, cyanide, thiourea, and thiosulfate. In the case of acid leaching various different acids in different ratios are involved, nitric acid, aqua regia (a mixture of hydrochloric and nitric acids), and sulfuric acid:H<sub>2</sub>O<sub>2</sub>. The most popular leaching method for metals in WEEE treatment is acid leaching, which provides high leaching rate and fast kinetics regardless of the corrosiveness. Leaching from cyanide is standard practice in gold mining; however, due to its high toxicity, it is not in practice at today's industry. It has been found that thiourea and thiosulfate leaching as the least hazardous techniques for the recovery of precious metals, however, are not cost-effective. In the case of thiourea, the stability is poor whereas, the leaching kinetics of thio-sulfate is slow and hence require large amounts of reagent, makes it unrealistic in large scale use. Finally, metals are recovered from the mixture through electrometallurgy or chemical reduction processes.

### 2.2.2.2.1 Acid/alkaline leaching

The acid or alkaline leaching is the basic and fundamental process of recovering precious metals such as Au, Ag, Pt, and Pd from E-waste, where the dissolution of selective precious metals taken place. However, the usage of aqua regia (the mixture of HCl and HNO<sub>3</sub> in 3:1 ratio) in the leaching process is a nonselective method for both precious and base metals. Numerous studies have investigated the usage of an inorganic acid such as HCl, HNO<sub>3</sub>, and H<sub>2</sub>SO<sub>4</sub> in recovering the precious metals from E-waste (Guo et al., 2016; Yang et al., 2017). Table 2.2 explains some inorganic acids leaching in urban mining.

Moreover, the usage of strong inorganic acids in the recovery of precious metals from E-waste may results, secondary contaminants formation: 540 tons of CO<sub>2</sub>, 1.4 tons of SO<sub>2</sub>, 2 kg of Sb, 98 kg of ethane, 130 kg of phosphate, and thousands of tons of tailings and similar amount of sludge, corrosion of the equipment, and spoilage of nonmetallic components (Innocenzi et al., 2017; Rocchetti et al., 2013). A special attention needs on the formed secondary contaminants before it dispose into the environment (Tesfaye et al., 2017).

Recently, the organic acids also have used to recover the metals from E-waste, especially cellphone batteries. The organic acids are considered as potentially harmless to the environment, efficiently leaching the metals, less corrosive, and biodegradable green chemicals (Fu et al., 2019; Musariri et al., 2019). Moreover, organic acids do not produce any secondary pollutants. Table 2.3 summarizes the recent

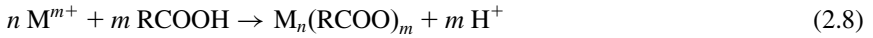
**Table 2.2** Urban mining of precious and base metals using inorganic acids.

Acid	Used E-waste	Recovered metal	References
2.0 M, HCl	Printed circuit boards (PBCs) of mobile phones	Au (5.0%) Cu (94.91%)	Kim et al. (2011)
0.1 M, HCl	PBCs of mobile phones	Au (93.06%) Cu (0.58%)	Kim et al. (2011)
2–5 M HNO <sub>3</sub>	TV board scraps	Cu (88.5%–99.9%)	Bas et al. (2014)
1–5 M HNO <sub>3</sub>		Ag (14%–68%)	
HNO <sub>3</sub>	PBCs of cell phones	Ag (100%)	Petter et al. (2014)
5.5 M HCl	PBCs	Sn (95.97%)	Jha et al. (2012)
2.0 M HCl	PBCs	Cu (71%) Zn (98%) Sn (96%) Pb (96%)	Kim et al. (2006)
0.5 M H <sub>2</sub> SO <sub>4</sub>	Lithium–ion batteries	Mn (100%) Co (99%) Ni (85%)	Yang et al. (2017)

**Table 2.3** Recovery of metals using organic acids as a leaching agent.

Acid	E-waste	Conditions	Metals recovered (%)		
			Co	Li	Ni
Citric acid	LIBs	Temp: 95 °C [Acid]: 1.5 M Reductant: H <sub>2</sub> O <sub>2</sub> 2 vol% Leaching time: 30 min	95	97	99
DL-malic acid	LIBs	Temp: 95 °C [Acid]: 1.0 M Reductant: H <sub>2</sub> O <sub>2</sub> 2 vol. % Leaching time: 30 min	98	96	99
Oxalic acid	LEDs	Temp: 90 °C [Acid]: 0.7 M Leaching time: 0 min	—	—	—
Benzenesulfonic acid	LIBs	Temp: 90 °C [Acid]: 0.75 M Reductant: H <sub>2</sub> O <sub>2</sub> 3 vol.% Leaching time: 80 min	96.53	99.58	

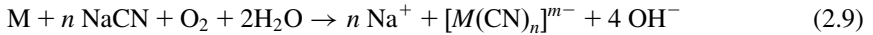
efforts of recovering precious metals using organic acid as leaching agents. The metal leaching from organic acids can be given by Eqs. (2.7) and (2.8):



where RCOOH is organic acid.

#### 2.2.2.2.2 Cyanide leaching

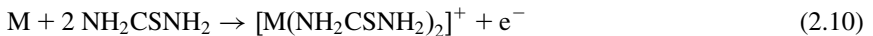
The utilization of cyanide ( $\text{CN}^-$ ) as a leaching agent in the recovery of precious metals is well known for more than 100 years (Cui and Zhang, 2008). The usage of cyanide is preferable due to its significant capacity on the recovery of precious metals. It is imperative to maintain the pH between 10 and 11 during the leaching process, since below pH 8.5,  $\text{CN}^-$  exist as HCN, which is a highly volatile and toxic substance. The temperature has to be maintained around 160 °C, to overcome the strength of metallic bonds present in metals during the chemical reaction and to oxidize metals in the alkaline medium under an oxygen-rich environment (Akciil et al., 2014; Chen and Huang, 2006; Naghavi et al., 2016). In the leaching process of precious metals under alkaline conditions, metals are oxidized while the oxygen is being reduced. The typical reaction involved in the metal recovery using cyanide is given in Eq. (2.9):

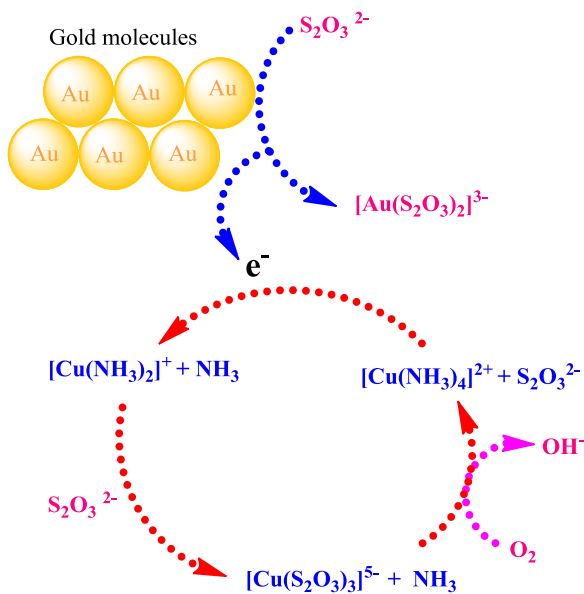


#### 2.2.2.2.3 Thiourea leaching

Thiourea ( $\text{NH}_2\text{CSNH}_2$ ) is an organosulfur compound, which is known as a sulfur-containing organic compound. Thiourea has the ability to bind with precious metals such as Ag and Au by coordination bonds since it has a lone pair of electrons on nitrogen and sulfur atoms. The low environmental impact, fast kinetics, and financial profitability considered thiourea as a right leaching agent in Au and Ag recovery process from WEEE (Gurung et al., 2013).

Utilization of thiourea for recovery of precious metals in alkaline medium is not feasible, because of the easy decomposition in alkaline solution, while thiourea exhibits a rapid recovery of leaching in an acidic environment. Furthermore, the reaction kinetic of thiourea leaching process in the acidic environment has been speeded up by introducing the iron (III) ( $\text{Fe}^{3+}$ ) ion into the reaction mixture (Gurung et al., 2013). In acidic medium, thiourea forms cationic coordination complexes with precious metals such as Au and Ag and the dissolution takes place by the anodic reaction indicated by chemical Eq. (2.10) (Jing-ying et al., 2012):





**Figure 2.3** The proposed mechanism of gold leaching from WEEE using thiosulfate agent.

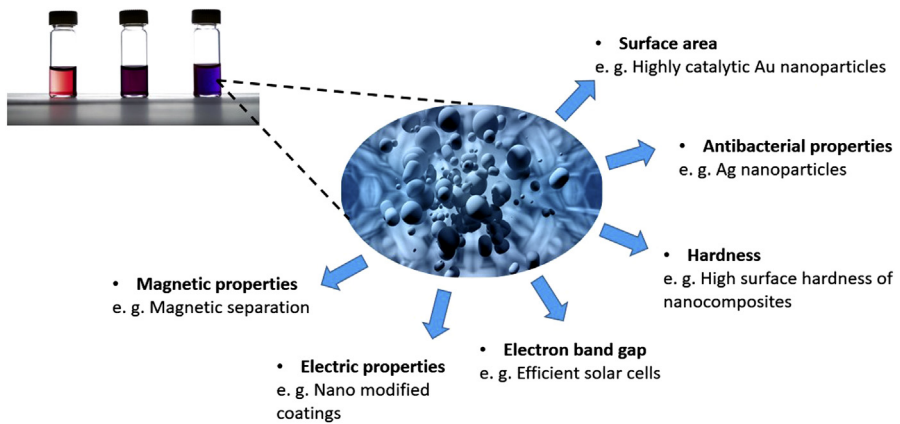
With this process, up to 100% of Au and Ag can be leach out from WEEE. The leaching rate of Au and Ag with thiourea influences by the pH of the solution, the strength of thiourea, the concentration of  $Fe^{3+}$  ion, leaching time, and particle size (Hilson and Monhemius, 2006).

Although, the recovery process is kinetically fast, less environmental influences compared to cyanide leaching process and insensitive to other metals such as Cu, As, Pb, and Zn, thiourea is still hidden from its commercial applications due to the high cost and the rapid oxidation in the reaction system. Therefore a large amount of thiourea needs in order to complete the recovery process, which is a significant drawback of the method (Hilson and Monhemius, 2006) (Fig. 2.3).

#### 2.2.2.2.4 Thiosulfate leaching

Thiosulfate ( $S_2O_3^{2-}$ ), an anionic chemical compound which is used in redox reactions as a reducing agent (Fig. 2.4). Since 20 years, it has been used to leach out the precious metals, instead of cyanide leaching method (Akciil et al., 2014). The usage of thiosulfate for the recovery of precious metals is peaceful to the environment since it is nontoxic and can be decomposed easily by the thio-bacteria in the environment (Wentzien et al., 1994). Leaching efficiencies of 98% and 93% of Au and Ag were recorded by ammonium thiosulfate leaching for 48 h (Ficeriová et al., 2011). Thiosulfate leaching process has been carried out in the alkaline medium since in low pH, thiosulfate has decomposed and formed elemental sulfur which covers the metal surface and prevents from the leaching (Hilson and Monhemius, 2006). Furthermore, the leaching kinetics of precious metals using thiosulfate solution, enhanced by the addition of copper (II) ions in the reaction mixture.





**Figure 2.4** The unique characteristics of nanomaterials, which are beneficial for basic electronic components.

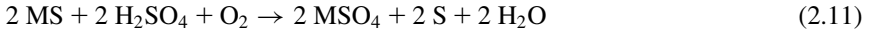
### 2.2.2.3 Biometallurgy

Biometallurgy has received recent attention due to low investment cost, low environmental impact, and low energy consumption and therefore has become a well-established pathway for recovering precious metals from WEEE. Biometallurgy is a two-step process: bioleaching and biosorption. Bioleaching employs diverse organisms for the extraction of metals where many factors can influence the extraction: microbial tolerance, microbial consortia, bacterial attachment, and abiotic factors including the metallic composition of the waste, pH, particle size, and the secondary reactions (Cui and Zhang, 2008). Two main types of bacteria: ferroxidans and thiooxidans, can solubilize metals specifically from metallic sulfides (Mahmoud et al., 2017; Morin et al., 2006). Biosorption process is different from bioleaching, a passive physicochemical interaction between the charged surface groups of microorganisms including algae, bacteria, yeasts and fungi, and ions in solution (Bandara et al., 2017). Biosorption-based recovery offers several advantages compared to the conventional methods including low operating costs, minimization of the volume of chemical and biological sludge to be handled, and high efficiency in detoxifying effluents.

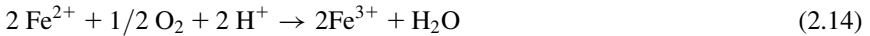
#### 2.2.2.3.1 Bioleaching

Bioleaching is a simple process for the recovery of metal particles from E-waste, with the use of microorganisms such as bacteria, fungi, and actinomycetes (Vakilchap et al., 2016). This particular process has considered as low energy consuming, highly efficient, environmental friendly, and a low operational cost process that can be carried out at room temperature and atmospheric pressure (Xiang et al., 2010). Generally, the microorganisms leach the metal particles from the metal sulfide, which presents in ore or E-waste by two types of mechanisms, which are known as direct action and indirect action mechanisms.

Indirect mechanism, microorganisms oxidized the metal sulfide directly, which means, the electron transfer takes place between the metal sulfides and the surface of the particular organism (Vera et al., 2013). Some bacteria such as *Acidithiobacillus ferrooxidans*, which has the ability to transfer the electrons between the cell and the mineral metals, are mediated by the secretion of extracellular polymeric substances (Zhao and Wang, 2019). However, studies on the direct action mechanism have to be further investigated (Zhao and Wang, 2019). Direct action mechanism has illustrated by Eqs. (2.11) and (2.12) (Cui and Zhang, 2008):



In the indirect mechanism, the microorganisms such as iron (II)-oxidizing bacteria regenerates the  $\text{Fe}^{3+}$  ions from  $\text{Fe}^{2+}$  ions by oxidization and then the  $\text{Fe}^{3+}$  ions oxidize the metal minerals by itself. This reaction represents in the chemical Eqs. (2.13) and (2.14):



The indirect mechanism further classified into two categories: thiosulfate pathway and polysulfide pathway. In the thiosulfate pathway, thiosulfate formed as an intermediate (Cui and Zhang, 2008). Generally, this mechanism plays on the acid insoluble metal sulfides such as molybdenum disulfide and iron disulfide. The thiosulfate pathway can be forwarded by *A. ferrooxidans* and *Leptospirillum ferrooxidans* bacteria (Balci et al., 2007).

In polysulfide pathway, acid soluble metal sulfides such as  $\text{FeS}$ ,  $\text{PbS}$ ,  $\text{MnS}_2$ ,  $\text{CuFeS}_2$ ,  $\text{As}_4\text{S}_4$ ,  $\text{Fe}_7\text{S}_8$ ,  $\text{As}_2\text{S}_3$ , and  $\text{ZnS}$  undergo oxidative attack by protons and/or  $\text{Fe}^{3+}$  ions and produced chemically inert elemental sulfur (Vera et al., 2013). However, the elemental sulfur can finally be oxidized biologically by bacteria to sulfuric acid, which produced enough protons for the dissolution of metal sulfide. This mechanism can be catalyzed by sulfur-compound oxidizing bacteria such as *A. ferrooxidans* and *Acidithiobacillus thiooxidans*.

Table 2.4 has summarized some previously studied documents about the bioleaching process in the recovery of precious and base metals using microorganisms. *A. ferrooxidans* and *A. thiooxidans* are the mostly utilized bacteria in the bioleaching process.

Although *A. ferrooxidans* and *A. thiooxidans* are frequently used in the metal recovery processes from E-waste (Table 2.4), some other bacteria such as *Chromobacterium violaceum* also have been used in the bioleaching of metals. *C. violaceum* is a gram-negative bacteria which has the ability to produce cyanide ions, where Au particles can be leach out from the WEEE (Liu et al., 2016). The chemical reaction about cyanide leaching of Au is explained nicely in Eq. (2.14). Over 70% of Au, biologically leached out from the WEEE using *C. violaceum* bacteria (Liu et al.,

**Table 2.4** Recovery percentage (%) of metals from different types of E-waste using bioleaching process.

E-waste	Organisms	Recovered metals	Recovered (%)	References
PCBs of computer	<i>Acidithiobacillus ferrooxidans</i>	Cu	94	Priya and Hait (2018)
		Zn	92	
		Pb	64	
		Ni	81	
LCDs	<i>Acidithiobacillus thiooxidans</i>	In	100	Jowkar et al. (2018)
PCBs	<i>A. ferrooxidans</i>	Sr	10	Yang et al. (2014)
		Zn	83.8	
		Cu	96.8	
Dust from WEEE shredding	<i>A. thiooxidans</i>	Al	75.4	Marra et al. (2018)
		Ce	>99	
		Eu	>99	
		Nd	>99	
		La	80	
		Y	80	

2016). The *Pseudomonas putida* is another type of gram-negative bacteria with the ability to generate cyanide ions. It is reported that 48% of Au has been recovered from the dust of WEEE, which is preleached with *A. thiooxidans*. It is also reported that no other precious metal such as Ag and Pd have been leached out from the preleached dust by *A. thiooxidans*. The bioleaching is an effective manner to recover the precious metals from the WEEE. Therefore it is necessary to study further in order to improve the leaching abilities and discover new species of microorganisms.

#### 2.2.2.3.2 Biosorption

Biosorption is another technique, which can be used in the recovery process of precious metals from WEEE. The biosorbent used in this process can be either dead or alive or product biomasses of bacteria, fungi, algae and protein, etc. The adsorption of metals take place due to the physiochemical interaction between the metals in solution and surface of biosorbents, while complex formation, microbial oxidation and reduction, chelation between biosorbent and metals, and microprecipitation are taken place as the chemical interactions. The physical interactions include ion exchange and electrostatic forces (De Vargas et al., 2004). The biosorption of metals by a particular biosorbent depends on the properties of the surface of biosorbent. Surface functional groups such as amine, amide, hydroxyl, carboxyl, and carbonyl have driven the adsorption of positively charged metals efficiently (Wang and Chen, 2006, 2009). The biosorption capacity of metals affected by several factors: temperature, solution pH, the dosage of biosorbents, and charge of metals. In order to achieve the highest biosorption capacity, the surface of biosorbent has chemically further modified. Polyethylenimine (PEI) modified bacteria *Corynebacterium glutamicum* has shown biosorption capacity of 110.5 mg/g for Ru

whereas raw bacterial biomass shown 16 mg/g of biosorption capacity which is determined by the Langmuir adsorption model (Kwak et al., 2013). The main drawback of the biosorption process is that the experiments cannot be carried out when the WEEE is in solid form. Once it leached out, the biosorption process can be carried out. From thiourea leachate of the discarded microprocessor of computer, 80% of Au has been recovered using chitin as the biosorbent and treating for 4 h with an ambient temperature (Côtés et al., 2015).

There are some bottlenecks on the biosorption of metals, it needs to be leached out the solid waste prior to carry out the biosorption, and the biosorbents are necessary to undergo a chemical surface modification to achieve maximum biosorption capacity. Due to these limitations, the biosorption process is carried out at the small scale and laboratory levels (Işıldar et al., 2019). Further implementation is needed for the biosorption process to industrial and commercial levels.

## 2.3 Extraction of nanometals from E-waste

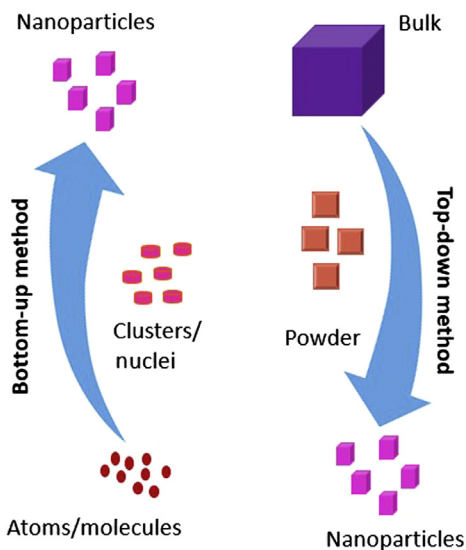
Recycling E-waste has been introduced as an effective solution for the massive accumulation of waste electrical and electronic equipment (WEEE), with a growth rate of 5% per year (Afroz et al., 2013). A wide range of waste types can be seen in electronic waste, such as plastics, precious metals (e.g., gold, silver, palladium, and platinum), base metals (e.g., copper, zinc, nickel, and ferrous), potentially toxic elements (e.g., lead, cadmium, and mercury), carbon-based insulate materials (e.g., quartz, silica and carbon material containing parts), and halogenated derivatives (Majumder, 2014). However, more than 90% of WEEE can be recycled and regenerate to reuse in new electronic devices (Afroz et al., 2013). The amount of E-waste generated due to limited utilization, low generating rate of E-waste compared to municipal solid waste and relatively large starting cost of recycling process are some of the drawbacks which limit the intention of recycling WEEE (Kim et al., 2017). Among different aspects of recycling E-waste, recovering metals in nanoscale results in high purity commercial grade nanometals (Deep et al., 2011).

Nanomaterials (NMs) have unique characteristics, which is very beneficial in electrical and electronic applications (Fig. 2.5). Synthesis of NMs can be carried out in two main pathways: top-down approach and bottom-up approach (Fig. 2.5). In the top-down approach, bulk materials have broken down to nanoscale particles, while nanoscale particles have built up starting from the atomic scale, in the bottom-up approach (Thakkar et al., 2009; Sinha et al., 2011). A variety of bottom-up methods, such as physical, chemical, and biological methods have been used to synthesize nanoscale metals and metal oxides particles from E-waste.

### 2.3.1 Pure metals

#### 2.3.1.1 Precious metals

Various chemical and physical techniques have been used in the case of precious metal extraction. However, recent attention is focused on biological extraction.



**Figure 2.5** Bottom-up and top-down approaches of synthesis of nanoparticles from E-waste using both chemical and biological methods.

Most of the precious metals have recycled to obtain nanoparticles, with the process which is known as bioleaching, by using microorganisms, weed extracts, and enzymes (Jain et al., 2010). Biosynthesis of nanoparticles is beneficial due to the formation of natural protein coat over the nanoparticle during the synthesis. This cover prevents aggregation, provides longer shelf life and stability due to less reactivity (Majumder, 2014). Microorganisms, which are known as mini biofactories of nanometal production, are able to produce metal particles in the range of 5 – 200 nm (Husseiny et al., 2007). They commonly extract, gold (Au), silver (Ag), and palladium (Pd) with bacteria, fungi, algae, yeast, and actinomycetes.

### 2.3.1.1.1 Gold (Au) nanoparticles

Extraction of nanogold from E-waste can be carried out in two pathways: chemically and biologically. Hydrometallurgical process of extracting metals results in a high recovery yield of metal with low temperature and cost. This method appropriates in small scale applications and therefore suits for small scale applications such as precious metal recovery (Ghosh et al., 2015). Extractions under hydrometallurgical process have done with different lixivants and solution pH values. Alkaline pH conditions were used with cyanide and thiosulfate leaching, while thiourea and halide leaching was done in acidic pH conditions (Tuncuk et al., 2012). Halide and cyanide complexes have expressed higher leaching rate of Au, with compared to thiosulfate and thiourea complexes. Overall, 97% of recovery of gold can be seen with  $\text{NaClO}_3\text{-HCl}$ ,  $\text{H}_2\text{O}_2\text{-H}_2\text{SO}_4$ , and iodine solutions under appropriate conditions (Ding et al., 2019). The hydrometallurgical process has been modified to leach out gold in nanoscale, to achieve high leaching rate (Behnamfard et al., 2013) and to

reduce environmental influence (Ding et al., 2019) with chloride/sodium chlorate to recover 99% of Au and with noncyanide leaching agents (e.g., thiourea, thiosulfate, and thiocyanate), respectively. Polyaniline powders, films, and coated fibers were used hydrometallurgical process, through spontaneous reduction to extract gold nanoparticles from E-waste (Wu et al., 2017). Traditional leaching methods also can be used to extract gold with cyanide as an active ingredient in the leaching process. However, due to high toxicity, noncyanide alternatives such as thiourea and thiosulfate have introduced by authorities to avoid environmental accidents (Ding et al., 2019).

Recovery of gold nanoparticles from WEEE also can be carried out with spent catalysts, which exhibits several advantages such as short production cycle, simple process, and eco-friendliness (Jha et al., 2013; Dong et al., 2015). Crushed spent catalysts mixed with fluxes such as  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$ , or  $\text{SiO}_2$  are used in the pyrometallurgical process, and chemical properties, mutual solubility, and melting point were considered (Ma et al., 2017).

In biological methods, nonmetal extraction with microorganisms plays a significant role. *Pseudomonas aeruginosa*, *Stenotrophomonas maltophilia*, *Plectonema boryanum*, and *Rhodospseudomonas capsulate* are some of the bacterial types, which is used in the biosynthesis of Au nanoparticles (He et al., 2008; Nangia et al., 2009). Other than bacteria, fungi types such as *Verticillium luteoalbum* and *trichothecium* species also can be used in bioleaching of nano Au (Ahmad et al., 2006; Maliszewska, 2012). *Yarrowia lipolytica*, a type of yeast and *Rhodococcus* sp., a type of actenomyces are reported as microorganisms for bioleach gold nanoparticles (Ramani et al., 2004; Pimprikar et al., 2009). Algae also have the ability to synthesized metal nanoparticles, and therefore *Calothrix pulvinata*, *Anabaena flos-aquae*, *Leptolyngbya foveolarum*, and *Laminaria japonica* algae species have been used in Au nanometal extraction (Brayner et al., 2007; Ghodake and Lee, 2011). Gold also can be extracted in nanoscale with weed extract with a range of 8–12 nm in size (Singaravelo et al., 2007).

#### 2.3.1.1.2 Silver (Ag) nanoparticles

Silver is a precious metal which is widely used in basic electrical components manufacturing. Therefore Ag can be commonly found in PCBs and other electrical appliances. Nanoscale silver can be extracted out from EEW into a cyanide solution by using traditional leaching out methods. Cyanide and aqua regia are used in traditional hydrometallurgy process to leach out silver, and the oxidant dosage, solution pH, temperature, and concentration of cyanide directly affect on the efficiency of leaching (Xie et al., 2014). Precious metals such as Ag, dissolve by complexation with  $\text{CN}^-$  in an optimal pH of 10.2. Considering the toxic effect of cyanide, to avoid environmental accidents, few noncyanide lixivants has been introduced by the authorities. Aqua regia exhibits a nonselective dissolution of precious metals and results in 98% of recovery of silver (Park and Fray, 2009). Even though aqua regia gives a high yield of Ag and Au, it expresses drawbacks such as toxicity, corrosiveness, and strong oxidative (Petter et al., 2014).

To extract nanosilver, noncyanide extraction technologies also can be used, and 48% of Ag could be recovered with thiourea leaching method (Jing-ying et al., 2012). The modified hydrometallurgical process to recover precious metals selectively and 71% of Ag can be obtained (Behnamfard et al., 2013). Extraction of Ag with iodine–iodide leaching is another method to take out silver in nanoscale with supercritical water oxidation (Xiu et al., 2015). Electrochemical methods also have been used in the extraction of Ag from E-waste. The chemical utilization in the recovery of metals is considerably low in electro-recycling process and results in nearly 97% of recovery of Ag (Lister et al., 2014).

Other than chemical methods, silver nanoparticles can be extracted by using biological methods suchlike microbial leaching and weed extraction. *Shewanella oneidensis*, *Escherichia coli*, and *Klebsiella pneumoniae* are some of the bacterial types that produce extracellular spherical silver in a range of 50–100 nm (Natarajan et al., 2010; Suresh et al., 2011). Fungal species, *Penicillium purpurogenum* NPMF, *Trichoderma reesei*, and *Aspergillus fumigatus*, are some of the many, which has the ability to synthesize silver nanoparticles less than 25 nm in scale (Pradhan et al., 2011; Vahabi et al., 2011). *C. pulvinata* and *Anabaena* species are algae, which is a type of microbe and contribute to the synthesis of nanosilver (Vahabi et al., 2011).

### 2.3.1.1.3 Platinum (Pt), palladium (Pd) and rhodium (Rh) nanoparticles

Plasma melting iron capture technology is the most commonly used and an effective way of recycling platinum group metals (PGM) using spent catalysts. Iron has been selected as the promising collector due to low cost and strong chemical affinity. The slag and the Fe-PGM alloy was separated using the significant density difference and the recovery of Pt, Pd, and Rh was above 98%, 98%, and 97%, respectively (He et al., 2016). Iron trapping method has introduced to overcome the high energy consumption of plasma melting technology and Pt, Pd, and Rh result in a recovery of 98.6%, 92%, and 97.6%, respectively (Ding et al., 2019). To leach PGMs from spent automotive catalysts, an eco-friendly electro-generated chlorine leaching method has been developed (Kim et al., 2013). To prepare the most effective chlorinated species such as  $\text{Cl}_3$  and  $\text{HClO}_2$  for dissolving Pt,  $\text{Cl}_2$  has fed into HCl solution. The dissolution of Pt is increased with  $\text{Cl}_3^-$  in a particular HCl concentration and exhibits leaching rates of 71%, 68%, and 60% Pt, Pd, and Rh (Upadhyay et al., 2013).

Aqua regia in nonselective dissolution method was used in both base and precious metals leaching and 93% of Pd could be possible to recover (Park and Fray, 2009). With a solid/liquid ratio of 1/10 at 25°C within 24 h, 100% of Pd was able to dissolve (Fontana et al., 2018). Recovery of platinum group metals (PGM) with copper smelting has been studied, and two types of recovery methods have proposed: wetting and settling mechanisms. Microparticles of PGM were used in metal separation process (Kolliopoulos et al., 2014).

Other than chemical methods, Pd can be biologically extracted by using bacteria. *Clostridium pasterianum*, *S. oneidensis*, and *Desulfovibrio desulfuricans* are

bacteria, which are used in biological methods. Metal particles of Pd are synthesized in the range of 1–50 nm (De Windt et al., 2006).

Matte acts as an excellent collector in matte trapping methods for extracting metal Rd, due to the high affinity for PGM and recovering Rd from spent organic Rd catalysts, high nickel matte has been used, and a recovery of 94.65% of Rd was observed (Xiaotang et al., 2012). Using nickel and sulfur as collectors in smelt spent catalysts in the presence of  $\text{Na}_2\text{CO}_3$  and  $\text{Na}_2\text{B}_4\text{O}_7$  at 1050 °C for 30 min with a recovery rate of 90%, 93%, and 88%, respectively (You et al., 2016).

### 2.3.1.2 Base metals

Other metals Cu, Sn, Zn, Al, and Ni are commonly used in electrical and electronic appliances also can be leached out in the E-waste recycling process. An alkali fusion-leaching-separation process has been developed with fluxing agents (e.g.,  $\text{NaNO}_3$ - $\text{NaOH}$ ) to recover metals from crushed metal enrichment (CME) from printed circuit boards (PCBs). In the fusion process, metals have oxidized and converted into soluble salts obtaining leaching rates of 97%, 91%, 98%, and 98% for Sn, Zn, Al, and Cu, respectively. Aqua regia has achieved 100% recovery of Cu with compared to thiourea, sulfuric acid, and ammonia (Lee et al., 2011). The developed hydrometallurgical process with two repeated leaching systems of  $\text{H}_2\text{SO}_4$ - $\text{H}_2\text{O}_2$  leaches Zn, Cu, Fe, Ni, and Sn in 100, 100, 59, and 94%, respectively (Birloaga et al., 2014).

An electrochemical process has developed to recover Cu from waste PCBs. The introduced process has the ability to recover Au simultaneously. Two different types of reactors coupled in series and one reactor for dissolution of base metals with a perforated rotating drum and the other reactor for leaching solution with the parallel electro-winning of copper. In the stage of Cu, Sn, and Ag recovered with  $\text{Fe}^{3+}$  in sulfate, 97% of Cu was recovered (Fogarasi et al., 2014).

Using biological methods, Cu can be extracted in nanoscale. Microorganisms such as bacteria (e.g., *Pseudomonas stutzeri*, *Morganella* sp. and *Pseudomonas* sp.), fungi (e.g., *Fusarium oxysporum*), and actinomycetes (e.g., *Streptomyces* sp.) have used to extract Cu as nanoparticles less than 150 nm (Usha et al., 2010; Majumder, 2012). Other than microbes, weeds also can be used to synthesize metal nanoparticles successfully. *Lantana camara* is an ornamental weed which considers as a green-approach for the synthesis of Cu nanoparticles (Majumder, 2012).

Besides of Cu, other metals such as Se, Ti, and Mn also can be extracted using biological methods. Using bacteria species and fungal species, metal particles in nanoscale have been extracted. *Pseudomonas alcaliphila*, *Lactobacillus* sp., and *Bacillus* sp. are some of the bacterial species that can be used in the extraction of nanoparticles of Se, Ti, and Mn (Sinha et al., 2011; Zhang et al., 2011).

### 2.3.1.3 Toxic metals

In printed circuit boards Pb is commonly used as a soldering material to create contact between basic electronic components. Therefore Pb is ubiquitous in E-waste



and can cause serious health issues by accumulating in the environment. Alkali fusion-leaching-separation process has been used with a fluxing agent (e.g.,  $\text{NaNO}_3\text{-NaOH}$ ) to recover Pb, by converting to a soluble salt in the fusion process. Under optimal conditions, 91% of Pb can be leach out (Guo et al., 2017). Mercury (Hg) and cadmium (Cd) are found in E-waste from small nonrecyclable fractions, and research has been carried out to extract and disposed of carefully (Ilankoon et al., 2018).

### 2.3.2 Metal oxides

Nanomaterials can be extracted in pure metal form as well as metal oxides. Zinc is one of the metal types, which can be extracted in metal oxide form. By using spent Zn–Mn dry alkaline batteries, pure zinc oxide (ZnO) nanoparticle in the range of 40–50 nm can be recovered. The extraction of ZnO nanoparticles can be carried out under Hydrometallurgy-precipitation and liquid–liquid extraction pathways resulting in a 99% recovery (Deep et al., 2011).

Nano- $\text{Al}_2\text{O}_3$  can be synthesized from the waste aluminum electrolytic solution with the co-precipitation method. Particles less than 200 nm was able to recover with a percentage of 99.9. The used ammonia during the recovery process could be recycled up to 80% and reused in the reaction process (Wu and Chang, 2016).

An effective synthesis of copper oxide ( $\text{Cu}_2\text{O}$ ) nanoparticles from E-waste (e.g., PCBs) has been developed. Highly uniform and monodisperse  $\text{Cu}_2\text{O}$  nanoparticles with a range of 5–40 nm in size could be able to synthesize using supercritical water, combined with an electrokinetic technique. Under optimized conditions, over 90% of Cu in E-waste have recovered as  $\text{Cu}_2\text{O}$  nanoparticles (Xiu and Zhang, 2012).

### 2.3.3 Metal nanocomposites

Recovery as a nanocomposite is one of the methods that can be used in extracting metals from E-waste. Using a facile physical mixing method,  $\text{MnO}_2$ /graphene nanocomposite can be prepared for the electrode materials for supercapacitors. Spent battery powder was used as a raw material in the precipitation process of synthesizing  $\text{MnO}_2$ /grapheme nanocomposite (Deng et al., 2015).

## 2.4 Challenges

Urban mining is a process, which recovers the resources such as precious metals and base metals from WEEE. This process will bring the landfills of E-waste to zero, will reduce the natural mining and industrial production processes. However, the collection of domestic WEEE highly costs due to the labor cost and the initial cost in the establishment of E-waste collection points, especially in developing countries.

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With the increasing usage of electronic and electrical equipment globally, the accumulation of WEEE gradually grows in the environment. As E-waste is a source rich in metals, it is important to recover those metals rather than disposing into the environment. The base metals and precious metals can be recovered from WEEE with high purity pyrometallurgy routes. Even though these routes achieved recovery of high purity metals, the major problem is identified as the environment pollution. During the smelting process of feed WEEE materials, it ignites at high temperature and releases a massive amount of hazardous gas to the environment. This hazardous gas contains dioxins, furans, polybrominated diphenyl ethers, and many hydrocarbons, which causes serious issues to both environment and living beings. Uncontrollable temperature elevation and high energy consumption are challenges and arise during the smelting of WEEE. Prevention of these environmental issues is a challengeable task, and it needs to be paid more attention to the pretreatment of hazardous waste gas prior to dispose of the environment.

Hydrometallurgy process is a highly efficient and environmentally friendly process compared to pyrometallurgy. Commonly, four methods are employed in hydrometallurgy process: acid leaching, cyanide leaching, thiourea leaching, and thiosulfate leaching. In acid leaching, the usage of acid, especially sulfuric acid in precious metal leaching from WEEE creates many secondary pollutants. Cyanide efficiently leaches the precious metals such as Au and Ag from WEEE in the urban mining process. However, in the presence of Cu, the leaching quantity of precious metals from WEEE become less and further implementation needed to eliminate the Cu from WEEE due to the most of WEEEs are abundant in Cu than other metals. Thiourea is a great leaching agent than cyanide and acid in precious metals leaching. Thiourea shows a complete recovery of Au and Ag from WEEEs. However, thiourea leaching has some disadvantages, which prevents the commercial applications of thiourea. A large amount of thiourea is needed in order to obtain the maximum recovery of precious metals since it undergoes oxidation in the solution. Although thiosulfate causes less environmental impacts and insensitive to other metals, currently, it is known as the best method to recover Au from WEEE. However, the major problem of using thiosulfate as leaching agent is high reagent consumption during the leaching process, and generally, it is slow in leaching of precious metals (Ficeriová et al., 2011).

Moreover, scientists put their footprint on the biohydrometallurgy using microorganisms such as bacteria and fungi, or products derived from microorganisms due to its reduced investment cost, less environmental impact, and low energy consumption. However, the selection of right species of organism and its pure culture is an essential task since the availability of a range of varieties and the low process speed (Priya and Hait, 2018). In case of biosorption, even it shows high sorption capacity with biosorbents, chemical surface modification has to be done and the recovery of metals is not possible with the solid initial mixture, without a pretreatment prior to the biosorption process. Therefore further studies are required in order to overcome these limitations in the urban mining process.

Transboundary WEEE is one of the major issues related to recycling and recovery as once WEEE reaches developing nations, there is no capacity for recycling

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and recovery due to limited financial assistance and willingness. Challenge is how to encourage the general public to proper discarding of WEEE and increase and improve the collection and transportation to recycling facilities. Even at a large scale recovery process of WEEE, nanometals may not be taken with care due to the process difficulties. At the same time, the gap between laboratory and real scale applications limits innovative techniques and inventions to be used in commercial scale to recover precious metals.

## 2.5 Future research developments

The urban mining of precious metals from WEEE is needed since WEEEs are highly rich in precious metals, and the accumulation of WEEE in the environment very frequent. All of the processes such as physical and chemical techniques involved in the urban mining and limitations of this processes are discussed in the previous sections (section 2.2.1 and 2.2.2). The major consideration of urban mining is the environmental impacts. The pyrometallurgy process created huge of toxic gases and sludge, and the hydrometallurgy process created fewer pollutants compared to the pyrometallurgy process. However, pretreatment of pollutants prior to open to the environment is a must. Therefore further studies are required in order to reduce the pollutant generated after the urban mining process.

Nevertheless, the bioleaching process is an efficient method as it is eco-friendly and which is mediated by the secretion of extracellular polymeric substances by the bacteria. However, the bioleaching is a very slow process it may take a few days to leach the metals from WEEE. Further studies are needed to be improved in the bioleaching process. According to currently available technologies, it is possible to genetically modified bacteria in order to secrete more extracellular polymeric substances which may promote more metal leaching from the WEEEs. However, the presence of many toxic substances in the WEEE may kill the microorganisms during the bioleaching. Hence, all toxic substances would be removed before attending the bioleaching process. Therefore further studies would essential to make it as efficient leaching in the future.

Using the ultra-small particles that were disintegrated, small circuit boards are being produced which will result comparatively a small final product. This particular advantage has done a revolutionary change in the market, which attract people to buy handy and portable instruments with high efficiency: liquid crystal display (LCD), solar cells, and chemically inert additives (e.g., carbon and silica polymer fillers). Nanometals are highly valuable resource embedded in WEEE in which the recovery is essential in terms of sustainable development. Although various techniques for nanometal extraction have been reported with promising results in laboratory scale, gaps present in upscaling into commercial use. Many research focused their efforts on precious nanometal extraction, for example, Au and Ag, while the base nanometal extraction is not paid enough attention other than Cu. Process developments is essential for nanometal extraction using cost effective top-down

and bottom-up techniques may be with novel catalysts. Pure nanometal extraction needs more attention over the metalloids or composites as pure metal has many uses and high worthiness. Therefore research must drive toward cost effective pure nanometal extraction. Physical disintegration may change the crystal structure of the metals may lead to the formation of composites and alloys through extraction should be taken care. Even though microorganism mediated nanometal extraction has been widely researched, however, lacking in real application due to the technical capacity. However, process development with biological extraction is highly valuable as it produces protein coated pure nanometals which will result noble precious and base nanometals. At the same time, research efforts should focus on nanometal usage in various applications may induce the willingness for recovery.

E-waste collection, handling, recycling and recovery is not solely a scientific method, it involves social and economic factors as well and therefore research on such should be encouraged. Research with direct benefits toward circular economy should be supported well. Gaps in transboundary WEEE flow needs to be secured for developing nations. Most of the countries do not have a WEEE inventory and it is essential to maintain such an inventory in order to understand the flow and recovery of WEEE.

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