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Advancements in the treatment and processing of electronic waste with sustainability: a review of metal extraction and recovery technologies

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The amount of electronic waste (e-waste) globally has doubled in just five years, from approximately 20 million tons to 40 million tons of e-waste generated per year. In 2016, the global amount of e-waste reached an all-time high of 44.7 million tons. E-waste is an invaluable unconventional resource due to its high metal content, as nearly 40% of e-waste is comprised of metals. Unfortunately, the rapid growth of e-waste is alarming due to severe environmental impacts and challenges associated with complex resource recovery that has led to the use of toxic chemicals. Furthermore, there is a very unfortunate ethical issue related to the flow of e-wastes from developed countries to developing countries. At this time, e-waste is often open pit burned and toxic chemicals are used without adequate regulations to recover metals such as copper. The recovered metals are eventually exported back to the developed countries. Thus, the current global circular economy of e-waste is not sustainable in terms of environmental impact as well as creation of ethical dilemmas. Although traditional metallurgical processes can be extended to e-waste treatment technologies, that is not enough. The complexity of e-waste requires the development of a new generation of metallurgical processes that can separate and extract metals from unconventional components such as polymers and a wide range of metals. This review focuses on the science and engineering of both conventional and innovative separation and recovery technologies for e-wastes with special attention being given to the overall sustainability. Physical separation processes, including disassembly, density separation, and magnetic separation, as well as thermal treatment of the polymeric component, such as pyrolysis, are discussed for the separation of metals and non-metals from e-wastes. The subsequent metal recovery processes through pyrometallurgy, hydrometallurgy, and bio-metallurgy are also discussed in depth. Finally, insights on future research towards sustainable treatment and recovery of e-waste are presented including the use of supercritical CO_2.

1. Introduction

Electronic waste (e-waste) is one of the most rapidly growing waste segments in the world and has become the fastest growing waste segment in the United States (U.S.). Currently, half of the world's population is online: 3.6 billion people are on the internet out of 7.4 billion people in the world, and this number will undoubtedly grow in the next few years.[1] The number of discarded computers, phones, and other appliances, often defined as Waste Electrical and Electronic Equipment (WEEE), doubled between 2009 and 2014 to 41.8 million tons per year globally and reached 44.7 million tons per year in 2016. Based upon detailed projections, the total amount of WEEE could exceed 50 million tons by 2021.[1–3] Fig. 1 illustrates these statistics and the projected trend of total global e-waste generation.

The Environmental Protection Agency (EPA) estimates that only 15–20% of e-waste is recycled, most recently reporting that only 20% of e-waste was recycled in 2016. The rest of the waste goes directly into landfills and incinerators. Safe disposal and poor regulation are two major concerns with regards to the management of e-waste, as the majority of e-waste is transported to poor, developing nations, such as China, India, and Africa.[4] In fact, 80% of e-waste in the United States (U.S.) is exported to Asia.[5] Africa has few to no laws on e-waste, and China and India have inefficient and inconsistent e-waste regulation. Fig. 2 depicts the flow of e-waste, as well as the top

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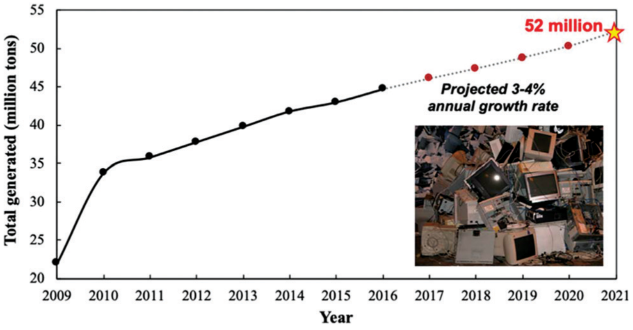

Fig. 1 The total amount of e-waste generated from 2009–2016 and projections. Data taken from ref. 1–3.

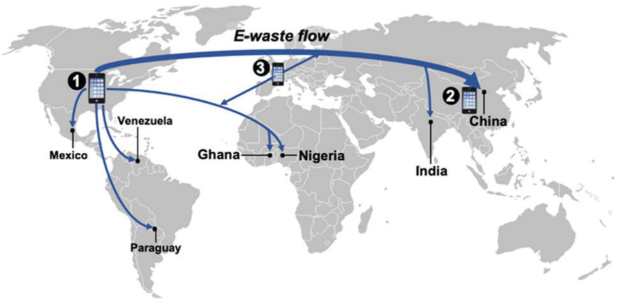

Fig. 2 The global flow of e-waste and the top three producers of e-waste, U.S., China, and Europe. Adapted from ref. 6.

three producers of e-waste, the U.S in first place, followed by China and Europe.[6]

Currently, disposal factories tend to recycle the non-toxic, valuable components of e-waste (metals) and release the toxic components into the surroundings, creating both human health and environmental hazards.[7] The large volume and flow of electronic waste can clearly lead to severe consequences, if not addressed in the near future. Thus, there has been a steady increase in the development of efficient recycling techniques for e-waste, especially with regards to the metallic components in the waste. Electronic waste is a complex mixture of metals, plastics, glass components, and more. Although they are not trivial to economically recover, the high economic value of precious metals, such as gold, silver, and palladium, in e-waste continues to drive recycling. Table 1 lists the compositions of metals, divided into heavy metals and precious metals, contained in various types of e-waste.[8–16] Printed circuit board and mobile phone scraps have the highest concentrations of precious metals, and a fair amount of base metals. Table 2 shows the values of these heavy and precious metals in printed circuit board scrap (PCBs) based upon the composition of PCB. The metal pricing data is from London Metal Exchange (LME) official prices for cash seller and settlement and New York Stock Exchange prices on June 24th, 2018. Note that copper has the second-highest monetary value, not because of its intrinsic value, but rather because of the high percentage of copper in PCB. Overall, the value of metals in WEEE amounted to approximately 52 billion U.S. dollars in 2014.[17] Furthermore, the metal content in WEEE is much higher than the metal content in ores; 1 ton of PCB contains 40–800 times the amount of Au and 30–40 times the amount of Cu mined from 1 ton of ore in the U.S.[18–20]

Printed circuit boards (PCB) are an integral component of all electronics, electrically connecting and mechanically supporting other electronic components. PCB represents approximately 8% of WEEE collected from small appliances and 3% of the total mass of global WEEE.[21,22] The structure of PCB is a generally a Cu-clad laminate comprised of glass fiber reinforced with epoxy resin, plastics, and metals.

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Katayun Barmak obtained her B.A. (First Class Hons.) and M.A. degrees in Natural Sciences, Metallurgy and Materials Science from the University of Cambridge, England. She completed her M.S. and Ph.D. in Materials Science at the Massachusetts Institute of Technology. She started her academic career at Carnegie Mellon University in 1999 and joined Columbia University as the Philips Electronics Professor of Applied Physics and Applied Mathematics and Materials Science and Engineering in 2011. She is an Associate Editor of the Journal of Electronic Materials. Her research interests include processing and structure relationships to electrical and magnetic properties of metal films.

Table 1 The compositions of metals by weight in various e-waste scraps[8–16]

	Weight (%)					Weight (ppm)			
Type of e-waste	Cu	Fe	Al	Ni	Pb	Ag	Au	Pd	Ref.
Printed circuit board	20	6	4	1	2.5	1000	250	90	8–14
Mobile phone	13	5	1	0.1	0.3	1380	350	210	9, 15 and 16
TV board	10	28	10	0.3	1	280	20	10	9, 15 and 16
Portable audio	21	23	1	0.03	0.14	150	10	4	9, 15 and 16
DVD player	5	62	2	0.05	0.3	115	15	4	9, 15 and 16
Calculator	3	4	5	0.5	0.1	260	50	5	9, 15 and 16

Table 2 The approximate monetary values of metals in PCB scrap

Metal	Value ($\$ g^{-1}$)	Value in 100 g of PCB ($)
Au	41	2.06
Cu	0.0075	0.15
Ag	0.53	0.083
Ni	0.017	0.018
Al	0.0024	0.011
Zn	0.0033	0.0066
Fe	0.000066	0.0003

PCBs can be single-sided, double-sided, or multi-layered. Conductive circuits on the substrate (glass fiber) are printed or etched with copper foil, and etch-resistant materials, such as gold, nickel, and tin, are used to protect the copper. The overall composition of PCB is estimated to be 40% metals, 30% organics, and 30% refractory.[23] The organics are most commonly comprised of the following polymers, Acrylonitrile Butadiene Styrene (ABS), Polycarbonate (PC), Polyvinyl Chloride (PVC), Polytetrafluoroethylene (PTFE), Polyethylene (PE), Polypropylene (PP), and High Impact Polystyrene (HIPS).[24] Refractory material generally consists of silica, titanates, alumina, and alkaline oxides. The toxicity of the materials found in PCB, particularly the plastics, is a significant concern in the characterization and treatment of waste PCB.

The solder material and plastics contained in PCB are the most toxic components, specifically the brominated flame retardants (BFRs) and the Pb/Sn solder. Although most solders are now Pb-free with Ag and Cu as substitute materials, many old PCBs still contain sizable amounts of Pb. In old waste PCBs, there is approximately 2–5% Pb in the solder.[25] Solder may contain Cd and Sb and the Surface Mount Device (SMD) chip resistors and semiconductors in PCB often contain Cd as well.[26] The BFRs, Poly-Brominated Diphenyl Ether (PBDPE) and Tetrabromo-bisphenol A (TBBA), are especially hazardous, since these compounds can react with oxygen to produce dioxins and furans. Making matters worse, copper can act as a catalyst for dioxin formation when the flame retardants are incinerated. Elemental analysis of PCB has revealed the following composition: 5.52 wt% C, 2.18 wt% H, 0.73 wt% N, and 7.86 wt% Br.[27] Antimony (Sb_2O_3) has also been found in the flame retarding materials, adding to the toxicity risks involved with PCB disposal and treatment.

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2. Key issues

The most pressing issues associated with waste PCB management are the environmental and human hazards posed by the waste, particularly those associated with current disposal techniques. As discussed previously, the toxicity of PCB presents a significant challenge for disposal and treatment, and much evidence of the adverse effects of PCB disposal on human health and the surrounding environment has been reported. Lead levels sampled in children's blood in the e-waste processing town of Guiyi, China were found to be three times of the safety limit recommended by the U.S. Centers for Disease Control and Prevention (CDC). Wildlife in California has been affected, as scientists recently found polybrominated diphenyl ethers (PBDPE), the flame-retardants in PCB, in the eggs of peregrine falcons.[28] The dioxins formed from the incineration of PCB could result in fatal liver damage and decreased thyroid function, while also severely disrupting the endocrine system.[29–31] Employees at e-waste recycling sites often suffer from respiratory issues, due to their prolonged exposure to dusts produced during pre-processing and concentrated acids used in metal recovery from PCB.[25]

The technical issues associated with treatment methods primarily stem from the energy and labor-intensive nature of the processing techniques, the potential for metal loss during treatment, and the low overall efficiency of the current recycling process. The transition from Pb-containing solders to Pb-free solders complicates recycling, as the finish of the two solders looks identical, and manufacturing of Pb-free solders is challenged by a high melting temperature requirement (>200 °C).[24] Disassembly and pre-processing, particularly crushing and shredding, require a significant amount of mechanical energy, and often involve human labor. Metal loss has been reported during pre-treatment/processing and smelting. In fact, shredding or grinding of PCB in steel mills can result in the loss of up to 40% of precious metals, as well as the formation of dangerous dusts and dioxins.[32] Smelting yields high Cu recovery, but often produces sludge that contains a mixture of different metals, such as Fe, Al, and precious metals. This sludge is not usually treated any further, and consequently, those metals are lost. The loss of metals in these processes, particularly the high-value precious metals, significantly affects the economics of the recycling process. Moreover, the overall efficiency of the recycling chain is quite low as shown in the example of a recycling sequence for gold recovery in Europe in Fig. 3.

While one process, in this case, smelting and refining, may have high operating efficiency, other processing steps may have lower efficiencies. Consequently, the overall efficiency of the process decreases, indicating how each individual process is just as important as the process as a whole. Integrated waste management will become an important issue, especially involving the 3R policy, which consists of three main factors-reduce, reuse, and recycle.[25,34] In summary, there are many challenges to overcome when developing new, more sustainable recycling methods for waste PCBs. The heterogeneity of PCBs, alluded to earlier in terms of the type, size, components, and especially composition, is a major issue. Waste PCBs are a complex mixture of plastics, refractory, and metals, and the composition of them continues to vary as toxic materials are phased out and new materials are developed. As highlighted in Tables 1 and 2, waste PCBs contain numerous metals in varying concentrations and the economic value differs from metal to metal. Hence, recycling initiatives have been focused on recovering the maximum amount of metals, with particular emphasis on the high-value precious metals. Yet, not much consideration has been put into developing recycling techniques that are greener and more sustainable.

3. Recycling of waste PCBs

The recycling of PCBs, a complex mixture of metals, oxides, and polymer materials, as depicted in Fig. 4, involves many steps and in the following sections, these steps and pathways are discussed in detail.

3.1. Pre-treatment: size reduction and separation

The pre-treatment of PCB generally consists of disassembly, solder removal, and physical processing, which then feeds into physical separation techniques. Fig. 5 summarizes the sequence of these steps, beginning with disassembly and ending with physical separation techniques for final separation into the non-metallic and metallic fractions of waste PCB.

The central objective of disassembly is to remove the hazardous components of PCB, minimizing the toxic materials in the main feed to the recycling process.[25] Reusable components are also targeted during disassembly. Selective and simultaneous disassembly are the two main types of disassembly, where selective disassembly is stepwise and simultaneous dis-

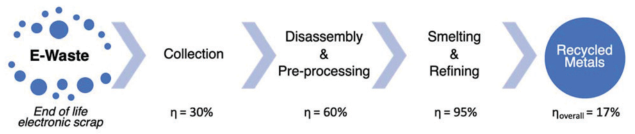

Fig. 3 Recycling sequence for gold recovery in EU with associated efficiencies of each unit process. Adapted from ref. 33.

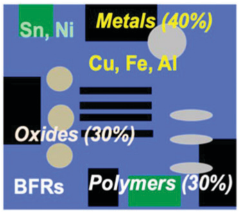

Fig. 4 Schematic of printed circuit board (PCB) with the approximate composition of metals, oxides, and polymers.

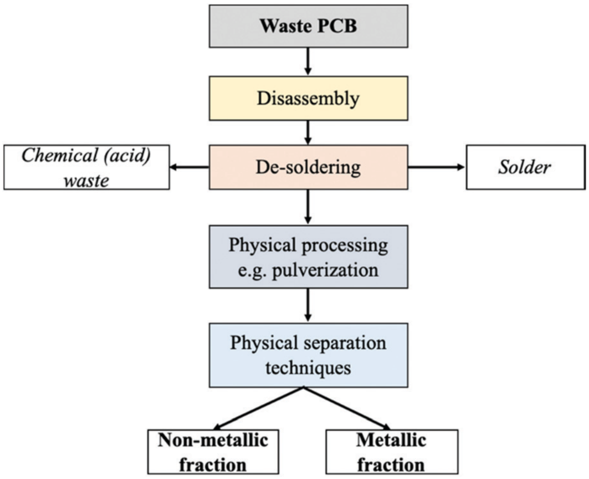

Fig. 5 Schematic of typical pre-treatment methodology for waste PCBs.

assembly occurs in just one step. During selective disassembly, specific components are located and removed individually with the guiding principle of "look and pick".[35,36] The identification of components is the most critical step during this process. In simultaneous disassembly, the PCB is heated to desolder components from the board simultaneously. The desoldered components are then identified and sorted by physical properties, such as size and shape. The guiding principle in simultaneous disassembly is "evacuate and sort". While simultaneous disassembly method has a high efficiency, it also runs the risk of damaging the components during heating. Since this method requires the additional sorting process, the processing time is longer and the cost is higher.[35] Recently, researchers have proposed the usage of different air and liquid materials as the heating medium for de-soldering, specifically air ovens and water-soluble ionic liquids.[36,37] Although the majority of disassembly processes remain manual, more attention is being given to automatic and semiautomatic systems now, with technological companies, such as Apple, at the forefront of automatic disassembly. There has been substantial advancement in the development of environmentally-friendly technologies for disassembly, reducing the risk of damage to components during heating and minimizing pollution from the off-gas.[38] While methods for automatic and semiautomatic disassembly have been reported in the past,[39] manual disassembly has remained the most popular technique. However, since Apple has developed robots, Liam and Daisy, that can mechanically disassemble several iPhones at once and recycle the components of the iPhones for reuse, the landscape of disassembly may begin to shift.

Upon removal of the hazardous and reusable components, the remaining waste PCB undergoes physical processing, *i.e.* crushing, shredding, and grinding. Different machinery and equipment, such as hammer crushers, cutting mills, and granulators, are used to crush the PCB and liberate the metals from the non-conducting, plastic substrates. Shredders and cutters may also be used to reduce the size of the boards, in the case that the crushers are not sufficient. Ball milling is then performed to pulverize the waste PCBs to powder.[40] It is worthwhile to note that in comparison to mineral ores during physical processing, PCBs do not have a specific size fraction when it comes to liberation. This is mainly due to the heterogeneity of PCBs. The non-metallic fractions are more brittle and tend to concentrate in finer fractions as opposed to the larger particle size metallic fractions.[41]

3.2. Separation of non-metallic fractions

The non-metallic fractions (NMF) in PCBs are primarily composed of the polymers and flame retarding-plastics. The polymers and plastics can be converted into high-grade fuel products; thus, much research has been done on the separation and recovery of NMF from waste PCBs through both physical and chemical techniques.

3.2.1. Physical techniques. The aim of physical recycling techniques is to recover the NMF without any loss of valuable metals. The physical properties of the particles, including size and shape, may influence the efficiency of the physical separation. Three main physical separation techniques are particle shape-based separation, electrostatic separation, and magnetic separation. Density separation falls under particle shape-based separation, and the most commonly-used form of electrostatic separation is eddy current separation. Fig. 6 outlines a physical separation scheme for the separation of the non-metallic fraction from the metallic fraction.[42,43]

During the grinding process, metals tend to take on a spherical shape because of their malleability and ductility, and non-metals (plastics, glass fibers, *etc.*) tend to remain non-spherical in shape, usually as rods or strands, due to stress. Particle-shape based separation takes advantage of this difference, along with differences between the densities of metals and the densities of NMF. Table 3 lists the density values of the metals and NMF contained in PCB.[14]

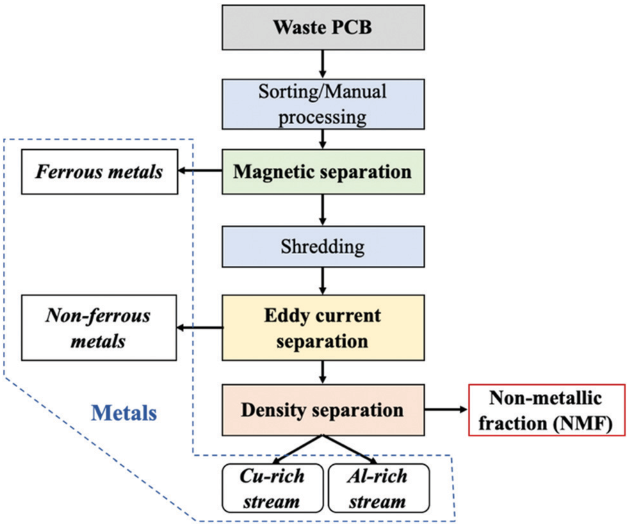

Fig. 6 Physical separation scheme for separation of NMF from metals.

Table 3 Density differences for the various PCB components (metals and NMF). Data taken from ref. 14

Material	Specific gravity (g cm^{-3})
Au, Pt, W	19.3–21.4
Pb, Ag, Mo	10.2–11.3
Cu, Ni, Fe, Zn	7.0–9.0
Al, Ti, Mg	1.7–4.5
Non-metallic fraction (NMF)	1.8–2.0

The feed PCB is separated into a light and heavy fraction, where the light fraction floats and the heavy fraction sinks. Metals are effectively separated from the plastics through the use of liquid mixtures, such as tetrabromoethane and acetone. However, the efficiency of this process is low, as the particle size and shape can have a significant impact on the efficiency. Certain metals are most effectively separated at a specific particle size; for Cu, this size is 149 microns.[40] Density separation has been completed in an inclined separation trough, where over 95% recovery of metals was achieved.[44] Researchers have also developed an air classification method that capitalizes on the settling velocity of particles.[45]

Electrostatic separation offers several advantages compared to the other physical techniques; it is less environmentally hazardous, requires less energy, and is easy to operate.[46] The basis of electrostatic separation is electrical conductivity. Electrostatics separates the non-conducting materials from the conducting ones, usually through a corona source or an eddy current. Researchers have reported a need for electrostatic separation to be performed as a multi-stage process to efficiently separate conductors from semi-conductors and non-conductors.[47] For corona discharging electrostatic separation, particle size is a limiting factor, along with the pinning effect of larger particles.[48] The efficiency of corona separation has been observed to decrease with finer particle size.[49] Recent studies on corona separation focus on novel electrode designs. Eddy current-based electrostatic separation depends on the flow of the particles induced by the eddy current and the external magnetic field. The eddy current and magnetic field aid in the separation of ferrous and non-ferrous metals and the separation of plastics from the plastic and metal mixture.[50] In addition to fine particles, coarse particles can also undergo eddy current separation. Thus, eddy current separation tends to be favored over corona separation. Fig. 7 illustrates a typical eddy current separation scheme. In recent years, researchers have investigated eddy current methods with rotating electrodes or pulsed excitation and have focused on optimizing specific operating conditions, the feeding speed and particle radius.[51,52] Overall, electrostatic separators are still limited to smaller particle sizes. After electrostatic separation, the NMF is sent through a vibrating screen.

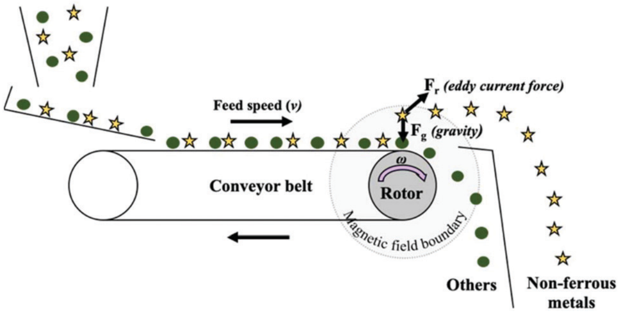

Fig. 7 Schematic of eddy current separation of non-ferrous metals from other components (metals, NMF).

Magnetic separation, which uses low special low-intensity drum separators, recovers ferrous materials from the non-magnetic fractions of PCB and is only effective for uncrushed PCB.[25] Therefore, as depicted in Fig. 5, magnetic separation is performed first, followed by shredding or grinding to fine particle size, and then electrostatic separation of the fines (eddy current separation).[53,54] The main challenge associated with these physical separation techniques, *i.e.* magnetic separation, electrostatic separation, and density separation, is the potential for loss of precious metals.

From the energy and economic standpoint, all of these physical treatments can incur high operating costs. The combined operating cost of wet and dry mechanical treatments (density separation, sieves, air separators, *etc.*) is estimated to be 1 MWH per ton. There is also a significant amount of wear and tear on the crushing tools, decreasing the overall efficiency of the process.[55] Recognizing this challenge, researchers have proposed and begun investigating a new physical separation technique, called opto-electronic sorting. Opto-electronic sorting uses X-rays to sort materials, and allows for separation of BFRs from heavy metals through laser-induced breakdown spectroscopy (LIBS) and X-ray Fluorescence (XRF) analysis.[42] Though the field of opto-electronic sorting is still developing, with support from agencies, such as Advanced Research Projects Agency-Energy (ARPA-E), opto-electronic sorting may become a promising alternative to traditional separation techniques.

3.2.2. Chemical techniques

3.2.2.1. Pyrolysis. Pyrolysis is one of the main routes for chemical recycling of the NMF in PCB. During pyrolysis, the plastics are degraded to oil, gases, and solid char, which can then be turned into high-grade fuel products and chemical feedstock. Pyrolysis has been carried out at a temperature range of 200–700 °C and experiments are generally performed in a fixed bed reactor.[56–65] Researchers have investigated fluidized bed reactors as well, reporting that pyrolysis in fluidized bed reactors results in more degradation than in fixed bed reactors.[59,66] Some researchers have studied different forms of pyrolysis, specifically comparing conventional pyrolysis to microwave-induced pyrolysis.[65] Pyrolysis of waste PCBs generates approximately 5–18 wt% oil, 5–14 wt% gases, and 77–81 wt% solids.[59,60,62] The oil contains aromatic compounds, such as phenols and the gases are usually composed of CO, CO_2, and hydrocarbons. Different characteristics of pyrolysis, particularly the particle size and temperature, were found to have varying effects on the degradation of the plastics. Although particle size did not have a significant effect on pyrolysis, the temperature was important, affecting the overall distribution of liquid, gas, and solid residue.[61] Pyrolysis at temperature greater than 500 °C was found to have minimal influence on the degradation of NMF and resulting products.[62] Overall, the composition of the pyrolysis products depends primarily on the reaction temperature, residence time in the reactor, and type of reactor. The pyrolysis oil has a high gross calorific value (30 kJ kg^{-1}) due to the aromatic and oxygenated compounds it contains. Similarly, the pyrolysis gases are rich in CO, CO_2, H_2, CH_4, resulting in high calorific values.[62] Yet, the major challenge associated with pyrolysis lies in the pyrolysis oil; the pyrolysis oil may contain large amounts of brominated compounds, hindering reuse of the oil, and the potential for dioxin formation still exists in the form of precursors, such as dibenzofurans.[65] Consequently, dehalogenation, the removal of the bromine and chlorine compounds, and removal of the dioxin precursors is a necessary step.[67] A significant amount of research on dehalogenation of plastics has been carried out, with an emphasis on the BFRs and the plastic components in PCB.[68–73] The governing chemical reaction for debromination of TBBPA during pyrolysis is highlighted in Fig. 8. Various additives, such as NaOH, CaO, CaOH, $CaCO_3$, Fe_2O_3, zeolite catalysts, and Pd–Fe catalysts, have been shown to aid in the removal of the brominated compounds from the pyrolysis oil.[27,65,74,75] Catalysts can transform PVC into non-toxic salts, such as $CaCl_2$, which can often then be re-used to regenerate the catalyst.[42]

3.2.2.2. Supercritical fluids and various solvent systems. Organic solvent systems and supercritical fluids for removing the plastic layers of waste PCBs have become an attractive alternative to thermal and physical treatments. Solvents, such as methanol, acetone, and dichloromethane, have been used to delaminate the PCBs and degrade the polymers. Recent work has built upon research on the chemical recycling of polymers, such as PC, a major constituent of PCB. Methanol–water mixtures with alkali catalysts, particularly NaOH, were shown to effectively recycle PC through alcoholysis at 120–140 °C and 10 MPa.[76] These solvent mixtures and alkali catalysts have since been applied to the recycling of plastics from e-waste and PCB. Chemical treatments with dichloromethane and chloroform in combination with pyrolysis at 550 °C were found to be most effective for recycling of PC from e-waste, while methanol, acetone, and toluene were found to be effective for other polymers. The dissolution of PC in these solvents was performed at temperatures of 25, 50, and 100 °C.[77] Computer simulations based on solubility relations have allowed for refinement of the list of existing, suitable solvents and optimization of solvent mixtures for enhanced recovery of the polymers from e-waste. A two-step extraction method with first a weak solvent followed by a strong solvent, acetone and then dichloromethane, was predicted to most readily dissolve the PC from e-waste.[78]

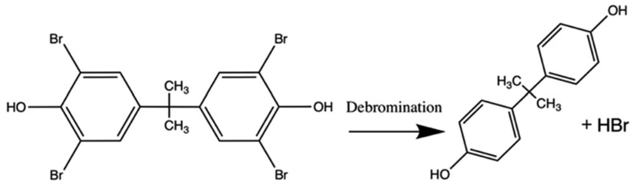

Fig. 8 The main chemical decomposition pathway during pyrolysis of TBBPA.

Both sub- and supercritical fluids have been used in the chemical recycling of plastics from e-waste and PCB, beginning with water and alcohols. Sub- and supercritical water and methanol treatments with Na_2CO_3 and phenol resin depolymerized the plastics, PC and Polyethylene terephthalate (PET).[79,80] Fig. 9 depicts the general methodology of a sub- and supercritical water treatment for waste PCB.

PC has been reported to readily decompose into phenol, bisphenol A, and *p*-isopropenylphenol, at 130–300 °C in water and Na_2CO_3, where the product yield reached 68% at 250 °C for just one hour.[80] Fig. 10 shows the chemical reactions that occur during the decomposition of PC in the supercritical water system.

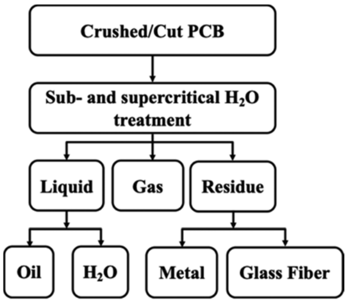

Fig. 9 Overview of sub- and supercritical water treatment methodology.

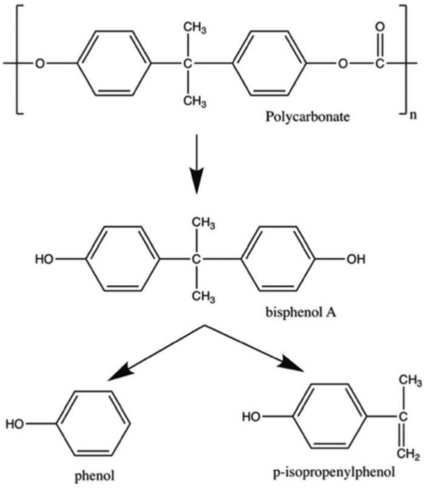

Fig. 10 Main decomposition mechanisms of polycarbonate (PC) during supercritical water treatment.

Meanwhile, supercritical fluids, including water, methanol, isopropanol, and acetone, have been extensively studied in the removal and recycling of the plastics from PCB.[81–83] Supercritical water (T_c > 374 °C, P_c > 22 MPa) was found to have the highest de-bromination efficiency of 97.6%, whereas supercritical isopropanol was found to have the highest oil yield for oil recovery from the BFR-containing plastic.[84] Since supercritical water, and other supercritical solvents have high critical temperatures and pressures, lower temperature and pressure conditions would be most optimal. Supercritical CO_2 (T > 31 °C, P > 7 MPa) is a better, greener option, with recent research reporting an environmentally benign supercritical CO_2 process for the delamination of PCB.[85] In this process, supercritical carbon dioxide was the main solvent and a small amount of water was incorporated into the solvent. It was found that the PCB scraps delaminated easily and could further be separated into copper foil, glass fiber, and polymer for recycling. Successful delamination of PCB was observed at 180 °C and 13.8 MPa, which is a lower temperature and pressure condition compared to previously studied supercritical solvent systems.[85]

3.3. Separation and recovery of metals

The central motivation for recycling of PCBs is the recovery of metals. The main routes of metal separation and recovery are pyrometallurgy and hydrometallurgy, where pyrometallurgy remains the most traditional, industrially-used treatment. Hydrometallurgy is a recent advancement and has gained traction with the burgeoning development of various hydrometallurgical techniques, such as bioleaching. Fig. 11 illustrates the schemes of the two foremost metal separation and recovery processes, pyrometallurgy and hydrometallurgy.[55]

3.3.1. Pyrometallurgy. Pyrometallurgy is the most traditional and commonly used route for metal separation and recovery, and involves incineration, smelting in plasma arc or blast furnaces, drossing, sintering, melting, and gas-phase reactions at high temperatures.[15,23] More than 70% of waste PCBs are treated in smelters, instead of mechanical processing.[15] Crushed PCB is essentially added to the raw materials in smelters for separation and recovery of copper and precious metals, Au and Ag. Copper smelting processes can be classified as either "bath" or "flash" smelting. In bath smelting, smelting and converting occurs predominantly in a molten or liquid bath, and the concentrate comes in contact with the liquid slag and matte. The matte is converted by air that is injected into or on top of the molten bath. In flash smelting, the concentrate is dispersed into an air stream and smelting and converting occurs while the concentrate is suspended in the air stream. The Noranda smelting process in Canada and the most state of the art Umicore smelting process in Belgium are prime examples of streamlined, industrial pyrometallurgical techniques. Essentially, the electronic scraps, PCBs, *etc.*, are first fed into a blast furnace, upgraded in a converter and anode furnace, and then electro-refined through electrolysis or electrowinning for metal recovery.[9,26,86,87] Fig. 12 depicts these processing steps in detail based on industrial schemes and shows all products streams and subsequent treatments of waste streams.[55,86] The Umicore process is more refined with its copper leaching and electrowinning step, followed by precious metal recovery steps for increased value of metal recovery. Furthermore, this process includes an advanced off-gas treatment that prevents release of toxic materials and reduces human and environmental hazards.

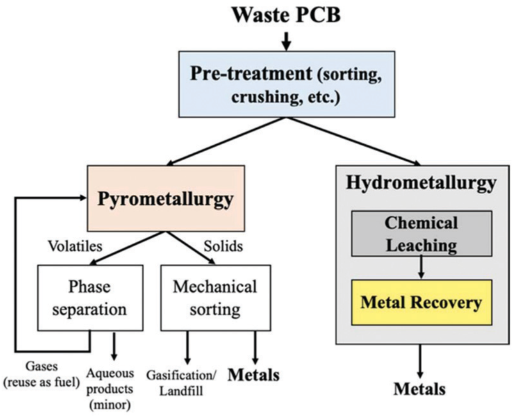

Fig. 11 Summary of main metal separation and recovery processes.

Pyrometallurgy is not without limitations and challenges. On the environmental side, the risk of toxic material release and dioxin formation is high, and state of the art smelters, such as the Umicore plant, which lower these risks through advanced emission control systems, are quite expensive. Smelting is undesirable as it leads to the formation of slag and more industrial wastes. On the technical side, integrated smelters cannot recover Al and Fe as metals, only Cu, and consequently, the Al and Fe becomes concentrated in the slag. Also, only partial separation of the metals is achieved, resulting in limited upgrading of metal value. Subsequent processing, such as electrorefining, is thus needed for complete separation of metals. The ceramics and glass components in PCB (refractory) contribute to more slag formation and higher losses of precious and base metals from PCB. Finally, precious metals require longer times to separate and recover during pyrometallurgy, and are usually not recovered until the end of the whole process.[26] Vacuum pyrometallurgy is another form of pyrometallurgy, in which metals with different vapor pressures are separated through distillation or sublimation and recovered with condensation. Researchers have proposed Vacuum Metallurgy Separation (VMS) for the recovery of Bi, Sb, Pb, and other heavy metals.[88] Molten salt mixtures, KOH–NaOH eutectic, at temperatures of approximately 250 °C, have been shown to dissolve the organics along with the refractory and ultimately recover Cu.[89] Recent technoeconomic 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 per year.[90]

3.3.2. Hydrometallurgy. Hydrometallurgy is readily controllable, more exact, predictable, and environmentally-friendly

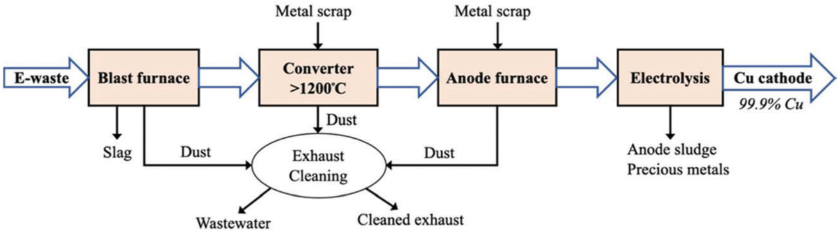

Fig. 12 Pyrometallurgical processing scheme based on industrial copper/e-waste smelting process. Adapted from ref. 55 and 86.

compared to pyrometallurgy. Hydrometallurgical techniques largely involve a series of acid or caustic leaches of e-waste 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. Chemical leaching processes have gained traction and a plethora of research on leaching has been done in recent years. Fig. 13 highlights the various branches of hydrometallurgy, specifically chemical leaching, where acid leaching is most pre-dominantly used, and the metal recovery routes that follow leaching.[16,91] Currently, cyanide leaching is being dismissed as a hydrometallurgical option due to its high toxicity. Other hydrometallurgical processes are either developing or in the early stages of research. Thiourea and thiosulfate leaching are the greenest processes compared to caustic acid leaching, while leaching with ligands, etching, and bioleaching are less developed and show less economic potential. Bioleaching is becoming an interesting and promising option, as recent research has shown, and will be discussed in detail later. After leaching, various metal recovery routes are utilized, where precipitation is the most commonly used technique. Electrowinning shows potential as an electrochemical technique that can be staged efficiently after chemical leaching, especially through simultaneous routes of leaching and electrodeposition.

3.3.2.1. Cu and precious metal recovery. In recent years, most articles have focused on the leaching of copper and precious metals from waste PCBs.[15,16,92–97] Table 4 details four main methods of chemical leaching, the key parameters of each extraction chemistry, and the overall chemical reactions that describe the leaching mechanisms. For the chemical reactions in acid leaching, three different reactions are depicted. These reactions involve nitric acid, aqua regia, and sulfuric acid : H_2O_2 mechanisms.[16,17,98–101] Acid leaching is currently the most popular leaching method and has many advantages, including high leaching rate and fast kinetics, but is quite corrosive. Cyanide leaching, which used to be the standard for gold mining, is being phased out due to its high toxicity. Thiourea and thiosulfate are the least hazardous leaching methods, but are not as economically feasible. Thiourea has poor stability, thiosulfate has slow kinetics, and both require large amounts of reagent.

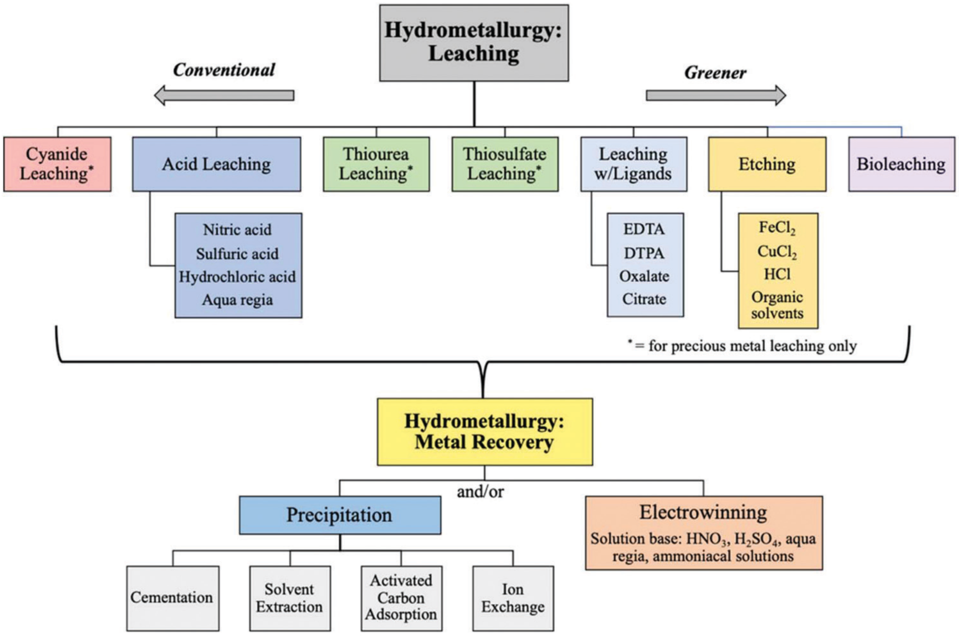

Fig. 13 Summary of hydrometallurgical leaching and metal recovery techniques.

Table 4 Chemistries of main leaching methods and key considerations in the assessment of each method

Leaching type	Example	Overall reactions	Considerations
Acid	HNO_3	$4HNO_3 + Cu \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$	Nitric acid cannot be used directly for electroplating
Acid	$H_2SO_4 : H_2O_2$	$Cu + 2H^+ + H_2O_2 \rightarrow Cu^{2+} + 2H_2O$	Stronger corrosion → stricter reactor requirements
Acid	Aqua regia	$2Au + 11HCl + 3HNO_3 \rightarrow 2HAuCl_4 + 3NOCl + 6H_2O$	Highly corrosive, metal specificity (targeted towards Cu recovery with chlorides)
Cyanide	NaCN	$4Au + 8CN^- \rightarrow 4Au(CN)_2{}^- + 4e^-$	Slow leaching rate, harmful wastewater
Thiourea	$CS(NH_2)_2$	$Au + 2CS(NH_2)_2 \rightarrow Au(CS(NH_2)_2)^{2+} + e^-$	Poor stability, high reagent consumption
Thiosulfate	$(S_2O_3)^{2-}$	$Au + 5S_2O_3{}^{2-} + Cu(NH_3)_4{}^{2+} \rightarrow Au(S_2O_3)_2{}^{3-} + Cu(S_2O_3)_3{}^{5-} + 4NH_3$	High selectivity, but high reagent consumption

Fig. 14 illustrates the rankings of acid, cyanide, thiourea, and thiosulfate leaching among five categories, leaching rate, kinetics, economic feasibility, toxicity, and research level, where a ranking of 3 is the most optimal. Studying leaching more closely reveals several drawbacks associated with different types of acids and extraction chemistries. Additionally, Table 4 highlights the important considerations for each type of chemistry.[98–101] Nitric acid (HNO_3) is the most commonly investigated leaching solution, particularly for the leaching of Cu, Pb, and Sn (solder removal) from waste PCBs.[92,102–104] Researchers progressed from HNO_3 to aqua regia for the extraction of precious metals, focusing on Au.[13,105–107] In general, the more concentrated the acid in the leaching solution and the longer the leaching time, the higher the extraction of metal. Researchers have also performed the simultaneous extraction and deposition of copper from waste PCBs in nitric acid and aqua regia media.[107] The results indicated that the nitric acid treatment yielded higher Cu recovery than the aqua regia treatment. However, the leaching solution could not be used directly for electrodeposition of Cu.

The high acid content in the leaching solution inhibited deposition of Cu.[107] Besides nitric acid, sulfuric acid has become a promising alternative option, and has proven to be effective, particularly when combined with an oxidizing agent, H_2O_2.[97,98,106,108–111] Leaching of waste PCBs, which had been crushed and magnetically separated, in piranha acid solution (2 M H_2SO_4 : 0.2 M H_2O_2) at 85 °C for 12 hours resulted in more than 95% Cu extraction.[98] The particle size of crushed PCB was found to have a significant impact on the Cu recovery, with studies showing that crushed PCB < 1 mm in size was optimal for Cu extraction.[108] When researchers compared sulfuric acid, sulfuric acid and hydrochloric acid, and nitric acid and hydrochloric acid (aqua regia), unsurprisingly, aqua regia yielded the highest Cu extraction.[106]

Aqua regia, known as the universal solvent, is effective for the leaching of Cu, Au, and Ag, but its highly corosive nature prevents it from being industrially realizable, especially when human exposure is involved. Sulfuric acid, on the other hand is mildly corrosive, lower in price, and much easier to regenerate from the industrial standpoint. Corrosion still remains an issue, as piranha acid (sulfuric acid in combination with hydrogen peroxide) is corrosive, but aqua regia is much more corrosive in comparison. With these issues in mind, researchers have proposed using alternative chemistries, particularly ammoniacal leaching, which has higher selectivity towards copper. Cu forms amine complexes with ammonia and the stability of the amine groups is tuned through pH, oxidation potential, and ammonia concentration. Ammonia-based leaching chemistries include ammonium carbonate, NH_3/NH_4Cl with $CuCl_2$ as the oxidant, *etc.*[93,112] Another unique leaching chemistry that was recently realized comprised of a Brønsted acidic ionic liquid with H_2O_2 for leaching of Cu from waste PCBs.[113] Ionic liquids have a wide liquid-phase temperature range and have numerous distinctive properties, such as negligible volatility, high conductivity, and a wide electrochemical window, making them a potentially promising replacement for traditional acid leaching systems.[114]

Precious metal recovery is often combined with Cu recovery, in a sequential leaching process involving two different leaching chemistries. The first chemistry is commonly an acid leaching chemistry, and the second chemistry is often cyanide, thiosulfate, or thiourea leaching solutions for precious metal extraction. Cyanide was traditionally used for gold and silver mining, but has since been slowly disregarded as a leaching technique due to its toxicity.[115] Current research has focused on thiosulfate leaching of gold and silver, thiourea solutions, and halide solutions (chlorides and iodide).[96,97,116–119] Researchers have demonstrated the potential of ammoniacal thiosulfate solutions, with 90% Au leached from PCB of

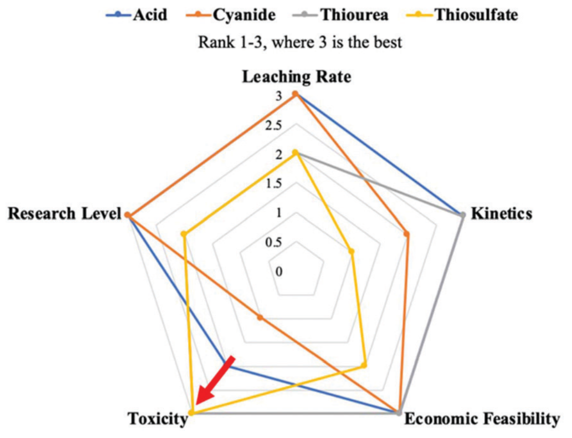

Fig. 14 Ranking of leaching chemistries among 5 categories, leaching rate, research level, kinetics, toxicity, and economic feasibility.

mobile phones using copper salt, thiosulfate and ammonia.[120,121] Although 95% Au and 100% Ag was extracted using thiosulfate solution, 0.2 M $(NH_4)_2S_2O_3$, 0.02 M $CuSO_4$, and 0.4 M NH_4OH, the reaction took a significant amount of time, 24 to 48 hours in total.[98] Similarly, thiourea leaching with ferric ion as an oxidant has yielded 86% Au and 71% Ag extraction.[97] Yet, the high cost and fast consumption of thiourea, are limiting factors in terms of process development and scale-up.[96,122,123] Chloride and iodide solutions have also been investigated, particularly using electro-generated chlorine for 99.9% Au recovery and using iodide solution with H_2O_2 for 95% Au recovery.[124–126]

The metal recovery techniques listed in Fig. 13 are for the most part, standard chemical processes. Each method brings about concerns related to the chemistry and physical mechanism of the technique. Table 5 illustrates the specific challenges of each metal recovery technique.[15]

Cementation and solvent extraction are regularly used for metal recovery after chemical leaching, but the need for additives, potential for passivation, and sensitivity to impurities are major constraints. Zinc cementation results in high reagent consumption and co-precipitation of metals, and solvent extraction requires different additives and steady control of the pH of the solution. Activated carbon adsorption does not adsorb the gold thiosulfate complex and ion exchange resins can lead to resin poisoning, resin swelling, co-adsorption, and passivation.[120] In recognition of these issues, researchers are developing new materials for adsorption and working to improve existing processes, through hybrid functionalized mesoporous silica gel adsorption and alternative resins.[104,120]

Electrowinning also has its challenges, including sensitivity to pH, high overpotentials, and re-dissolution of metals. It is worthwhile to note how recent research on electrowinning has elevated it to nearly the same level of popularity as cementation and solvent extraction. Many researchers have successfully used electrowinning for Cu and Sn recovery.[92,127–132] The electrodeposition of Cu in membrane electrowinning has low power consumption compared to the other metal recovery techniques.[129] Furthermore, electrowinning of precious metals has been performed, especially for recovery of gold from ammoniacial thiosulfate leaching solutions.[133–135] The successive electrowinning of multiple metals, particularly with Cu and Ni and Cu and Au, in sulfuric acid and aqua regia baths, presents a promising option for combination of individual electrowinning steps. These electrowinning schemes take advantage of differences in the potentials, *E* (V). Fig. 15 details these electrowinning pathways.[131,134] Since electrochemical techniques have the potential to reduce power consumption and minimized chemical input, recent research has explored the direct electrolysis of waste PCBs to produce Cu powder and investigated the integration of leaching and electrochemical recovery processes.[136–139] Researchers examined the effects of $CuSO_4{\cdot}5H_2O$, NaCl, and H_2SO_4 concentrations, the current density, and the electrolysis time on the current efficiency and size of the recovered Cu powder in direct electrolysis.[136] A recent article proposed an integrated scheme with a leaching reactor and electrochemical reactor in series for regeneration of the leaching solution; in this configuration, parallel electrowinning of copper can be performed.[138]

3.3.3. Biometallurgy. Biometallurgy has gradually become a well-established pathway for recovering metals, especially copper and gold, from waste PCBs, and is particularly favorable due to low investment cost, low environmental impact, and low energy consumption.[15] The technique of biometallurgy can be summarized in two main steps: bioleaching and biosorption.[101] Essentially, bioleaching employs acidophilic groups of bacteria, most commonly acidithiobacillus ferroxidans and thiooxidans.[16,101,140,141] Biosorption is similar to the metal recovery techniques discussed earlier but involves biological materials. Bioleaching is strongly influenced by the chemical composition of the culture media, the particle size of the ground PCBs, and the pH of the solution. The particle size affects the leaching time.[142] Two main types of cultures are

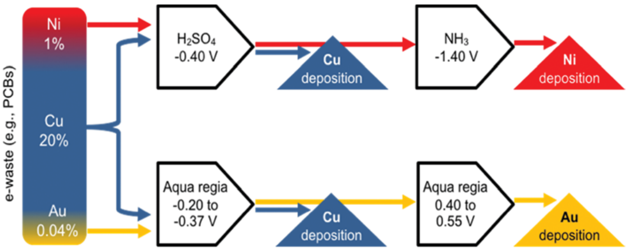

Fig. 15 Two electrowinning schemes for Cu, Ni, and Au recovery.

Table 5 Detailed breakdown and analysis of major metal recovery techniques

Precipitation		Electrowinning
Cementation	Zinc (Merrill-Crowe), sodium borohydride **Concerns:** impurities, passivation (ZnOH)	• Aqua regia, HNO_3, HCl • H_2SO_4 • Ammoniacal solutions **Concerns:** ≻ Re-dissolution of copper ≻ NO_3^- decreases efficiency ≻ Impurities from other metals ≻ High overpotential **Advantage:** high purities of deposition
Solvent extraction	LIX-79, Cyanex 921, NaOH, alkyl phosphorous esters **Concerns:** pH control, need for additives	
Activated carbon adsorption	Carbon in-pulp (CIP) and carbon in-leach (CIL) **Concerns:** kinetics, isotherms	
Ion-exchange	Resins: Dowex G51, amberlite, RIP, RIL **Concerns:** impurities in bath, reagent degradation	

ferroxidans and thiooxidans, and these bacteria can solubilize Cu, Al, Zn, and Ni. Fig. 16 shows the mechanism by which ferroxidans solubilize Cu in solution.

An example of the composition of a culture media is $(NH_4)_2SO_4$, KCl, K_2HPO_4, $Ca(NO_3)_2$, and $FeSO_4{\cdot}7H_2O$.[142] When researchers studied the bioleaching of Cu from waste PCBs using ferroxidans, they found that the optimum pH for A. ferroxidans was in the range of 1.8–2.5 and that a higher concentration of Fe^{3+} ions led to faster rates of Cu leaching, reaching 99% Cu extraction.[143] The mobilization of Cu ions into solution consumes Fe^{3+}, which is evident in the governing chemical reactions for bioleaching with ferroxidans as shown in eqn (1) and (2). Eqn (2) proceeds in a thermodynamically favorable manner with $\Delta G = -82.90$ kJ mol^{-1}.

$$2Fe^{2+} + \frac{1}{2}O_2 + H^+ \rightarrow 2Fe^{3+} + H_2O \tag{1}$$

$$2Fe^{3+} + Cu^0 \rightarrow 2Fe^{2+} + Cu^{2+} \tag{2}$$

Beyond Cu extraction, a recent article reported successful bioleaching of 97% Cu, 84% Zn, and 75% Al after 72 hours by ferroxidans.[144] In this work, the kinetics of H^+ consumption and metal recovery in the bioleaching of waste PCBs was represented by a second order kinetic model with the shrinking core model for precipitate production. Novel and new developments on culture media include bioleaching using biosurfactant producing bacteria for enhanced Zn recovery (no enhancement in Cu and Al recovery) and bioleaching of Cu from PCB using mesophilic bacteria, specifically ferroxidans and thiooxidans.[145,146] The novelty of the article on mesophilic bacteria was the incorporation of pyrite, specifically 5–50 g L^{-1} PyC, as a source of iron and sulfur.[146] Pyrite was supplied from a nearby mine and the pH was maintained at 1.7 using sulfuric acid. The addition of pyrite enhanced Cu extraction from 24 to 84% at the maximum pyrite concentration of 50 g L^{-1} PyC, and further decreased the acid consumption by 62%. Researchers attributed the enhancing effect of pyrite to the chemical oxidation of Fe(II) released from PyC, which is catalyzed by Cu^{2+} in the solution.[146] Bioleaching of precious metals, Au and Ag, requires different bacterial strains. Chromobacterium violaceum (CV) is the most commonly used bacteria for precious metal extraction. CV produces CN^- and is effective for Au and Ag extraction, yielding over 70% gold leaching efficiency.[147] The chemical mechanism of Au leaching using CV is shown in eqn (3).

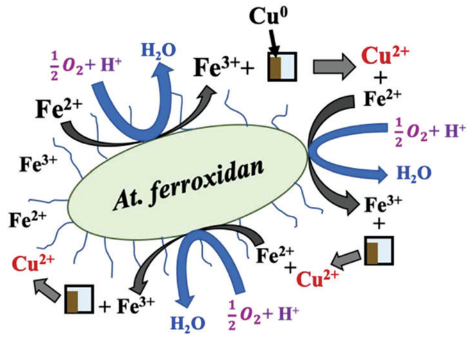

Fig. 16 The bioleaching mechanism of At. ferroxidans in solution with shredded PCB.

$$4Au + 8CN^- + O_2 + 2H_2O \rightarrow 4Au(CN)_2{}^- + 4OH^- \tag{3}$$

Cyanogenic microorganisms, like CV, produce the cyanide lixiviant which reacts with Au for leaching, but the cyanide lixiviant is a limiting factor. The lixiviant is derived from secondary metabolite HCN produced from glycine using the enzyme HCN synthase, but the HCN metabolite (cyanide) produced turns out to be quite limited. Only about 20 mg of cyanide are produced for every 1 L of bacteria culture, making scale up to an industrial level a daunting task.[147] Another challenge is the difficulty of harvesting CV, as it grows in tropic and subtropical regions and has stringent living conditions.[148] As such, a new bacterial strain for leaching Au, Ag, and Cu has been developed, pseudomonas chlororaphis (PC), which produces CN^- similarly. Pseudomonas strains are easily harvested and currently already employed in industrial applications for recovering precious metals from waste PCBs, but are not as strong as CV for the production of CN^-. Consequently, leaching with PC resulted in just 8.2% Au, 12.1% Ag, and 52.3% Cu extraction.[148]

Biosorption is a physico-chemical and metabolism-independent process, involving mechanisms such as chelation, coordination, ion-exchange, and complexation, for the removal of metals from solution by biological materials.[25,101] The physico-chemical interactions occur between the metal ions and the charged surface groups of microorganisms. Usually, inactive or dead biomass materials are used, as they bind and concentrate metal ions from solutions. Examples of biomass include fungi, algae, and yeasts. Brown alga, specifically Fucus vesiculosus, was proven effective for the recovery of Au(III), where the optimum gold uptake occurred at pH = 7.[149] Marine alga, was also investigated, particularly the species Sargassum natans, with fungal cells of *Aspergillus niger*, *Mucor rouxii*, and *Rhizopus arrhizus* as additives.[150] Researchers examined biopolymer derivatives for biosorption as well, DEAE-cellulose, for Au recovery and reported Au recovery rates over 99%.[151]

Table 6 is a complete summary of the bioleaching techniques in biometallurgy organized by the microorganism, with the metal recovery percentages as well as pH and temperature conditions.

3.3.4. Use of Supercritical CO_2 and Greener Physical Treatments

3.3.4.1. Treatment with Supercritical CO_2. The wide range of hydrometallurgical techniques and chemical treatments for separation of plastics has inspired researchers to explore combinations of various processing methods. Some researchers have performed experiments with supercritical water and acid leaching for metal extraction from waste PCBs.[164,165] These experiments involved two pre-treatment processes, supercritical water oxidation (SCWO) and supercritical water depolymerization (SCWD), in combination with HCl leaching. Both SCWO and SCWD were determined to be effective for the recovery of

Table 6 Summary of bioleaching techniques separated by microorganism

Microorganism	Metal recovery (%)	pH	Temp. (°C)	Ref.
Aspergillus niger	Cu, Sn 65%	2.5–2.7	30	152
Penicillium simplicissimum	Al, Ni, Pb, Zn > 95%	2.5–2.7	30	152
Thiobacillus thiooxidans and *Thiobacillus ferrooxidans*	Cu, Ni, Al, Zn > 90%	2.5–2.7	30	152
Acidithiobacillus ferroxidans	Cu 99%	1.5	30	143
Acidithiobacillus ferroxidans	Cu 99%	2.5	28	142
Acidithiobacillus thiooxidans	Cu 74.9%	2.5	28	
At. ferroxidans and *At. thiooxidans*	Cu 99.9%	2.5	28	
At. ferroxidans, *L. ferroxidans*, and *At. thiooxidans*	Cu 95%	1.70	35	146
Acidithiobacillus thiooxidans	Cu 98%	<1.0	30	141
Acidithiobacillus ferrooxidans	Cu 96.8%, Zn 83.8%, Al 75.4%	2.25	30	144
Acidithiobacillus sp. and *Leptospirillum* sp.	Cu, Ni 100%	1.5	25	153
Acidiphilium acidophilum (ATCC 27807)	Cu 3.6%, Ni 86%	3.5	26	154
genera Acidithiobacillus and *Gallionella*	Cu 95%	1.5	30	155
genera Acidithiobacillus and *Gallionella*	Cu 96.8%, Al 88.2%, Zn 91.6%	2	30	156
At. ferrivorans, *At. thiooxidans*, *Pseudomonas fluorescens*, and *Pseudomonas putida*	Cu 98.4%, Au 44%	1.0–1.6, 7.3–8.6	23	157
Sulfobacillus thermosulfidooxidans and *Thermoplasma acidophilim*	Cu 86%, Zn 80%, Al 64%, Ni 74%	3.4	45	158
Chromobacterium violaceum	Au 22.5%	9.5	30	159
Chromobacterium violaceum	Au 11.31%, Cu 24.6%	8–11	30	160
C. violaceum, *P. fluorescens* and *P. plecoglossicida*	Au 68.5%	7.2	30	161
C. violaceum, *P. aeruginosa* and *P. fluorescens*	Au 73%, Cu 83%, Zn 49%, Fe 24%, Ag 8%	7.2	30	162
Sulfur-oxidizing bacteria and *mixed culture of biosurfactant-producing bacteria* and *sulfur-oxidizing bacteria*	Cu 53%, Zn 48%, Ni 48.5%, Cd 93%	6–8	37	145
Acidaianus brierleyi, *A. manzaensis*, *M. sedula* and *S. metallicus*	Cu 81.4%, Ni 83.7%	1.5	65	163
Pseudomonas chlororaphis	Au 8.2%, Cu 52.3%, Ag 12.1%	7	25	148

Cu, reaching 99.8% Cu recovery, as well as 90% recovery of other metals, Sn, Zn, Cr, Cd, and Mn.[165] Researchers have similarly used this approach for precious metal recovery.[166,167] The sole disadvantage of incorporating supercritical water into acid leaching is the high temperature requirement (420–440 °C). Thus, supercritical CO_2, which has a lower critical temperature, presents a greener alternative. As noted by the red arrow in Fig. 14, greener treatment processes need to have minimal toxicity, and supercritical CO_2 fulfills this need.

A recent article investigated the use of supercritical CO_2 in a piranha acid leaching system and reported favorable results with respect to Cu recovery. The supercritical CO_2 extraction was much faster than atmospheric pressure extraction, and 90% of the Cu in the finely-ground PCB was extracted after only 20 minutes of leaching.[168] We have investigated supercritical CO_2 ($scCO_2$) extraction using crushed PCB. The selected reaction conditions included pressures in the range of 75–100 bar and temperatures ranging from 35–70 °C, where the reaction time was varied from 20 to 60 minutes. The solvent system was controlled at 2 M H_2SO_4 : 0.2 M H_2O_2 (piranha acid) and the solid to liquid ratio was lowered to 1 : 35 compared to 1 : 100 for leaching of pyrolyzed residue in the absence of CO_2. Fig. 17 illustrates the ICP-OES measurement results of concentrations for the Cu extracted from the crushed PCB in the novel solvent system with $scCO_2$.

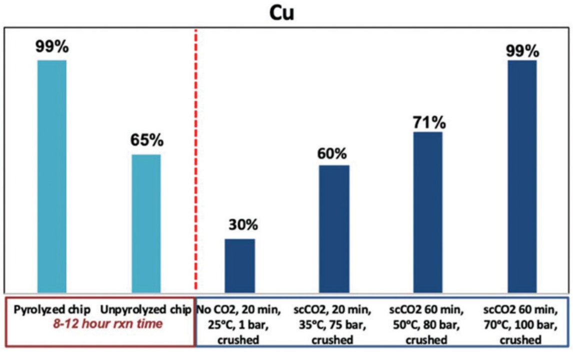

Fig. 17 Cu extraction results for pyrolyzed *vs.* unpyrolyzed, no CO_2, and $scCO_2$ leaching solutions of PCB.

These results are compared to prior results from unpyrolyzed and pyrolyzed chips (no CO_2) and a blank case (no CO_2) conducted at ambient pressure and temperature. The percentages in the figure represent estimated Cu recoveries into solution. It is evident that as the reaction temperature, pressure, and time increase, the amount of Cu extracted into solution increases. The $scCO_2$ solvent system appears to reduce the reaction time needed to reach high metal recovery and yields higher Cu extraction compared to the batch experiment in a beaker at ambient temperature and pressure under the 20-minute reaction condition.

In order to elucidate the effects of $scCO_2$ on the leaching of Cu from PCB, control PCB samples with polycarbonate (PC) and copper were synthesized and reacted with $scCO_2$. The control PCB particles were placed into the same solvent system (piranha acid) as in the experiments with real PCB particles and the solid to liquid ratio was maintained at 1 : 40. A reaction temperature of 120 °C and a reaction pressure of 150 bar were used respectively. The total reaction time was 6 hours. Fig. 18 illustrates the physical differences in the control PCB sample after the 6-hour reaction in the $scCO_2$ solvent system.

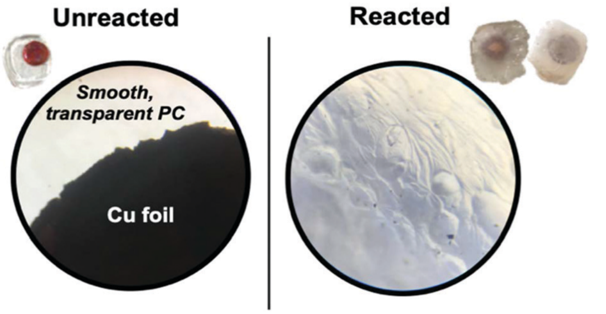

Fig. 18 A comparison of the unreacted control PCB particle (Cu in PC) and the reacted control PCB particle (reaction in $scCO_2$ solvent system).

It can be seen that the polycarbonate surface swelled at the reaction conditions, likely due to free volume expansion of the polymer, and the surface of the control particle became roughened and translucent, making it difficult to see the copper inside.

Based upon these observations and results, it was determined that the $scCO_2$ appears to physically change and swell the organic polymers (plastics) thereby enhancing metal leaching. The morphological change induced by the $scCO_2$ solvent system was found to be permanent and investigation into the polymer stability confirmed that the effects were not chemical, only physical. Further investigation into the precise effects of $scCO_2$ on the extraction of metal, specifically on leaching kinetics and transport phenomena, is needed to fully understand the fundamental mechanisms in which the $scCO_2$ solvent system improves metal leaching. Focused efforts on incorporating $scCO_2$ into the e-waste treatment scheme for improved sustainability of the metal separation process are underway.

3.3.4.2. Greener physical treatment. Another novel, recently proposed approach to recycling the metals from waste PCBs is cryo-milling, essentially freezing, the waste.[169] Researchers proposed a low-temperature ball milling method that degrades the PCB into nanoscale particles allowing for convenient separation into the polymer, oxide, and metal constituents. This method is scalable and environmentally friendly due to low operating temperatures and minimal waste generation, but requires more energy than hydrometallurgical methods. More studies on improving the efficiency of the cryo-milling technique are necessary to develop this mechanical process into a more sustainable, economical treatment for e-waste.

4. Conclusions and perspectives

The mounting volume and flow of electronic waste can clearly lead to severe environmental and human consequences, if not addressed in the near future. As more and more PCBs are landfilled, the availability of easily mineable elements, particularly metals, decreases, disturbing the overall material cycle. The economic value and high content of the metals, base and precious metals, in PCB continue to drive the recycling of e-waste. Currently, the processing and treatment of PCB is not sustainable; thus, new, environmentally-friendly approaches to recycle and recover valuable components from waste PCBs are urgently needed. The processing and recycling of PCB is a multi-faceted challenge, as demonstrated by the detailed analyses of the various treatment methods. Every individual process is just as imperative as the collective process, beginning with the collection of the electronic scrap and ending with the metal recovery for reuse. The heterogeneity in the chemical composition of PCB and the toxicity of the materials contained in PCB present important challenges to the recycling methodology. Disassembly of the waste PCBs, particularly separation of the hazardous components from the non-hazardous materials, is a crucial step in the minimization of toxicity concerns during processing. Upon the dismantling of PCB, physical techniques are used to separate the non-metals from the metals in PCB. Reduction of the PCB to fine particle sizes below 150 μm is the first step followed by physical separation. Density separation is the most popular option for physical separation of the NMF from the metals. Electrostatic separation (corona and eddy current) and magnetic separation are also used to separate materials based on differences in electrical conductivity and magnetism (ferrous *vs.* non-ferrous). The NMF can often be recycled for reuse in filler materials and composites. One growing field of research in physical processing is Disassembly Process Planning (DPP), which focuses on the innovation of disassembly facilities. The objective of DPP is to develop procedures and tools for improved disassembly strategies and configuration of disassembly systems.[26] Disassembly could become a more attractive and feasible option for the recycling of small devices, such as mobile phones, since smaller scraps are easier to disassemble. Apple has capitalized on this concept *via* their iPhone dismantling robots, Liam and Daisy. As scientists develop new materials and smarter designs for electronic equipment, the low cost and high technological concepts of these new electronic components could weaken the long-term feasibility of component recycling by physical techniques. Regardless, nearly all existing and potential treatments for PCB require mechanical processing; even the most advanced hydrometallurgical methods involve some form of mechanical treatment. Chemical techniques for the separation of the NMF from the metals generally involve degradation of the plastics through either chemical solvents, pyrolysis, or supercritical fluids. Pyrolysis is the main method used to decompose the plastics, whereas supercritical fluids are a newer development. One of the major concerns during pyrolysis is the presence of dioxin precursors in the pyrolysis oil. Thus, different compounds and catalysts, such as $CaCO_3$ and Fe_2O_3, are often added to subdue these precursors. More recently, a number of research articles on supercritical fluids have shown that supercritical H_2O and other supercritical solvents are effective in the removal of plastics from PCB. With more research on the efficacy of supercritical fluids for the decomposition of plastics underway, pyrolysis may no longer be the most popular option for chemical separation of the non-metallic fraction from the metals in PCB. For the extraction of metals from PCB, pyrometallurgy is the most traditional route. Pyrometallurgy is advantageous since the feed can be any form of electronic scrap, but the drawback is that the product stream is hard to control. The refining processes are not selective, and as a result, many metals are lost during smelting in either the slag or the sludge. Pyrometallurgy also runs the risk of dioxin formation and toxin release, especially when the process does not include a dust containment/filter system and thorough off-gas treatment process for prevention and containment. Hydrometallurgy offers better control, more precision, and is a greener option compared to the high operating temperatures of pyrometallurgy. Most hydrometallurgical processing focuses on copper and precious metal recovery. Acid leaching is most frequently used, where sulfuric acid is the superior reagent for Cu leaching. Nitric acid is another effective reagent, but these inorganic acids, sulfuric and nitric acid, have poor leaching selectivity in subsequent processing steps. Alternatively, ammoniacal-based leaching has high selectivity towards copper. For Au leaching, thiosulfate and thiourea seem to be promising leaching options that could replace cyanide solutions. Thiosulfate and thiourea are greener solvent systems, but tend to consume large amounts of reagent and can suffer from poor stability and slow kinetics. Biometallurgy, which utilizes microorganisms, usually acidophilic groups of bacteria, is the most environmentally-friendly route for extraction and recovery of metals from PCB. Bioleaching is feasible for the extraction of Cu and precious metals, Au and Ag. Yet, bioleaching suffers from low reaction rates, metal precipitation, long reaction times, and bacterial toxicity. Hydrometallurgical routes produce solutions containing a mixture of metals and the recovery of these metals turns out to be a challenging task. Cementation using zinc powders and sodium borohydride, solvent extraction using lixiviants, and Cu electrowinning are some of the main techniques for metal recovery. While these processes, particularly precipitation techniques, cementation and solvent extraction, are well-established, several issues with regards to metal recovery from the leached-PCB solution still remain. It is evident that new, sustainable technologies for the recycling of PCBs are urgently needed. More studies on effective, efficient, and green metal separation and recovery techniques are necessary to overcome the challenges involved with PCB disposal and recycling. Supercritical fluids, particularly $scCO_2$, shows potential as a greener solvent for the separation and extraction of metals from PCB. New research areas to advance include smarter design (automated disassembly, shape memory metals and polymers), dry capture technologies (nanotechnology, cryo-milling), biotechnological capture technologies (biomaterials, new microorganisms), and sensing technologies (opto-electronic sorting, X-rays).[22] Engineers, lawmakers, and other stakeholders must work together to find the gaps in achieving a more economical and environmentally-friendly recycling process.

Conflicts of interest

There are no conflicts to declare.

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