Chapter 1

Introduction

1. Introduction

1.1. Electronic waste (e-waste)

Electronic devices have become an essential component of society due to modern era's significant revolution in science and technology. The swift progress in electronics and computing, coupled with frequent alterations in device designs and operating systems and the strong desire for fast digital connectivity among consumers, has led to the creation of sophisticated electrical and electronic equipment with limited lifespans. Electronic waste is defined as all Electrical and electronic equipments (EEEs) that have no value to their owners and have been discarded as waste without the intention of re-use (Balde et al., 2014). For instance, from 1992 to 2005, the average life of a personal computer decreased from 4.5 years to 2-3 years (Yazici and Deveci, 2013). This trend results in the production of significant amounts of e-waste (Rao et al., 2020), which is three times greater than the amount of waste produced by other categories (Cucchiella et al., 2015). This possesses a significant environmental challenge. The consumption of Electrical and electronic equipment is further increased worldwide due to the covid-19 as the pandemic forced people to stay indoors and on devices. Electronic waste comprises of mobile phones, personal computers, laptops, tablets, printers, calculators, televisions, refrigerators, air conditioners, washing machines, photovoltaic panels, etc. as shown in *Figure 1.1*.

Researchers have found that only 17% of the e-waste produced is being recycled every year and 83% of treatment is unknown likely landfilled, traded or recycled in unauthorized recycling sectors in unhealthy environmental practices (Cucchiella et al. 2015). The developing countries still use some informal activities for recycling such as open burning, backyard recycling and land filling, often disregarding the necessary environmental protocols (Cucchiella et al. 2015). Consequently, this results in the loss of precious resources and possesses severe ecological threats. Thus e-waste is becoming a significant problem due to exorbitant generation rate and low reclamation rate.

Figure 1.1 Different components of electronic waste

1.1.1. Global e-waste generation statistics

According to global transboundary e-waste flows monitor 2022 *(Figure 1.2)* the worldwide generation of Waste Electrical and Electronic Equipments (WEEEs) reached 41.8 million tonnes (Mt) in 2014, which increased to 44.7 Mt in 2016 and 53.6 Mt in 2019, and is expected to reach 74.7 Mt by 2030 and 110 Mt by 2050

(Baldé et al., 2022; Gautam et al., 2023). WEEE is experiencing a rapid growth rate and is now recognized as one of the most swiftly expanding forms of solid waste globally, with an annual surge ranging from 3% to 5% (Gautam et al., 2022a). According to the UNU study, the discarded waste in the year 2019, including precious metals and recyclable plastics, was valued at around 57 billion USD (Baldé et al., 2022).

Figure 1.3 shows the continent-wise generation of e-waste. In 2019, the largest amount of e-waste totalling 24.9 Mt, was produced in Asia. Following Asia, the Americas generated 13.1 Mt. Europe produced 12 Mt, Africa generated 2.9 Mt, and Oceania contributed 0.7 Mt. Out of 24.9 Mt e-waste generated, Asia recycles only 2.9 Mt (nearly 11.7%) of it (Gautam et al., 2022a). Primarily, this stems from insufficient e-waste management and infrastructure, the existence of an informal sector driven by the search for valuable components, and the presence of unregulated dumping sites. The majority of cross-border e-waste movement is concentrated in East Asia and Southeast Asia, given their status as electronics manufacturing hubs. These regions serve not only their own markets but also cater to global consumption. Europe boasts the highest e-waste recycling rate of 42.5%, attributed to the advanced policy and regulatory framework established within the European Union. Africa exhibits the lowest recycling rate of 0.9% owing to the absence of adequate e-waste management and recycling infrastructure. This is compounded by the proliferation of informal, undocumented recycling units, along with the practice of dumping and burning e-waste. However, in the case of per-capita generation, Europe and Oceania ranked first with 16 kg per capita, followed by the Americas (13.3 kg), Asia (5.6 kg) and Africa (2.5 kg) (Forti et al., 2020).

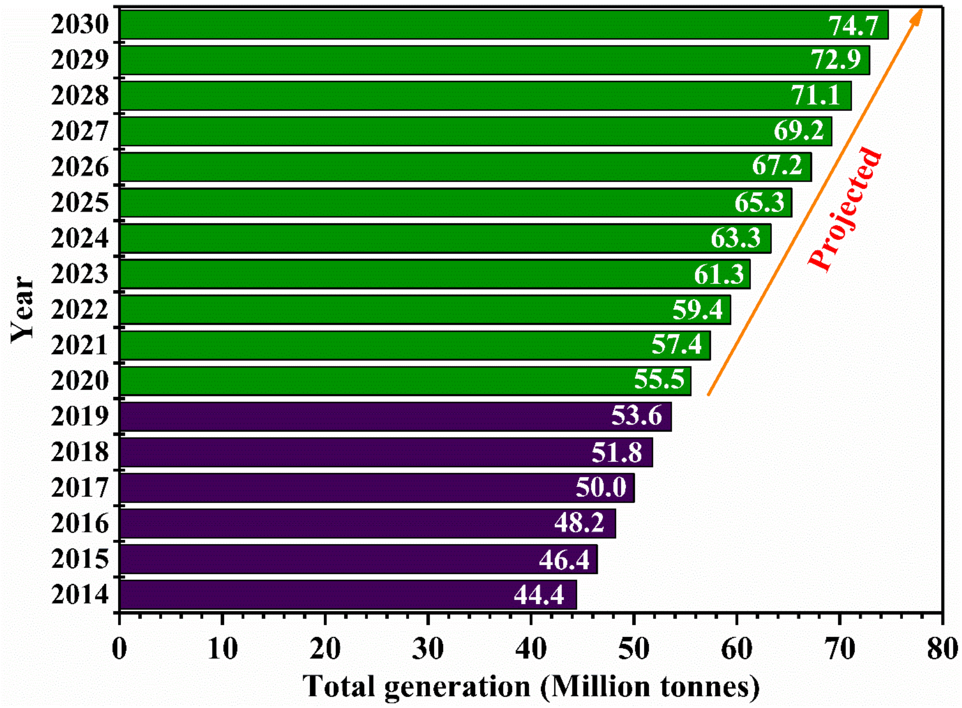

Figure 1.2 Global e-waste generation from 2014 to 2019 and projection from 2020 to 2030 (modified from (Forti et al., 2020; Panda et al., 2021)) (Effect of COVID 19 is not included in the projected data)

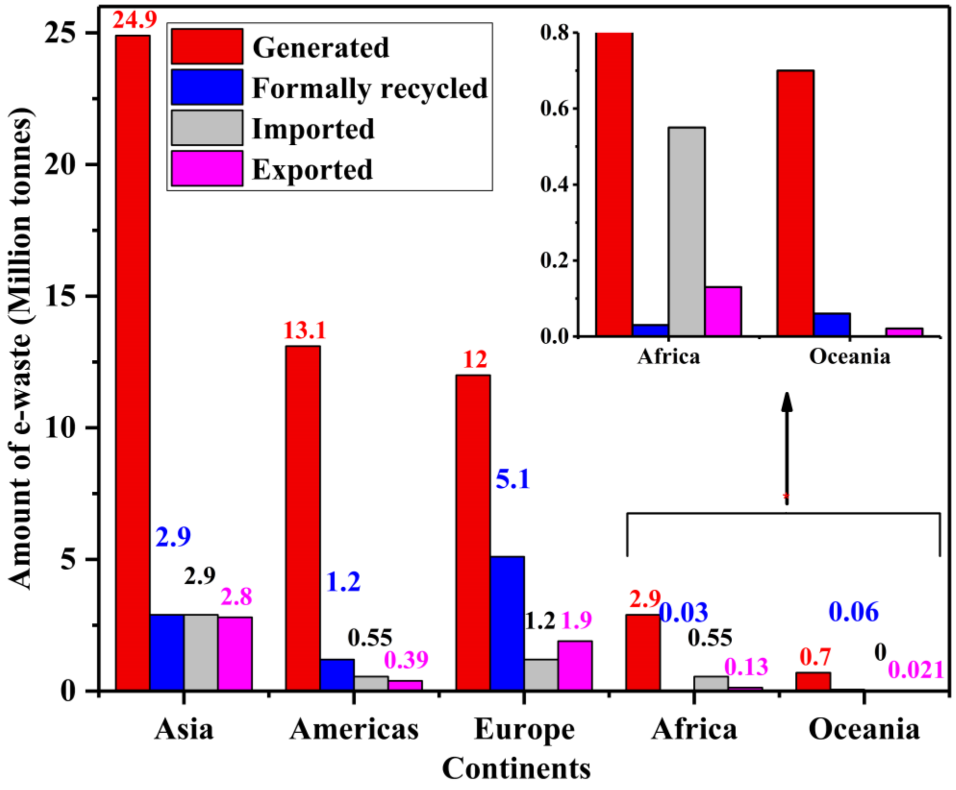

Figure 1.3 Total e-waste generated and recycled continent-wise in 2019

India is one of the developing country and occupies third position in e-waste generation in the world after China and USA. The Associated Chambers of Commerce and Industry of India (ASSOCHAM) reported in 2020 that the annual generation of e-waste reached 3.23 Mt and increased 43% during 2018-2020. The report highlighted that 0.2 Mt of WEEE was generated annually from Delhi, Mumbai and Bangalore only (Kumari and Baby, 2016). The availability of e-waste generation data in India is a primary constraint due to Informal sector participation in e-waste management, grey market domination and collection and waste collection, processing is not under mercantile transactions (Bhattacharya, 2009).

1.1.2. Classification of e-waste and its composition

E-waste encompasses ten distinct categories. These groups encompass a range of items such as information technology and communication devices, large and small household appliances, consumer electronics, non-industrial electrical and electronic devices, lighting fixtures, toys, sports equipment, relaxation gadgets, non-contaminated medical devices, control and monitoring units, as well as automated dispensers (Seif et al., 2023). Notably, accessories constitute about 10%, electronic equipment makes up 14%, communication devices comprise 34%, and home appliances represent the largest share at 42% (Forti et al., 2020).

1.2. Printed circuit boards

Printed Circuit Boards (PCBs), a significant part of all electronic products, form nearly 6% of the total e-waste (Barragan et al., 2020). Waste PCBs are complex materials that could contain up to 63 different elements (Hong et al., 2020). A standard PCB’s composition, as shown in *Figure 1.4* consists of upto 40% metals, 30% ceramics and 30% polymers (Rao et al., 2020). PCBs contain a high concentration of base metals (Cu, Ni, Al, Pb, Fe) and precious metals (Au, Ag, Pt, Pd) than their respective primary ores making it a potential secondary source for metal recovery (Barragan et al., 2020). That is why e-waste is often mentioned as "urban ore" or "secondary ore". This urban ore contains 30-40 times more copper and 130 times more gold than in its one tonne primary ore (Gautam et al., 2022a; Jha et al., 2020; Rao et al., 2020). Recycling one tonne of mobile phones can recover 130 kg Cu, 0.34 kg Au, 3.5 kg Ag, and 0.14 kg Pd (Rao et al., 2020). Such metal recovery techniques from e-waste is termed as “Urban Mining” (Awual and Ismael, 2014). Apart from prioritizing the recovery of base and precious metals from economic point of view, it is important to recover hazardous and heavy metals which potentially leach to water, soil and land in landfill disposal from environmental perspective and affect human health (Widmer et al., 2005). The incineration of PCBs releases toxins such as furans, dioxins, polyhalogenated organics, and aromatic compounds because resin, plastics, and glass fiber are present (Jadhav and Hocheng, 2015), resulting in harmful health effects (Wang and Gaustad, 2012). An effective recycling process can replace the existing promising technologies for energy saving and valuables recovery enhancement.

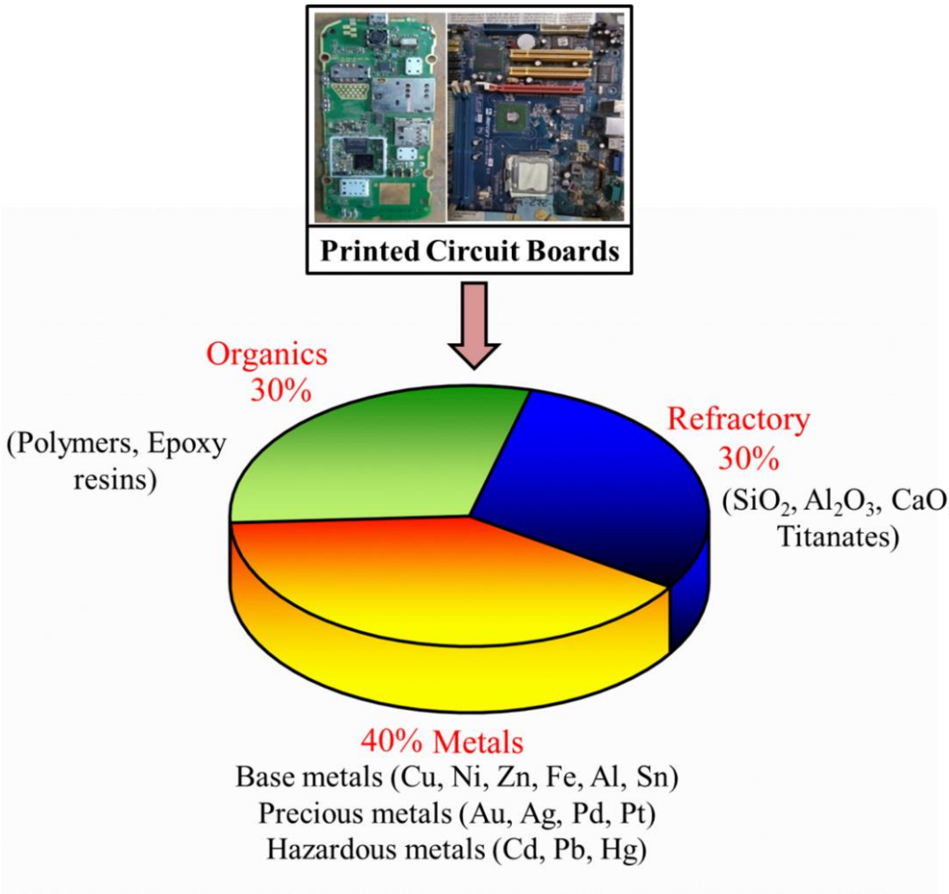

Figure 1.4 Composition of printed circuit boards (Kaya, 2016)

1.3. Recycling and recovering copper from e-waste

Copper and precious metals like gold account for more than 95% of the total value of WPCB (Hagelüken and Corti, 2010). Cu and alloys make 67% of the total metal and alloy content in PCBs (Tiwary et al., 2017). Additionally, it is estimated that the global PCB market is growing at an annual growth rate of 3.2% (Awasthi et al., 2017). Recycling metals from these secondary resources compared to their extraction from their naturally occurring ores saves substantial energy of 95% for aluminum, 90% for nickel, 85% for copper, 74% for iron and steel, 60% for zinc, and >80% for plastics (Chakraborty et al., 2022; Cui and Forssberg, 2003). Producing 1 ton of Cu from ores typically requires 1400−1700 kg of standard coal, generating 20 tons of wastewater and 3 tons of hazardous materials (Qiu et al., 2020; Zeng et al., 2017). Hence it is worth recovering copper from waste than its naturally occurring ores (Salhofer et al., 2016). The metallic portion within PCBs comprises varying percentages: 8–38% Fe, 10–27% Cu, 2–19% Al, 1–3% Pb, 0.3–2% Ni, along with concentrations ranging from 200–3000 ppm Ag, 20–1200 ppm Au, and 10–300 ppm Pd, all contingent upon the specific electronic device (Arshadi et al., 2018; Arya and Kumar, 2020). So more copper is present in PCBs (10-27%) than their primary ore (0.5-3%) (Abdelbasir et al., 2020). Recycling rate of copper is 43%, which enables the generation of 274 Kt of copper as a secondary resource, substituting the need for primary copper (Graedel et al., 2011). Between 2017–18 and 2021–22, the average copper price remained approximately at 6046 USD per ton. Consequently, the economic potential of copper recovery during this period is estimated at around 2 billion dollars (Panchal et al., 2021). In 2020, global refined copper consumption reached 24.989 Mt, surpassing world mine production, which totaled 20.634 million tonnes of copper metal. Refined copper production stood at 24.51 million tonnes during the same period (International Copper Study Group, 2022). From June 2022 to May 2023, worldwide copper production from mines accounted for 22.088 Mt, whereas refined copper production accounted at 26.461 Mt. The consumption of refined copper amounts to 26.527 Mt (“Monthly Summary on Minerals & non-ferrous metals, July 2023, Government of India, Ministry of Mines,” 2023). We can clearly see a gap in the demand and supply of copper where the consumption is higher than the production. So copper can be recovered from secondary resources, replacing the need for primary copper. Besides, according to International Copper Study Group's (ICSG) estimation, the Electrical and Telecommunication Industry comprises 56% of the total consumption of copper produced worldwide, followed by Transport (8%), Consumer Durables (7%), Building & Construction (7%), General Engineering goods (6%), and other industries, including Process Industries (16%) (IBM (Indian Bureau of Mines), 2023). Thus, recovering Cu from WPCB recycling offers a triple benefit:

conserving primary resources, reducing solid waste, and preventing environmental pollution caused by Cu release.

1.4. E-waste recycling techniques

Various recycling practices have been developed to address the challenges in the recovery of materials from PCBs (*Figure 1.5*), which are widely divided into three stages: pretreatment stage, physical recycling stage, and chemical recycling stage (Sohaili et al., 2012).

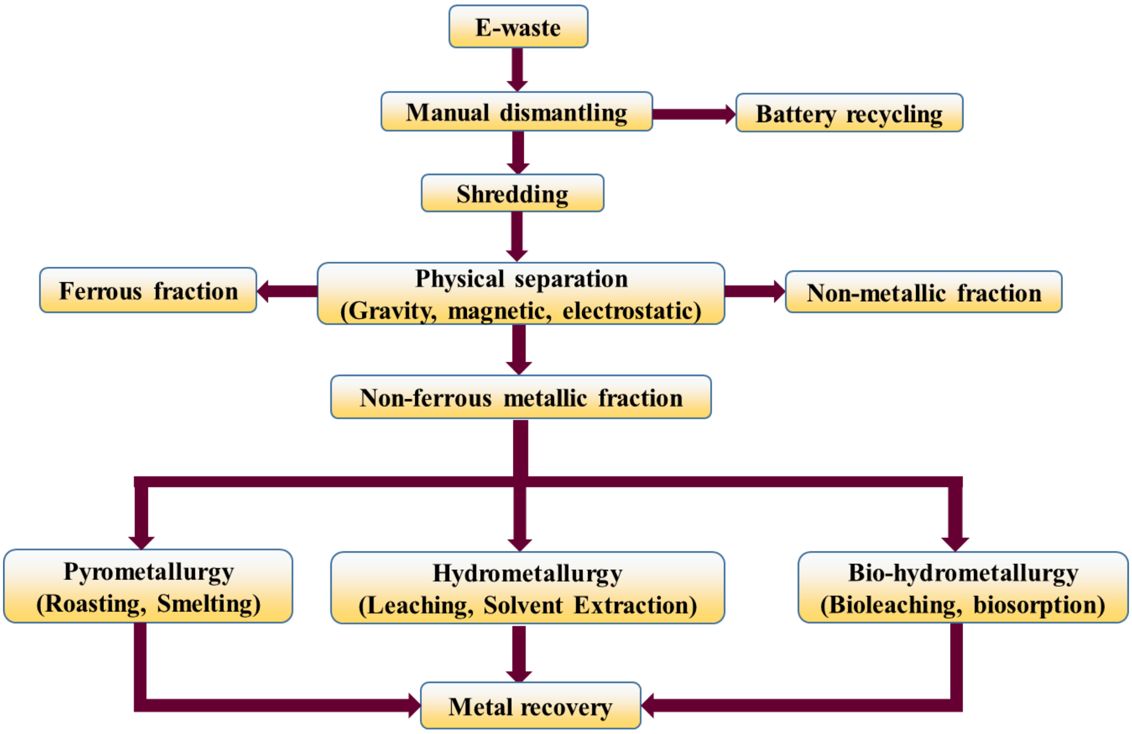

Figure 1.5 Overview of stages involved in metal recycling from electronic waste (Rao et al., 2020)

1.4.1. Pretreatment of e-waste

The pre-separation treatment of scrap electronics consists of disassembly, desoldering, dismantling, and physical processing techniques. Disassembly is done to remove the reusable and hazardous components of WPCB. Here specific components are selectively disassembled by either the “look and pick” principle or by heating the PCB to desolder components from the board (Rao et al., 2020). After manual separation, the remaining WPCB is subject to the physical processing stage, which consists of crushing, shredding, and grinding to reduce the size and liberate the metals from the non-metals. For maximum separation, e-waste should be milled to fine particle size, generally below 5 or 10 mm. PCBs do not have a specific size fraction to help the liberation of metals due to their complex composition (Koyanaka et al., 1999). Mechanical recycling practices for upgrading scrap electronics have been reported by Cui and Forssberg (Cui and Forssberg, 2003). Ball milling to pulverize the WPCBs to finer powder is also reported (Hanafi et al., 2012).

1.4.2. Physical recycling

The physical recycling techniques followed to recover the NMF without any metal loss are based on particle shape (density separation), electrical conductivity (eddy current separation) and magnetic properties (magnetic separation). 95% of metals have been recovered by the density separation route (Peng et al., 2004). There is a need for multi-stage electrostatic separation to effectively separate conductors from semi- and non-conductors (Xue et al., 2012). The efficiency of corona separation reduces with finer or larger particle size (Li et al., 2007). Eddy current separation is more favourable than corona separation as eddy current-based electrostatic separation aids the separation of ferrous and non-ferrous metals and plastics from the plastic-metal mixture (Schlett et al., 2002). Also, both fine and coarse particles can be subject to eddy current separation. Low-intensity drum separators are used to recover magnetic materials from non-magnetic fractions of uncrushed PCBs (Ghosh et al., 2015). So magnetic separation is followed by grinding and electrostatic separation of fines (Yoo et al., 2009). There may be potential loss of precious metals associated with the above-stated physical separation routes. Besides, they incur high operating costs from the energy and economic viewpoint. So, researchers have proposed optoelectronic sorting as an alternative new physical separation method. Here x-rays are used to sort materials and separate BFRs from heavy metals by laser-induced breakdown spectroscopy and x-ray fluorescence analysis (Vermeşan et al., 2020).

1.4.3. Chemical recycling

Chemical recycling delaminates the PCBs to separate organic and metallic parts by decomposing polymers into monomers by chemical reactions (Kaya, 2016). It includes pyrolysis, gasification, and the application of supercritical fluids (Guo et al., 2009). Further separation of metallic fraction from the non-metallic fraction is done by following metallurgical routes such as pyrometallurgy, hydrometallurgy, and biometallurgy (Rao et al., 2020).

1.4.3.1. Incineration, Pyrolysis, and Gasification

Incineration is the burning of waste in the presence of oxygen, whereas pyrolysis is the degradation of material by heating in the absence of oxygen to recover energy and other valuable materials. The epoxy resin in scrap PCB can be thermally cracked to its original form of energy, i.e., fuel oil by pyrolysis. Pyrolysis is a chemical recycling route for treating non-metallic fractions in PCBs, accomplished at the 200-700°C temperature range in fixed or fluidized bed reactors (Chien et al., 2000). During pyrolysis, plastics degenerate to solid char, oil, and gases which can be later transformed into top-grade fuel products and chemical feeds (De Marco et al., 2008; Jadhao et al., 2020; Panda et al., 2020). Pyrolysis of WPCBs generates nearly 77-81 wt% solids, 5-18 wt% oil, and 5-14 wt% gases (De Marco et al., 2008). The distribution of pyrolysis products depends on the pyrolysis temperature, residence time, and the type of reactor used, with particle size having no significant effect on pyrolysis (Chiang et al., 2007). However, this process involves the formation of toxic compounds at elevated temperatures and is costly due to the association of high energy and consumption of reagents. The gaseous products formed are identical for both pyrolysis and gasification (Havlik et al., 2010). Phenolic boards of PCBs were subjected to steam gasification in the presence of ternary LNK carbonate mixture (Li_2CO_3, Na_2CO_3, K_2CO_3) at 823-948 K to yield clean hydrogen gas (Salbidegoitia et al., 2015).

1.4.3.2. Super critical fluids systems

Sub- and supercritical fluids and organic solvents have been explored as an alternative to physical and thermal treatments for the removal of plastics from WPCBs. Supercritical fluids such as water, methanol, isopropanol, acetone, dichloromethane, CO_2 have been reported in the removal of plastics from PCBs (Wang and Xu, 2014).

The main motive behind PCB recycling is the recycling of metals which is done by techniques such as pyrometallurgy, hydrometallurgy, and bio-hydrometallurgy.

1.4.3.3. Pyrometallurgy

Pyrometallurgy includes incineration, smelting, melting, sintering, etc. (Rao et al., 2020). Here the solid waste is melt, resulting in the slag formation into which precious metals are accumulated. Pyrometallurgy focuses on the production of precious metal-loaded copper bullion from which high-purity copper can be extracted by electrolytic refining technique (Tuncuk et al., 2012). In this process, only a partial separation of metals is achieved, so other processes such as hydrometallurgy and electrochemistry are required (Cui and Zhang, 2008). Vacuum metallurgy separation is an effective method for recovering heavy metals such as Sb, Pb, Cd, or Bi (Zhan and Xu, 2009).

1.4.3.4. Hydrometallurgy

Hydrometallurgy is more exact, easily controllable, predictable, and more environment-friendly than pyrometallurgy. Hydrometallurgy routes involve leaching in specific reagents followed by purification methods such as cementation, solvent extraction, and ion exchange to separate and concentrate preferential metals from the leach liquor. Cyanide leaching, being highly toxic, is not used nowadays. Acid leaching is mainly used among all chemical leaching processes (Pant et al., 2012). Leaching using mineral acids and oxidants such as HCl, H_2SO_4/H_2O_2, HNO_3, $HClO_4$, aqua regia, sodium hypochlorite has been extensively reported. Selective recovery of copper, gold, and nickel has been studied using nitric acid leaching followed by solvent extraction (Rao et al., 2021). Precipitation is predominantly used to recover metals after leaching. Electrowinning can refine metals during the recovery stage after chemical leaching (Sethurajan et al., 2019). Recently some studies have compiled the techniques for metal recovery from scrap electronics using hydrometallurgy (Pant et al., 2012). Thiourea and thiosulfate leachings are greener processes, while other methods using ligands, etchants, or bioleaching are in the developing stage. Chemical leaching involving complexation of ligands with metals using chelating agents such as EDTA (Cheikh et al., 2010), DTPA (Hong et al., 2002), NTA (He et al., 2011), oxalate (Elliott and Shastri, 1999), which have been studied for extraction of metals from soil can be applied for the recovery of metals (Cu, Pb, Cr, Zn) from ores and e-waste. Hydrometallurgical etching using chemicals such as HCl, $FeCl_3$, and $CuCl_2$ has been used to recover precious metals (Barbieri et al., 2010). Studies involving organic solvents for the recovery of heavy metals such as Cu, Ni, Al, Fe, Au, and Ag have also been reported (Lee et al., 2009). Treatment of WPCB by green solvent ionic liquid has been reported. In one such study WPCBs were dissolved in $[EMIM^+][BF4^-]$ for delamination of PCBs to separate copper foils and glass fibers (Zhu et al., 2012b, 2012a).

1.4.3.5. Bio-hydrometallurgy

Bio-hydrometallurgy is predominantly used for recovering metals such as copper and gold from WPCBs because of low cost, low energy consumption, and less pollution (Cui and Zhang, 2008). Bio-hydrometallurgy is mainly bioleaching and biosorption (Zhang and Xu, 2016a). Bioleaching uses acidophilic bacteria, mostly ferrooxidans and thiooxidans to solubilize metals such as Cu, Al, Zn, and Ni (Yang et al., 2014). *Desulfovibrio desulfuricans* are used to recover Cu, Au, and Pt from e-waste (Creamer et al., 2006). The particle size of the milled PCBs influences bioleaching as it affects the duration of leaching. Biosorption is a physicochemical process involving chelation, ion exchange, complexation, and coordination for the recovery of metals from solution using biological materials such as yeast, fungi, and algae (Zhang and Xu, 2016b). Researchers have reported recovery of 99% Au by biosorption (Tasdelen et al., 2009).

1.4.3.6. Other greener treatments

Cryo-milling has been lately explored for recycling metals from WPCBs (Tiwary et al., 2017). This mechanical process involves low-temperature ball milling, which degrades the PCB into nanoparticles from which metals can be separated. This route is scalable and environment-friendly as it generates minimum waste and involves low operating temperatures. Due to its high separation selectivity ability, membrane filtration is a developing green approach for extracting metals from PCB solutions (Chauhan et al., 2018; Jha et al., 2020). The interwoven metallic and non-metallic layers in a PCB bonded with halogenated epoxy resin can be delaminated by organic solvents such as dimethylformamide and dimethylacetamide (Verma et al., 2017a, 2017b, 2017c).

1.5. Non-metallic fraction recycling

The non-metallic fraction (NMF) represents a significant part of WPCB mass (nearly 60%). While techniques such as float-sink and triboelectric separation have been developed to recycle NMF, most studies focus on the direct recovery of metals due to the complexity and low economic benefits of NMF recycling (Vermeşan et al., 2020). The recovered metal and non-metal can help mitigate the shortage of material resources for the electronics industry and composite materials application (*Table 1.1*).

Table 1.1 Broad use of recycled components of different parts of WPCBs

Part of WPCB	End-use	Ref.
Enriched multi-metal fraction	Raw material feed to metallurgy plants say copper smelting plants	(Yang et al., 2012)
Non-metallic fraction	Modified phenolic molding compounds, non-metallic plates, filler for sound-absorbing material, reinforcing material in production of flame retardants and construction materials	(Yang et al., 2012; Zhu et al., 2016)
Recovered woven fiberglass layers	Filler to improve the mechanical behavior of wood, plastic, and concrete composites	(Sommerhuber et al., 2016)
Recovered epoxy resin	Composite structural materials	(Chen et al., 2019)
Recycled polymers and plastics	Wood-plastic composites	(Sommerhuber et al., 2016)

1.6. High added-value products recovered from e-waste

Recycling with the sole motive of end-of-life (EoL) waste treatment is not an attractive scenario in developing countries where economic benefits supersede environmental obligations. It is necessary to shift from WPCB recycling to remanufacturing stage to re-utilize the recovered metal as starting raw material to synthesize higher valued products and marketable commodities, say nanoparticles (Dutta et al., 2018). Such initiatives would help realize a circular economy's objective for the huge quantity of electronic scrap generated annually. Hence closing the materials loops, reducing inputs, reuse, and recycling waste to maximize sustainable use of resources, minimizes waste, develop innovative products, and benefits both economy and environment (Bocken et al., 2016; Homrich et al., 2018).

High added-value products are saleable products that have been enhanced with additional properties that make it worth a higher price than the initial raw material used to make it, which here is discarded e-waste. Nanomaterials possess unique properties compared to their bulk counterparts due to considerable surface area, reactivity, shape, size, and morphology (Petit et al., 1990). Hence they are applied in various fields such as catalysis (Judai et al., 2011), bio labeling, detection (Misra et al., 2010), drug delivery system (Patri et al., 2002), removal of pollutants from different media like wastewater and air (Abdelbasir et al., 2020) and others. A bottom-up or top-down approach can synthesize engineered nanomaterials. In a top-down approach, the bulk material is reduced to nanosize by cutting, grinding, and scattering techniques. It includes laser (pulse) ablation, vacuum vapor deposition, pulsed wire discharge, and mechanical milling. In the bottom-up approach, the nanomaterials are synthesized by atoms, molecules, or clusters. It includes micro-emulsion processes, chemical reduction, microwave-assisted methods, electrochemical, hydrothermal, and biosynthesis (Ealias and Saravanakumar, 2017). The choice of synthetic approach depends on the cost-effectiveness and characteristic properties desired in the nanomaterial, such as size, morphology, crystal structure, etc. (Stankic et al., 2016).

The recovery of nanomaterials from e-waste recycling marked the start of a new phase in nanotechnology. E-waste used for obtaining nanomaterials includes PCBs of mobile phones, computer motherboards, Television (TV) board; solders of PCBs; waste etchants generated in the manufacturing of PCBs; rejected organic solar cells; Low temperature co-fired ceramic (LTCC) scrap; electrical components mounted on PCBs such as capacitors, memory slots, through-hole solder joints (THSJs); compact discs; glass components of monitor screens and plastic shells of computers; waste toners derived from printer cartridges, etc. Recovered high purity metals have been reported in *Figure 1.6*. In the forthcoming section we summarize the reported literature on the recovery and synthesis of various high added value products (HAVP) i.e. nanomaterials in the form of nanoparticles, nanostructured alloys, nanocomposites, microparticles from various forms of electronic scraps. Literature related to battery recycling is not included in this section.

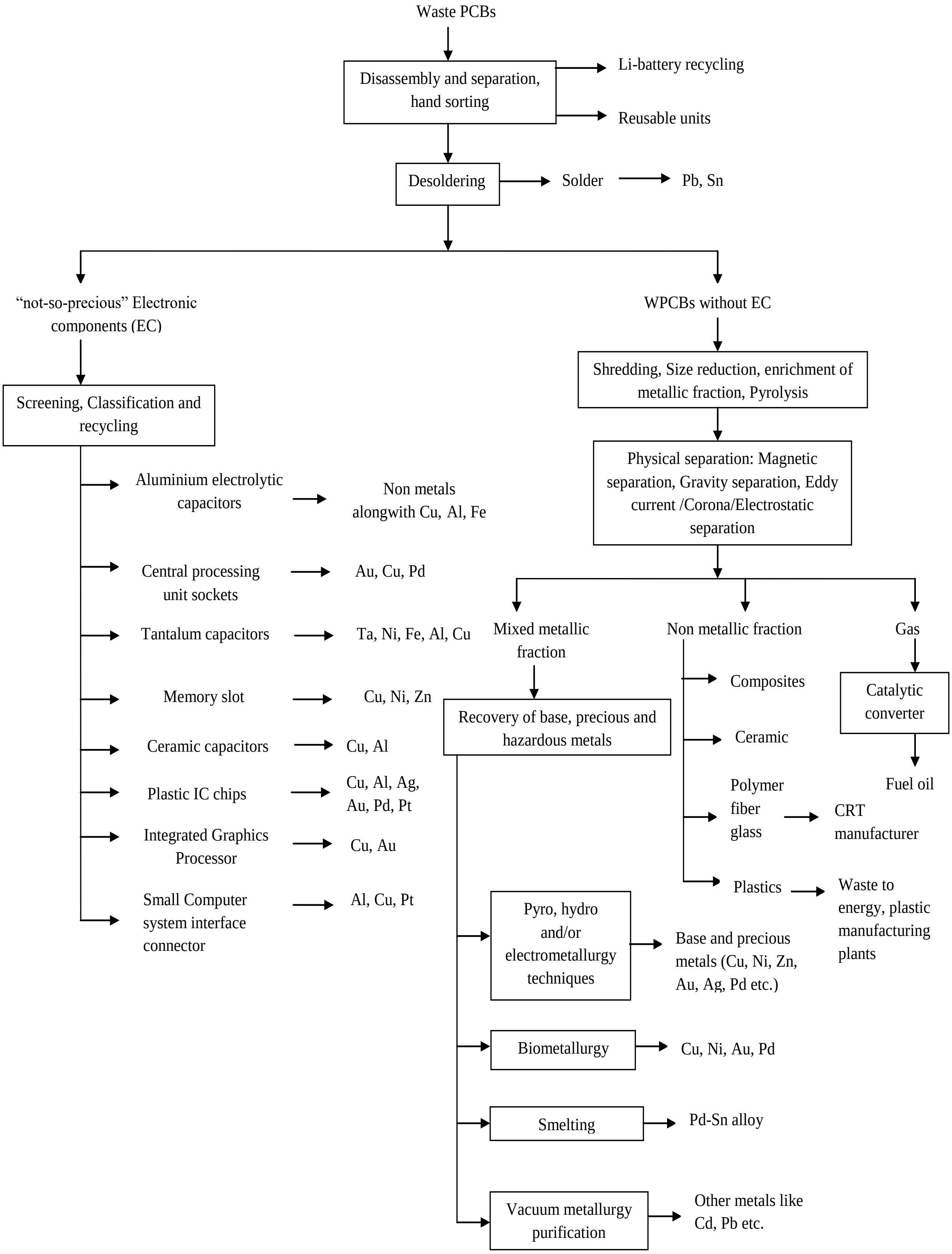

Figure 1.6 Integrated process for the recycling of PCBs (based on the work of (Gautam et al., 2022a; Nayak et al., 2019; Wang and Xu, 2017; Wang et al., 2016))

1.6.1. *Precious metal nanoparticles*

PCBs contain less than 1 wt% of precious metals, but they account for nearly 80% of their total intrinsic value, making precious metal recovery from electronic waste essential. Gold is widely used in electrical and electronic devices components because of its ductility, high electrical conductivity, and resistance to oxidative corrosion (Akcil et al., 2015; Vats and Singh, 2015). The sustainability of gold is of great concern as the grade of gold ore is declining (Mudd, 2007). So there is a need to develop techniques to recycle gold from gold-containing wastes.

Gold nanoparticles (20 nm) and 98 wt% of the silver present have been recovered along with high purity precious metals from PCBs through aqua regia leaching. 93 wt% of the input palladium is collected as red $Pd(NH_4)_2Cl_6$ precipitates. 97 wt% of input gold is selectively recovered via liquid-liquid extraction with toluene. Gold NPs are obtained after adding dodecanethiol and sodium borohydride solution (Park and Fray, 2009).

Gold NPs have been synthesized from PCBs of personal computers in four steps. Firstly, the PCBs were leached in H_2O_2-H_2SO_4 solution, followed by leaching in microwave-assisted aqua regia. The Au(III) was adsorbed in Mg/Al-hydrotalcite and desorbed in NaOH solution. Gold from desorption solution was used to synthesize gold nanoparticles using glutamic acid and trisodium citrate (Alfanaar et al., 2020). Oestreicher et al. proposed a series of physical and chemical recycling steps to recover gold from microprocessors of discarded computers and synthesize stable gold NPs. Gold was concentrated in the metallic fraction by milling and magnetic separation. Two-step hydrochloric acid leaching was performed to obtain Au (III) rich solution. Gold NPs with spherical and triangular-shaped morphology were synthesized by following a combination of reducing agents sodium citrate and ascorbic acid and PVP as a stabilizing agent. This e-waste upcycling study demonstrates the use of e-waste as secondary raw materials to obtain valuable nanomaterials for the sustainable development of nanotechnologies (Oestreicher et al., 2020).

Finer gold nanoparticles from worn electronics have been reported using phospholipids stabilized electrochemical extraction. The electrodes made of waste containing gold were immersed in HEPES buffer solution containing dispersed DOPC phospholipid, and AC voltage was applied to the electrodes for 5 sec. The prepared spherical gold NPs with a mean diameter of 13.9 nm demonstrated good potential for biomedical applications and catalysis (Moriwaki et al., 2017).

Gold has been bio-extracted from nitric acid pretreated electronic scrap material using a cyanogenic bacterium *Chromobacterium violaceum*. The bio-leached gold is mineralized using the *Delftia acidovorans* bacterium to get spherical crystalline precipitate with an average size of 31±2 nm (Das et al., 2017). In another study, spherical crystalline gold nanoparticles with an average size of 22±0.2 nm were generated by the bacterium *Delftia acidovorans* using invitro reduction of thiourea leachate from electronic scrap material (ESM) (Das and Ting, 2017).

Gold nanoparticles have been prepared from gold-containing scrap (transistor pins) of electronic waste. The pins were dissolved in chloronitric acid, followed by gold ion concentration by a floto-extraction method and their reduction by glucose in direct micelles of cationic amphiphile, resulting in the formation of 100 nm aggregates of gold nanoparticles. The nanosized gold was used as a catalyst in polypyrrole polymerization from pyrrole with a yield of 95% (Mirgorod et al., 2014).

Multilayer ceramic capacitors (MLCCs) used in various electronic devices contain most of the palladium used in a single computer PCB (Delfini et al., 2011). Palladium NPs are recovered from waste MLCCs by enrichment and a two-step electrodeposition route. Pd is first enriched by the copper capture method, then separated, leached in nitric acid, and purified using the potential-controlled electrodeposition technique. High-purity Pd (>99%) is recovered with a 99.02% recovery rate. Electrodeposited Pd has a grain size of about 20 nm (Liu et al., 2020).

Tin oxide and silver NPs have been synthesized by ultrasound assistance and microwave irradiation of nitric acid-leached PCB solution (Cerchier et al., 2017a). After precipitation of SnO_2, hydrochloric acid was added to the leached solution, inducing silver chloride precipitation. Silver chloride was further reduced to metallic silver NPs in ammonia solution by adding glucose syrup as the reductant and the capping agent. The SnO_2 NPs were <10 nm in size, while the Ag NPs obtained were approximately 2 nm and 0.7 nm with microwave and ultrasound assistance, respectively. Microwaves and ultrasound irradiations produce NPs by reducing the particle dimensions due to micro-cavitation and localized hotspot heating effects (Bang and Suslick, 2010).

Solar cell wafers (SCWs) consist of Si substrate, Ag electrode tracks, Al electrode layer, an anti-reflective coating (Lee and Ebong, 2017). Al nanocrystals, Si microparticles, and Ag have been recovered from rejected SCWs (RSCWs). Ag is recovered as AgCl with a 98% recovery rate by ultrasound-assisted nitric acid leaching of broken RSCWs and subsequent addition of HCl. Al nanocrystals with an average 25 nm size and yield>91% are separated from the leached solution by centrifugation. Si is recovered as high purity micro powder with 50 µm average size, at a recycling rate >98% by micro-filtration of the leached solution followed by purification with fluoric acid (HF) etching. The recovered Si microparticles and Al nanocrystals can be used as catalysts, metal alloys, drug delivery systems, lithium-ion batteries, etc. (Yousef et al., 2018a).

Joda and Rashchi reported the recovery of silver (87 wt%) and copper (98 wt%) by leaching personal computer board scraps. Nitric acid, hydrochloric acid, aqua regia, potassium persulfate, and ammonium persulfate were tested as leachates. The leaching process was improved using response surface methodology (RSM). With nitric acid leaching, ultrafine-grained silver particles were obtained by precipitation, and copper NPs were obtained by electrowinning (Naseri Joda and Rashchi, 2012).

Isotropic silver nanoparticles were obtained from a mixture of spent PCBs, processors, mobile phones, and TV boards. Two routes were followed: an electrokinetic route in which silver metal recovered from nitric acid leached solution of e-waste was deposited on carbon substrate; another chemical adsorption route in which silver nitrate solution is adsorbed on the carbon substrate followed by reduction with hydrazine hydrate. Hydrazine hydrate reduced silver nitrate to yield nanosized silver metal (4-10 nm) (Rabah, 2013).

The Asia-pacific region is the largest producer of Ag-bearing LTCC products and LTCC industrial waste scrap during fabrication. LTCC e-wastes are recovered from multichip ceramic modules, radio frequency microwave circuits, sensors, and MEMs (Gongora-Rubio et al., 1999, 2001). 99% of submicron silver powder could be recovered from Ag-containing LTCC scrap. Silver was selectively precipitated as AgCl by leaching in HCl. The precipitates of AgCl were further dissolved in ammonium hydroxide and reduced to pure metallic silver nanopowder using hydrazine as a reducing agent, polyvinyl pyrrolidone (PVP) as a stabilizer, polyethylene glycol (PEG) as both reductant and stabilizer (Swain et al., 2018).

1.6.2. *Base metal and base metal oxide nanoparticles*

1.6.2.1. Copper nanoparticles

High purity copper nanoparticles were synthesized from the WPCBs of desktop computers via electrospinning. The obtained copper NPs have a small average diameter of ~5 nm and narrow size distribution ±2 nm with a honeycomb-like structured layer (Yousef et al., 2018b). These NPs show antimicrobial activity and can have applications in electronics, sensors, optics, medicines, catalysis, and solar/photovoltaic energy conversion. Zhu et al. synthesized high purity nano-copper bearing particle size 10-50 nm from WPCBs by physical enrichment and ammoniacal/ammonium chloride solution leaching and reduction by ascorbic acid under ultrasonic condition. The physical recycling route consisted of gravity separation, mechanical grinding of concentrate, and flotation to remove impurities (X. Zhu et al., 2021).

Antibacterial copper nanoparticles were investigated by Tatariants et al.. In this study Cu foils were liberated from three types of as-received WPCBs of a motherboard, video card, and random access memory (RAM) by the BER dissolution ultrasonic treatment recycling approach using DMF. The recovered copper foils were leached in nitric acid to give $Cu(NO_3)_2$. Subsequently, sodium hydroxide was added to produce copper hydroxide, to which sulphuric acid was added to form copper sulfate. Aqueous $CuSO_4$ solution was chemically reduced by ascorbic acid and β-NCD stabilizer to synthesize Cu-NPs. Quasi-spherical NPs of average 7 nm size were obtained. Cu-NPs synthesized from the RAM sample exhibited good antimicrobial activity (Tatariants et al., 2018).

El-Nasr et al. selectively extracted copper by leaching PCB powders of obsolete computers in ammoniacal/ammonium salt solutions. Spherical copper NPs with particle size range 5-

32 nm were synthesized from the leachate solution using L-ascorbic acid reductant and CTAB surfactant at room temperature (Seif El-Nasr et al., 2020). Cerchier et al. recovered pure copper from a nitric acid leached solution of PCBs of spent mobile phones by cementation with iron. The copper dissolved in nitric acid was neutralized with sodium hydroxide, and metallic copper NPs were synthesized via ultrasound-assisted reduction with L-ascorbic acid and sodium borohydride reducing agents. The Cu NPs have dimensions ~5 nm and remain stable in the solutions for days (Cerchier et al., 2017b).

Adsorption combined with cementation has the potential to prepare self-assembled nanostructured metals. Ultrafine copper powders have been recovered from ammoniacal spent etching solutions of PCBs by cementation on helical iron scrap chips. Self-assembled copper nanocubes of 200 nm size with >99% purity have been obtained (Fouad and Abdel Basir, 2005).

The improper disposal of waste etchants generated from printed circuit board fabrication units leads to environmental problems and economic losses (Misra and Pandey, 2005). Copper NPs have been recycled from copper-containing waste etchant solution via a microemulsion process with sodium borohydride ($NaBH_4$) at controlled ambient conditions. These were used in Cu-based nanofluids to improve the heat exchange system thermal conductivity (Mdlovu et al., 2018).

Copper from worn PCBs can be reprocessed as NPs via bioleaching using *Ocimum sanctum* (tulsi) leaf extract as a reducing agent. The as-obtained spherical, relatively uniform Cu NPs with an average size of less than 20 nm are used to decolorize synthetic dyes and treat industrial effluents (Swarnambiga et al., 2019). Spherical copper nanoparticles have been synthesized using the leaf extracts of *Lantana camara*, a weed mostly found in Maharashtra, and microorganisms *Fusarium oxysporum* and *Pseudomonas* sp. under ambient conditions. Particle size studies show that *Pseudomonas* sp. leached out copper NPs of size 84-130 nm, whereas *F. oxysporum* leached out copper NPs in size range of 93-115 nm (Majumder, 2012). Such eco-friendly NPs can be applied in antimicrobial, wound healing, and electronic applications, making this green chemistry approach potentially exciting for large-scale synthesis of other inorganic NPs, hence justifying 'Waste to health'. This study sets an example of the bioremediation of copper.

Nascimento et al. synthesized polymetallic nanoparticles from PCBs (PN-PCBs) via a chemical reduction route. The PN-PCBs were potentially tested for the removal of reactive blue 4 (RB4), a textile dye. The spent PCBs were crushed, hammer milled and digested in a potassium persulfate/sulphuric acid system. NaOH solution was added to adjust the pH of liquor to 3, followed by the addition of reductant sodium borohydride. The obtained polymetallic NPs which consisted of Cu, Ni, Zn, and Fe metals exhibited spherical morphology with 30 nm diameter, 693 m^2g^{-1} surface area (Nascimento et al., 2018).

1.6.2.2. Copper-based nanostructured alloys

Direct transformation of WPCBs to useful alloys saves energy, preserves valuable resources, and prevents environmental pollution. In this context, copper-based alloys (*Table 1.2*) i.e., Cu-Sn, Cu-Ni-Sn, have been synthesized via thermal transformation and mechanical alloying from PCB scraps.

Table 1.2 Nanostructured alloys recovered from waste PCBs

HAVP	**E-waste source**	**Process of recovery**	**Size obtained**	**Morphology**	**Recovery (%)**	**Property/ application studied**	**Ref.**
Cu-Sn, Cu-Ni-Sn	PCB	Thermal transformation at 500°C	-	-	-	Electrical conductivity	(Ulman et al., 2018)
Cu79-Zn13-Fe3-Sn3-Ni1	WPCB of motherboards and modem board	Solid-state mechanical alloying	40 nm	-	-	Electrical conductivity (nanofluid)	(Nekouei et al., 2018)
CuNi	PCB of computers + NiMH battery	Thermal transformation at 1550°C, reduction	-	-	-	-	(Farzana et al., 2019)
Cu-Sn NPs	PCB	Selective thermal transformation of cryo-milled PCB at 900°C	<500 nm	-	-	-	(Shokri et al., 2017)
Cu-Fe-Sn	50% e-waste of computers + 50% waste copper slag	Thermal heating at 1350°C in air	-	-	-	-	(Kim et al., 2009)

En dash (-) indicates data unavailable or not reported in respective literature

1.6.2.3. Copper oxide NPs

Ultrafine copper materials were prepared from waste PCBs by the supercritical methanol (SCM) method after two succeeding nitric acid pretreatments. A mixture of spherical irregular-shaped zero-valent copper and Cu_2O with particle diameter in the range of 50-500 nm was obtained (Xiu et al., 2017).

A size-controlled process for preparing Cu_2O NPs from WPCBs from discarded telephones, PCs, and other electrical equipment is reported by combining supercritical water (SCW) with the electrokinetic (EK) process. Spherical, uniform, pure Cu_2O NPs with particle size 5-40 nm are obtained with nanoparticle stabilizer PVP. Copper is selectively leached out from powdered WPCBs in ammonia/ammonium salt solutions with 90% yield (Xiu and Zhang, 2012). Rajkumar et al. reported the recovery of CuO NPs from end-of-life SIM cards of mobile phones via wet chemical route and examined its supercapacitive behaviour for application in portable electronic equipment. The SIM cards were leached in a 1:1 acid mixture of conc. nitric acid and conc. Hydrochloric acid. Few drops of NaOH were added to precipitate copper oxide which was further calcined at 450°C for 6 hours (Rajkumar et al., 2022, 2020).

Panda et al. dissolved BER from WPCBs and recovered more than 93% copper as cupric oxide nanoparticles by ammonium chloride roasting of PCBs at 275°C for 180 min. Ammonia solution was used to precipitate copper from the leached solution, which was further calcined at 500°C to achieve 98% pure CuO NPs with 100 nm particle length and irregular morphology (Panda et al., 2021).

Yi and Chandren synthesized CuO NPs from waste SIM cards by NaOH precipitation at 100°C, followed by calcination, and utilized it as a photocatalyst for phenol photodegradation. A degradation rate of 58.5% and 45.3% was observed under visible light and UV light exposure respectively, after 5 h irradiation time (Yi and Chandren, 2022). Ravi et al. developed CuO NPs from WPCBs via a green synthesis route with the involvement of *Cathantharaus roseus* plant extract as reducing agent (Ravi et al., 2023). Zhu et al. fabricated waste-based Cu_2O photocatalyst and investigated the photoreduction of Cr(VI). It exhibited a photocatalytic reduction efficiency of 40.91% (P. Zhu et al., 2021).

1.6.2.4. Nanocomposites

The nanocomposite particle sizes and shapes are determined by the preparation method, precursors used, the relative combinations of the constituent materials, and the calcination temperature. Researchers have reported the synthesis of various nanocomposites, which show promising applications. Cu_2O/TiO_2 nanocomposite was prepared from WPCBs. The WPCBs were initially treated by Super Critical Water Oxidation (SCWO), then introduced into an electrokinetic (EK) system with nano-TiO_2 dissolution as the catholyte. The average size of Cu_2O deposited was about 40 nm. The photocatalytic efficiency of the obtained nanocomposite was examined against methylene blue (MB) degradation. The highest photocatalytic activity was obtained for 6 hours EK treated 4.53 wt% Cu_2O/TiO_2 photocatalyst, which was much higher than commercial photocatalyst P25 (Xiu and Zhang, 2009).

Photocatalytic ZnO/CuO nanocomposites have been synthesized by recycling "not-so precious" electric components, i.e., waste memory slots mounted on discarded computer

PCBs. Nitric acid leaching was followed by alkaline hydrothermal treatment using supercritical water to obtain the metal oxide nanocomposite with shell-core morphology. The recovered nanocomposite showed good visible light photocatalytic behavior in the presence of H_2O_2 against Methyl Orange (MO), a model dye pollutant (Nayak et al., 2019).

Hossain et al. reported a strategy for synthesis of NiO doped CuO nanoflakes from problematic waste flexible PCBs via chemothermal microrecycling technique. Subsequently, the nanomaterial was employed to create a sensor for detecting ammonia at ambient temperature. This sensor exhibited a fast response within 11.7 sec, stable performance, and enhanced selectivity for detecting 200 ppm of ammonia gas at ambient temperature (20°C) (Hossain et al., 2022a). In another study, this NiO-doped CuO nanoflakes were applied for water-splitting application (Hossain et al., 2022b).

1.7. Research gaps

Following the review of literature on extracting added value products from e-waste, several gaps emerged. These gaps pave the way for research directions in the current study, elaborated upon below:

1. It was observed that there are very limited research articles available on the direct recovery of metal oxide (say CuO) from delaminated PCBs. Therefore, more research work is needed in this area to provide an economically significant process for recovery of copper and fabrication of copper oxide nanomaterials from recovered copper.

2. Most of the previous studies (Hossain et al., 2022b; Rajkumar et al., 2022, 2020; Yi and Chandren, 2022) have used concentrated acid (mixture of nitric acid and hydrochloric acid) and alkali solution (sodium hydroxide) to leach the metal content and precipitate copper oxide from the solution respectively. Therefore, a combination of methods needs to be developed for the genesis of copper oxide nanoparticles from WPCBs of computer motherboards by combining leaching, precipitation, and calcination of the dried powder.

3. Very limited research has been conducted on the recovery of added-value material from purified stripped solution obtained after selective extraction of valuable metals from PCBs. Therefore, more research work is needed in this area to provide an integrated method for recovery of copper oxide nanostructure from WPCBs of mobile phones.

4. Application of waste-derived copper oxide nanoparticles for supercapacitor material (Rajkumar et al., 2022, 2020), Cr(VI) degradation (P. Zhu et al., 2021), and phenol degradation (Yi and Chandren, 2022) has been reported. Other potential applications can be explored.

1.8. Research objectives

1. **To maximize the recovery of copper from WPCBs of computer motherboards using hydrometallurgical route.**

A one-stage leaching method was developed for recovery of copper from waste PCBs of computer motherboards. Various leaching parameters such as time, temperature, concentration of leaching reagent, pulp density, and stirring speed were optimized to maximize the recovery of the target metal (copper) with desired purity.

2. **To recover Copper oxide nanoparticles from recovered copper without the use of any chemical precursor.**

A facile method was developed to fabricate copper oxide nanoparticles from the pregnant leach solution, without the use of any chemical precursor as initial starting material for copper source or any chemical source as surfactant, substrate, template, or particle size stabilizer.

3. **To investigate its photocatalytic activity by studying degradation behaviour of textile dyes.**

The as-recovered nanoproduct is further explored as a potential photocatalyst for degradation of textile dyes, here congo red and methylene blue, in presence of visible light.

4. **To fabricate nanostructures from purified strip solution obtained after selective extraction of valuable metals from mobile phone PCBs.**

A sustainable CuO nanoparticle and hybrid $Cu(OH)_2$/CuO nanostructure recovery process from the Cu-rich strip solution of spent mobile phone PCBs is investigated. Here also, no chemical precursor, surfactant, substrate, template, particle size stabilizer is used for nanoproduct synthesis.

1.9. Organisation of the thesis

The overall thesis is divided into 7 chapters followed by scope of future work, references, and publications/conferences details. A brief about each chapter is discussed in the following paragraphs.

In the preceding sections, **Chapter 1** provided an overview of e-waste, printed circuit boards, copper recovery, recycling methods, and the diverse range of valuable materials obtained from e-waste. Extensive scrutiny was given to literature on recovering high added-value materials from different components of e-waste, particularly focusing on the retrieval of value-added products based on copper. After reviewing the literature, the study pinpointed an existing research gap, from which the objectives of this study were derived.

Following the establishment of the objectives for this project, the experiments were devised. **Chapter 2** elaborates extensively on the materials and methodologies utilized for the retrieval of the desired value-added nanoproducts. To begin with, the information regarding the assortment of diverse raw materials essential for conducting the experiments is provided. Following that, a detailed description is provided regarding the experimental procedure employed for both synthesis and the subsequent measurement of photocatalytic activity during the experiments. The varied characterizations and chemical analysis methods employed for examining liquid, solid, and powder samples after each stage are succinctly addressed. These methods include atomic absorption spectroscopy (AAS), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), Scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectroscopy (EDS), High-resolution scanning electron microscopy (HR-SEM), Transmission electron microscopy

(TEM), X-ray photoelectron spectroscopy (XPS), surface area measurement using the BET method, solid-state UV-visible reflectance spectrophotometry, and UV-visible spectrophotometry.

The outcomes of this study are categorized into four chapters spanning from chapter 3-6. In **Chapter 3**, results of copper and zinc recovery from waste printed circuit boards of computer motherboards is described. Firstly, the results of pre-processing (to separate the metallic fraction and non-metallic fraction) and characterization of printed circuit board and its separated metallic fraction are presented in detail to understand it’s structure. After this, the outcomes of copper recovery are described for the chosen recovery pathway i.e. nitric acid leaching route. The study's optimization results concerning the acidic leaching route are outlined. Kinetic study findings are deliberated upon to elucidate the leaching mechanism and ascertain the activation energy for the reaction. A comprehensive description is provided regarding the outcomes of copper and zinc recovery subsequent to leaching.

In **Chapter 4**, results of genesis of copper oxide nanoparticles from copper-rich solution is described. The pregnant leach liquor obtained after acidic leaching route was processed for selective precipitation of copper, and further synthesis of copper oxide nanoparticles. The as-recovered nanoproduct is characterized by various techniques to confirm its structure, phase, shape, size, morphology, surface area, and associated bandgap energy.

In **Chapter 5**, results of evaluation of photocatalytic behaviour of synthesized nanoproducts are described in detail. In this regard, the as-synthesized nanoparticles are used to degrade textile dyes congo red and methylene blue. The reason behind the photocatalytic behaviour of the nanoparticles is also mentioned.

In **Chapter 6**, the recovery of $Cu(OH)_2$/CuO and CuO nanostructures by alkaline precipitation and low-temperature aging methods from strip solution originated from laboratory-scale spent mobile phone printed circuit board recovery process is explored. The recovered nanostructure is characterized to confirm its phase, shape, morphology, and associated bandgap energy. The as-synthesized nanostructures were assessed of their photocatalytic activity by verifying rhodamine blue degradation.

Towards the end, **Chapter 7** encapsulates the major conclusions derived from the present research endeavour. Subsequently, it delves into the prospects for future work, includes the bibliography encompassing cited references, and provides information regarding publications and conference details.