

A critical review on the recycling of copper and precious metals from waste printed circuit boards using hydrometallurgy

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HIGHLIGHTS

- Waste PCBs have a high content of valuable metals.
- Hydrometallurgical technology has been widely used to extract valuable metal.
- The recycling of waste PCBs using hydrometallurgy was critically reviewed.

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GRAPHIC ABSTRACT



ABSTRACT

Currently, increasing amounts of end-of-life (EoL) electronic products are being generated due to their reduced life spans and the unavailability of suitable recycling technologies. In particular, waste printed circuit boards (PCBs) have become of global concern with regard to environmental issues because of their high metal and toxic material contents, which are pollutants. There are many environmental threats owed to the disposal of electronic waste; off-gasses, such as dioxins, furans, polybrominated organic pollutants, and polycyclic aromatic hydrocarbons, can be generated during thermal treatments, which can cause serious health problems if effective off-gas cleaning systems are not developed and improved. Moreover, heavy metals will dissolve, and release into the ground water from the landfill sites. Such waste PCBs contain precious metals which are of monetary value. Therefore, it is beneficial to recover the metal content and protect the environment from pollution. Hydrometallurgy is a successful technique used worldwide for the recovery of precious metals (especially gold and silver) from ores, concentrates, and waste materials. It is generally preferred over other methods because it can offer high recovery rates at a relatively low cost. This article reviews the recent trends and developments with regard to the recycling of precious metals from waste PCBs through hydrometallurgical techniques, such as leaching and recovery.

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1 Introduction

Owing to the current rapid development of electronic technology, electrical and electronic equipment (EEE), such as televisions (TVs), computers, printers, telephones, modems, fax machines, copy machines, light emitting

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diode (LED)/liquid crystal display (LCD) monitors, laptops, printed circuit boards (PCBs), and medical equipment, have a shorter life span compared to products produced in the past. It is summarized that electrical and electronic devices currently have a shorter lifespan because of the availability of inexpensive, highly technically advanced products that have more features [1]. There has been rapid growth in the lifestyles of human beings, who are increasingly likely to have modern facilities along with user-friendly EEE. Thus, there is stiff competition among manufacturers to produce superior products based on advanced technologies.

Simultaneously, the resultant short life spans of EEE have generated large amounts of waste electrical and electronic equipment (WEEE), known as “e-waste.” The United Nations Environment Program estimates that the global annual production of e-waste will be approximately 50 million tons in 2018; approximately one-third of this waste is from the USA and one-quarter is from Europe [2,3]. It is reported more than 7-8 million tons of e-waste are generated annually in the USA. In Europe, the amount of e-waste generated annually is increasing at a rate of 3%-5%, which is about three times that of municipal waste. E-waste accounts for more than 5% of the total amount of municipal waste produced [4,5]. There are also extremely high quantities of e-waste generated in China, where the e-waste growth rate (about 5%–10% per year) is higher than the average growth rate of the rest of the world [6]. Following the industrial age, when metallurgical-, chemical-, paper-making-, printing-, and dye-waste pollution emerged worldwide, e-waste is currently becoming an emerging contaminant. Therefore, it is necessary to manage and dispose of e-waste effectively. Useful compo-

nents can be recovered from e-waste to save resources. This can minimize the emission of environmental pollutants associated with e-waste that are harmful to human health as well as ecological systems [7]. Developed countries already have e-waste recycling and processing systems that are relatively mature. Japan, Germany, and Switzerland are world leaders with regard to the recycling of e-waste. Developed countries use e-waste recycling systems to reduce pollution and recycle resources. Large-scale networks and resource-collection systems are built on industrial parks, to achieve the centralized disposal of e-waste [8]. For example, since 2001, Japan has implemented a “home appliance recycling law” to help manufacturers collect e-waste. In addition, Germany has a ‘divided product responsibility’ system (shown in Fig. 1), which was established through the Elektro G regulations, and therefore, manufacturers are obliged to recycle e-waste [9]. Switzerland was the first country to establish a management system for the recycling of e-waste, which has two sets of effective recycling management systems, known as the Swiss Association for Information, Communication, and Organizational Technology (SWICO) and the Foundation for Disposal in Switzerland (SENS). These systems are used for the classified management of waste computers, electronic information technology equipment, and household appliances [8–10].

There has been increasing concern over global environmental issues in recent years. The vast quantity of e-waste generated from PCBs has compelled researchers, scientists, industries, and government authorities to execute several recycling strategies for metal recovery. This is because e-waste from PCBs has a high metal content, especially precious metals [11].

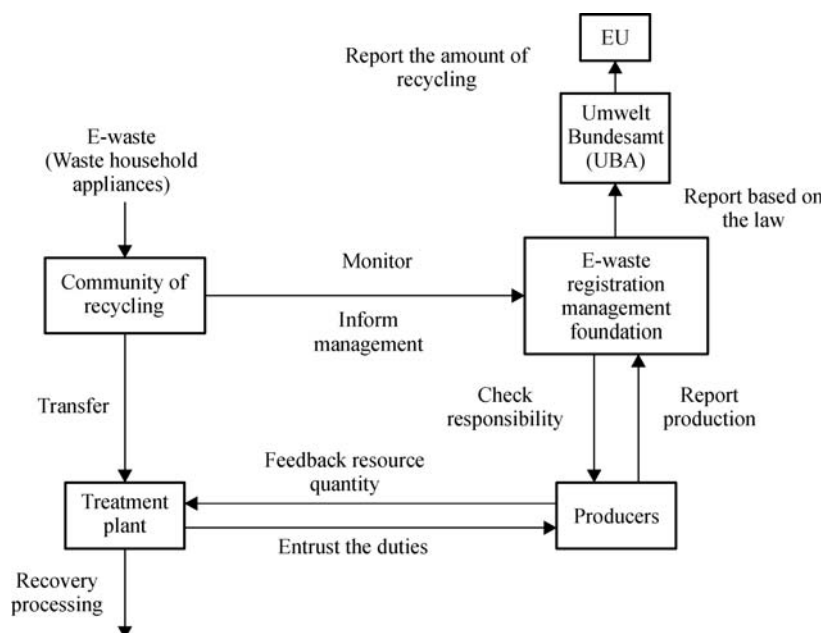


Fig. 1 E-waste retrieval and recycling system in Germany

Waste PCBs are generated from electronic and consumer devices, ranging from larger items, such as fridges, washing machines, TVs, personal computers, and laptops, to smaller items, such as mobile phones, CD/DVD players, radios, shavers, modems, and cameras. PCBs are the most important component of electronic products and have a complex elemental composition. About 1.5 Mt/year of waste PCBs is generated in the world [12]. The weight percentages of the metals obtained from PCBs are shown in Table 1. In addition, different types of PCBs have different metal contents, especially with regard to precious metals. For example, a typical computer circuit board contains 20% copper, 1000 ppm silver, 250 ppm gold, and 110ppm palladium. A mobile phone circuit board contains 13% copper, 1380 ppm silver, 350 ppm gold, and 210 ppm palladium.

However, a TV circuit board contains 10% copper, 280 ppm silver, 20 ppm gold, and 10 ppm palladium [17]. The precious metal content of the PCBs of telephones and calculators is about 70% while it is approximately 40% in the case of TV boards and DVD players [17]. Compared with primary metal resources, such as ores and concentrates, waste PCBs have a low precious metal content; however, it is noteworthy that that PCBs have gold, platinum-group, and copper contents that are 50-100, 7-200, and 50 times higher than those of primary metal resources respectively, and therefore have become a secondary metal resource. In addition, owing to their value, gold, silver, and platinum-group metals account for more than 70% of the total value of the metal within e-waste, and thus their recovery has become the main economic driving force for electronic waste recycling [17,18]. Gold is with the highest recovery priority, followed by copper, palladium, aluminum, tin, lead, platinum, nickel, zinc, and silver [19].

However, without the use of appropriate methods, many environmental issues will occur. According to the US Environmental Protection Agency (EPA), 80%–85% (by

weight) of e-waste is traditionally destined for landfills, where their leachage would undoubtedly contaminate the soil and groundwater in adjacent regions [20–23]. Another major disposal route involves incineration, in which a number of associated problems have been identified, including the production of estrogenic compounds [24,25] and the presence of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) and polybrominated diphenyl ethers (PBDD/Fs) [26–29] in emissions. In addition, following incineration, the fly and bottom ashes become enriched with heavy metals; the vaporization of these heavy metals leads to their emission in the exhaust gas [30,31]. Therefore, it is advantageous to recycle precious metals from waste PCBs because of both economic and environmental reasons. During recovering precious metals, large quantities of toxic materials are often produced and separation methods are required; therefore, despite the high value of precious metals, the exploitation of materials recovery from PCB waste has been limited. The current methods used to recycle precious metals from waste PCBs involve various technologies, such as physical separation, metallurgical (pyrometallurgical, hydrometallurgical, and biometallurgical) processing, or pooling techniques; these methods have been studied [17,32]. Compared with other methods, hydrometallurgical methods are favored for the recovery of precious metals from e-waste, because they are relatively simple and inexpensive. In this article, the authors review the current status of the hydrometallurgy processes used to recycle waste PCBs, and introduce recycling processes based on leaching and reduction.

2 Recycling of precious metals via hydrometallurgical techniques

Hydrometallurgy is an essential part of metallurgy. In this type of recycling, precious metals within the e-waste are

Table 1 Metal concentrations in printed circuit boards based on metal analysis

Source/Weight (%)	PCB scrap			PCB-MP		PCB-PC
	(1)	(2)	(3)	(4)	(5)	(5)
Silver	-	3300 g·t ⁻¹	0.10	0.21	0.054	0.16
Palladium	-	-	0.010	-	-	-
Aluminum	-	4.7	5.00	0.26	-	5.7
Gold	-	80 g·t ⁻¹	0.025	0.00	0.0043	0.13
Copper	25.06	26.80	16.00	34.49	39.86	20.19
Iron	0.66	5.30	5.00	10.57	-	7.33
Nickel	0.0024	0.47	1.00	2.63	0.39	0.43
Lead	0.80	-	2.00	1.87	-	5.53
Tin	-	1.00	3.00	3.39	-	8.83
Zinc	0.04	1.50	1.00	5.92	0.46	4.48

Note: (1): Yang et al. [13], (2): Guo et al. [3], (3): Park and Fray [14], (4): Yamane et al. [15], (5): Li et al. [16]. MP-mobile phone; PC-personal computer

initially leached by acid or salt, and then separated by a variety of methods to obtain purified metals. Hydrometallurgical techniques include the use of chemical leaching, bioleaching, and supercritical fluids which are performed by various researchers under laboratory conditions. In most industries, the recycling of e-waste is restricted to the use of physical and pyrometallurgical processes [17]. Compared with the use of pyrometallurgical methods, hydrometallurgy methods offer many advantages. There are no/low levels of toxic gases released and little or no dust is generated. The processes consume relatively little energy and offer a high recovery rate. There is no slag generated except for a few plastics. In addition, such processes have simple working conditions and low equipment costs [33,34].

Figure 2 shows a flow chart describing the hydrometallurgy methods used to recover precious and base metals from waste PCBs. First, the waste PCBs are physically pretreated; for example, this includes the collection, sorting, shredding, and magnetic separation of the PCBs. Following pretreatment, the waste PCBs are dissolved using acid to achieve separation; the leach liquor and residue are rich in copper and precious metals, respectively. During the subsequent step, the residue is leached by lixivants (chemical or biological). Subsequently, the leaching solutions, which contain precious and base metals, are subjected to separation and purification

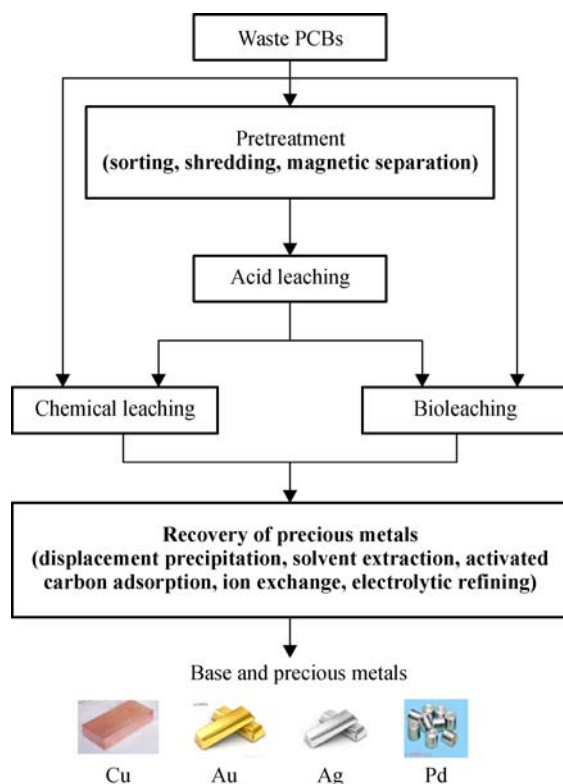


Fig. 2 Flow chart showing hydrometallurgy routes for the recycling of metals from waste PCBs

techniques, such as the precipitation of impurities, solvent extraction, absorption, and ion-exchange, to isolate and concentrate the metals of interest. Nevertheless, when PCBs are recycled via hydrometallurgy, leaching is the most important step because it dissolves the greatest metal content into the solution [1]. The leaching of precious metals from waste PCBs has been investigated by many researchers and industries to test potential lixivants, such as halogens, cyanide, thiourea, thiosulfate, and aqua regia.

2.1 Chemical leaching

2.1.1 Cyanide leaching

Cyanidation is a traditional method used to leach gold and silver, which commenced in 1887 [35]. Compared with non-cyanide lixiviant systems, it is simple, efficient, and widely used in industry. Owing to the oxygen in the cyanide solution, cyanide can be used to selectively dissolve gold, silver, and some of their complexes. If the dissolution reaction is considered as an electrochemical erosion process, then the gold dissolution process can be represented by gold that is dissolved into the solution (Fig. 3). When oxygen is present at the cathode surface, the reactions at the anode and cathode surface are:

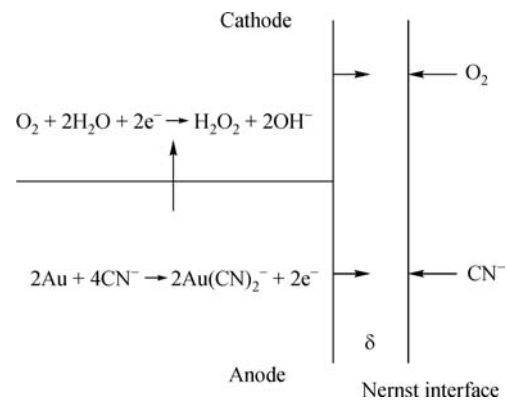
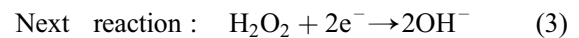
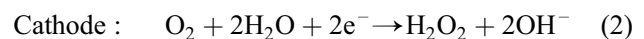
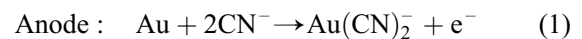
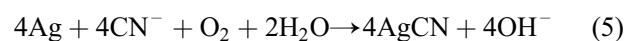
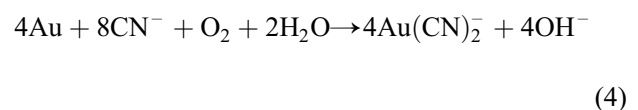
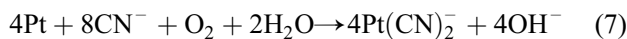
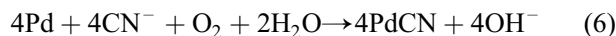


Fig. 3 Dissolution of gold in the cyanide solution



The reactions between the cyanide and precious metals are shown below.



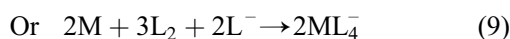
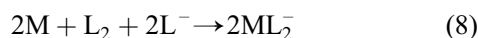


Although cyanide is toxic to human beings and harmful to the environment, it is largely used for the leaching of precious metals from waste PCBs. It has been applied for centuries because of its advantages; it offers highly efficient recovery and is inexpensive and simple to use [36]. Moreover, some researchers have also investigated the use of pressure cyanide leaching as a new technique for the recycling of precious metals [37]. First, the leaching of gold from refractory gold ore was studied. Later, in the USA, this method was introduced to dispose of catalysts used to purify automotive exhaust emissions; platinum, palladium, and rhodium were recovered from the catalysts [38]. However, few studies have focused on the recovery of precious metals from PCBs. Cyanide leaching could be used to recover precious metals from PCBs. However, owing to its toxicity, many researchers currently prefer to study non-cyanide methods.

Akcil et al. [1] summarized a number of studies that focused on the recovery of precious metals from e-waste by cyanide, as shown in **Table 2**.

2.1.2 Halide leaching

This method includes chloride leaching [41,42], bromide leaching [43], and iodide leaching [44–46]. Their reaction principles are similar, as shown below:



Where, M represents the precious metal element, L represent the halogen element (include chlorine, bromine and iodine). L_2 is the oxidizing agent, and L^- is the complexant.

The halogenation method has been used to recover precious metals (mainly gold) from gold ore for many years. For years it has been investigated by a large number of researchers with regard to the recovery of precious metals from PCBs. Several investigations have been undertaken to determine the effectiveness of chlorine [47]. Liu et al. [48] conducted a comparative experiment on the efficiency of various chlorination (Cl_2 , NaClO , NaClO_3) methods with regard to the leaching of gold. The

results showed that for gold leaching, the best lixiviant is sodium chlorate. In addition, all the lixiviants offered a low leaching rate of below 60%. Behnamfard et al. [41] developed multi-step hydrometallurgical process for recycling waste PCBs. First, Cu was dissolved in $\text{H}_2\text{SO}_4\text{-H}_2\text{O}_2$ solution, then Au and Ag in the leaching residue dissolved in $\text{CS}(\text{NH}_2)_2\text{-Fe}^{3+}$ system, and finally Pd and the remaining Au dissolved in $\text{NaClO-HCl-H}_2\text{O}_2$ system. The process achieved the selective recovery of Cu, Au, Ag and Pd.

Moses and Petersen [43] conducted a dynamic research study on separation techniques with regard to the coal-gold agglomeration process. They determined that the vapor pressures of bromine are 10 KPa and 28 KPa at temperatures of 0°C and 35°C , respectively. When the bromide leaching process is used, specialist equipment is required for safety and health reasons, and this restricts its use in industrial applications.

Iodide leaching is a promising technology with regard to non-cyanide leaching processes. Iodide leaching has many advantages. It achieves rapid leaching and is non-toxic. It offers good selectivity, which results in less leaching of the base metal. It is easy to regenerate iodide; the iodine is reduced while the gold is recovered at the anode region. In addition, no corrosion occurs because iodide leaching is conducted in a weakly alkaline medium [49]. Moreover, among the complexes formed by gold and the halogen elements, the complexes formed by gold and iodine are the most stable. However, iodide leaching consumes a great amount of reagent, and iodine is relatively expensive. In addition, the efficiency of the electrolytic deposition of gold should be improved. All these issues must be resolved before iodide is applied for the leaching of gold in industry.

2.1.3 Thiourea leaching

In 1941, scholars of the former Soviet Union were the first to report that silver and gold could be dissolved in a thiourea solution. However, this was largely ignored until the late 1960s, when many researchers began to theoretically and experimentally investigate the leaching of gold by thiourea; the research has been conducted on this topic [50]. It was reported that in 1977, scientists in France started to leach gold and silver using thiourea from zinc calcine. In 1982, mineral companies in Mexico and Colorado started to dispose of gold tailing ores using thiourea. In 1984, the New England Antimony Company

Table 2 Studies on the recovery of precious metals from e-waste using cyanide [1]

Source of waste	Medium conditions	Recovery (%)	References
E-waste	Cyanide leaching (pH>10 and temperature of 25°C), applied to chloride leaching tailings	Ag-93% Au-95% Pd-99%	[39]
PCB of cell phones	Commercial cyanide process (potassium cyanide concentration of 6%–8%, 25°C , 2–4 h, pH = 12.5, at S/L of 1/20)	Au-60%-70%	[40]

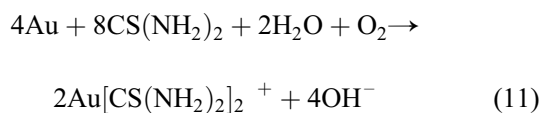
of Australia began to leach gold from gold antimony ores using thiourea. In addition, in the 1980s, the former Soviet Union began to recover gold using thiourea [51]. Therefore, it is apparent that thiourea can be used to leach precious metals from PCBs. Therefore, in recent years, the use of thiourea for the recovery of precious metals (mainly gold) has gained attention worldwide because of its relatively low environmental impact.

Under acidic conditions, thiourea can be used to dissolve gold effectively under the action of an oxidizing agent (mainly Fe^{3+}), as demonstrated by the following reaction (Tu represents the thiourea, SCN_2H_4):



Li et al. [16] extracted gold and silver from PCBs of waste mobile phones using thiourea leaching method. The influence of thiourea and Fe^{3+} concentrations, reaction temperature, and particle size on the leaching of gold and silver from mobile phones was investigated. Birloaga and Vegliò [52] studied multi-step thiourea methods, used to extract the valuable content of gold, silver, and copper from waste PCBs, and they determined the optimal conditions for the dissolution of the three metals. In the case of copper dissolution via a two-step counter current leaching procedure, the optimal conditions were achieved using $1.7 \text{ mol} \cdot \text{L}^{-1} \text{ H}_2\text{SO}_4$ (98%), 17% H_2O_2 (30%), solid/liquid ratio of 1:5, with a continuous stirring rate of 200 rpm for 1 h at 25°C . In the case of gold and silver dissolution, the optimal conditions were achieved using $20 \text{ g} \cdot \text{L}^{-1}$ of thiourea, $6 \text{ g} \cdot \text{L}^{-1}$ of ferric ions, $0.1 \text{ mol} \cdot \text{L}^{-1}$ sulfuric acid, with vigorous agitation at 200 rpm for 1 h at ambient temperature.

However, thiourea is not stable under acidic conditions; it is easily oxidized to formamidine disulfide. Therefore, under acidic conditions, the thiourea solutions used to recover precious metals have a series of disadvantages. However, under alkaline conditions, thiourea is stable; therefore, methods involving the use of alkaline thiourea have been focused on by many researchers. The gold is leached by the alkaline thiourea, as shown by the reaction below:



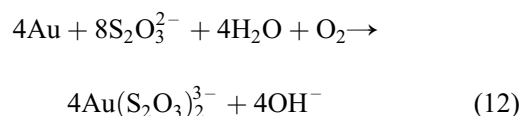
At present, methods involving gold dissolution by alkaline thiourea have been successively improved; researchers identified a cheap and efficient stabilizer, which was efficient, non-toxic, and offered rapid gold leaching. Senanayake [53] conducted electrochemical tests involving the leaching of gold using alkaline thiourea, and determined the electrodynamic parameters for the gold leaching. Moreover, they explored the electrochemical behavior that occurred during gold dissolution in an

alkaline thiourea solution containing Na_2SO_3 , as well as the associated thermodynamics.

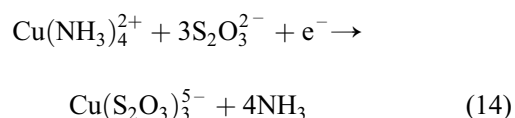
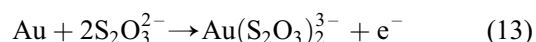
However, this method is still in an early stage of development. It is difficult to adapt this method when gold ore with a high sulfur content is used. The products formed due to the oxidation of the thiourea influences the stability of the alkaline thiourea. In addition, there is a lack of awareness regarding the selectivity associated with the gold leaching. The stabilizers used can only inhibit the irreversible decomposition of the thiourea to a certain degree. In the case of gold leaching by alkaline thiourea, the leaching rate cannot attain that achieved with cyanide leaching, and therefore this limits its use in industry.

2.1.4 Thiosulfate leaching

The thiosulfate method has been well-recognized with regard to the development of cleaner and safer gold-ore processing techniques using hydrometallurgy. Moreover, this method has been investigated with regard to the recovery of precious metals from PCBs. Ammonium thiosulfate and sodium hyposulfite, which are easily dissolved in water, are mainly used in the thiosulfate process [52]; the sulfate radical is unstable in an acidic solution, and is converted into sulfuric acid. Therefore, it should react in alkaline medium. The reaction principle is shown below:



The electrochemical-catalytic mechanism of gold leaching by ammoniacal thiosulfate was investigated by Aylmore and Muir [54]. It was proposed that $\text{Cu}(\text{NH}_3)_4^{2+}$ species present in solution acquires electrons on the cathodic portion of the gold surface and is directly reduced to $\text{Cu}(\text{NH}_3)_2^+$. At the same time, either ammonia or thiosulfate ions react with Au^+ ions on the anodic surface of gold and enter the solution to form either $\text{Au}(\text{NH}_3)_2^+$ or $\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$. Depending on the concentration of $\text{S}_2\text{O}_3^{2-}$, $\text{Cu}(\text{NH}_3)_2^+$ converts to $\text{Cu}(\text{S}_2\text{O}_3)_3^{5-}$ ions, and likewise for $\text{Au}(\text{NH}_3)_2^+$. Both the $\text{Cu}(\text{S}_2\text{O}_3)_3^{5-}$ species and the $\text{Cu}(\text{NH}_3)_2^+$ species in solution are then oxidized to $\text{Cu}(\text{NH}_3)_4^{2+}$ with oxygen. The leaching of gold in a thiosulfate solution containing copper and ammonia can be represented by an electrochemical reaction, as shown in Eqs. (13) and (14) [1].

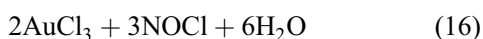
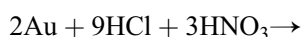
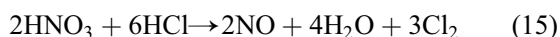


In a study by Ha et al. [55], gold was leached from waste PCBs using thiosulfate leaching under a copper-ammonia-thiosulfate solution, and the kinetics of the associated electrochemical reaction was studied. The obtained results showed that the leaching rate depends on the concentrations of the thiosulfate, Cu^{2+} , and ammonia. The optimal conditions were achieved using 20 mM copper, 0.12 M thiosulfate, and 0.2M ammonia. A leaching rate of 98% was achieved. Ficeriova et al. [56] determined that the recovery of gold and silver from waste material using ammonium thiosulfate was both economical and eco-friendly. Meanwhile, a high gold leaching rate was also achieved.

Thiosulfate leaching has many advantages; it is non-toxic, non-corrosive, and offers high selectivity. However, the principal problem associated with thiosulfate leaching involves the high consumption of the reagent during extraction. It is reported that thiosulfate losses of up to 50% occur in ammoniacal thiosulfate solutions containing copper [52]. In general, the high reagent consumption renders most thiosulfate systems uneconomical, despite their potential environmental benefits.

2.1.5 Aqua regia leaching

Aqua regia is effective with regard to the leaching of precious metals because of its good oxidation properties. The chemical reactions associated with this gold leaching method are shown in Eqs. (15)–(17).



However, in industry, aqua regia is just used for digestion processes, to determine the precious metal content rather than for the leaching of precious metals. The use of aqua regia results in the release of toxic gases,

such as nitrogen oxide. It is also highly corrosive, dangerous, and results in high consumption. Therefore, aqua regia has not been widely used as a lixiviant to leach precious metals. Under laboratory conditions, many researchers use it for the one-step leaching of precious metals. Using three stages, Sheng and Etsell [57] used aqua regia as a lixiviant to leach gold from computer circuit board scrap. The first and second stages involved nitric-acid leaching to separate the gold and base metals; the third stage involved aqua regia leaching to recover the gold.

2.1.6 Ionic liquid acid leaching

Ionic liquid is a salt; it is a liquid at low temperature and has a wide liquidus temperature range. It typically consists of an organic cation with an inorganic or organic anion [58]. Globally, it has been increasingly investigated with regard to organic syntheses, catalytic reactions, electrochemical applications, separation, biochemistry, and materials engineering [59–62]. As for ionic liquid leaching for recovering precious metals from WPCBs, the best advantages are high metal selectivity and recovery efficiency without second pollution generated during the process. However, the obvious limitation of this technique is high cost.

Chen et al. [63–65] conducted much work regarding the leaching of copper from waste PCBs using ionic liquid acid; this is summarized in Table 3.

2.1.7 Other hydrometallurgical methods

Table 4 summarizes the results of several studies with regard to the recovery ratio of certain metals in e-waste with the use of other lixiviants. There are many types of chemical lixiviant. However, each lixiviant is associated with their specific advantages and disadvantages. Zhang et al. [49] compared these using a three-scale analytic hierarchy process (AHP) to determine the weight of evaluation indices of various leaching methods. They determined a basic score for each leaching method with regard to five indices (leaching rate, reagent cost,

Table 3 Leaching of copper from waste PCBs by ionic liquid acid

Source of waste	Used amount of chemicals	Medium conditions	Recovery (%)	References
PCB	Bronsted acidic ionic liquid	particle size of 0.1–0.25 mm, 25 mL 80% (v/v) ionic liquid, 10 mL 30% H_2O_2 , S/L of 1/25, 70°C, 2 h	99% Cu	[63]
PCB	[BSO ₄ HPy]HSO ₄ , [BSO ₃ HMIIm]HSO ₄ [MIm]HSO ₄ [BSO ₃ HMIIm]OTf [BSO ₃ HPy]OTf	particle size of 0.1–0.25 mm, 10%–80% (v/v) ionic liquid, 30 wt.% H_2O_2 , S/L of 1/1–1/15, 40°C–70°C, 0–2 h	100% Cu	[64]
PCB	[BSO ₃ HMIIm]OTf [BSO ₃ HPy]OTf	particle size of 0.5–1.0 mm, 10%–80% (v/v) ionic liquid 10 mL 30% H_2O_2 , S/L of 1/1–1/15, 40°C–70°C, 0–8 h	30% Pb	[65]

Table 4 Studies regarding metal recovery with other lixivants

Source of waste	Amount of chemicals used	Medium conditions	Recovery (%)	References
PCB	In chloride medium (HCl and NaCl) oxidative leaching (HNO ₃ and H ₂ O ₂)	75°C	93%–95% Pd	[39]
PCB of cell phones	1/3 (v/v) HNO ₃	25 and 60°C, 2 h, S/L of 1/20	100% Ag	[40]
Poly cracker ash of PCBs	4 M HNO ₃	90°C, 1 h, stirring speed of 250 rpm	99.9% Cu, Fe, Pb, 57.01% Ni	[61]
PCB	0.3 kmol/m ³ Cu(II) 5 kmol/m ³ NH ₃ 1 kmol/m ³ (NH ₄) ₂ SO ₄	1.5 mm particle size, 10 g PCB, 25°C, 5 h	82% Cu	[66]
PCB	0.5–7.5 g/L Cu ²⁺ 4.7–46.6 g/L Cl [−]	20°C–80°C, solids ratio (1%–15% w/v), A/O of 2–4, 2 h	>91%Cu, Ni, Fe, Ag	[67]
PCB	2 M H ₂ SO ₄ , in 20 ml 30% H ₂ O ₂ (for 100mL solution)	30°C, 2 h	90% Au	[68]
PCB	10% Diisoamyl sulphide (S201, >98.5%)	A/O of 5, and 2 min extraction	99.5% Pd	[69]

Table 5 Final scores of various leaching methods [49]

Leaching methods	Cyanide	Aqua regia	Thiourea	Thiosulfate	Chloride	Bromide	Iodide
Score	4.457	3.483	4.000	2.711	3.251	2.249	3.640

corrosive, toxicity, and reliability), which was multiplied by its relevant weight. The final scores for each method are shown in Table 5. It was determined that the use of thiourea and iodide is likely to reduce the cost of the process and be more reliable with regard to the replacement of cyanide leaching.

2.2 Bioleaching methods

Metals from e-waste can be recovered using a bioleaching process; this process commenced in the 1980s. The principle of the method involves using the interactions between the microorganisms and e-waste to recycle the metals. The biological method has only been used relatively recently; however, through the efforts of many scientists, it has been significantly developed. The microorganisms used can be divided into autotrophic bacteria and heterotrophic bacteria. The autotrophic bacteria include *Acidithiobacillus thiooxidans* (*At. thiooxidans*) and *Acidithiobacillus ferrooxidans* (*At. ferrooxidans*). The heterotrophic bacteria include *Aspergillus niger* and *Penicillium simplicissimum*. The bioleaching process requires low investment costs, has a lower environment impact, consumes less energy, and is easily controlled compared with the conventional pyrometallurgy and hydrometallurgy routes [70]. However, biotechnology is also with obvious limitation on industrial application. Bioleaching process takes a long time to reach high recovery rates of precious metals from WPCBs.

In recent years, bioleaching has also been applied to recover metal from waste PCBs. Wang et al. [71] used *Acidithiobacillus thiooxidans* (*At. thiooxidans*) and *Acid-*

ithiobacillus ferrooxidans (*At. ferrooxidans*) to leach copper from waste PCBs; a leaching rate of greater than 90% was achieved. Moreover, mixed culture of *Acidithiobacillus thiooxidans* (*At. thiooxidans*) and *Acidithiobacillus Ferrooxidans* (*At. ferrooxidans*) were investigated by Liang et al. [72]. They found that the extraction efficiency of copper, nickel, zinc and lead were enhanced when mixed culture were applied compared to the individual cultures. They attributed this bioleaching enhancement to the increased redox potential and lowered pH value in the case of mixed culture. Arshadi et al. [73] used *Bacillus megaterium*, a cyanogenic bacterium, to extract Au and Cu from PCBs of mobile phone. Under the optimal condition, about 72% of Cu and 65 g Au/ton PCBs was extracted. When Cu/Au ratio is high, the elimination of Cu can improve Au recovery. Table 6 summarizes a number of reported results regarding the extraction of metal from waste PCBs using various types of microorganisms.

2.3 Supercritical fluids

A novel method, which uses supercritical fluids for metal-nonmetal separation, is attracting increasing attention. The temperature and pressure of a supercritical fluid are above the critical point; these liquids have many unique properties, such as their viscosity, density, diffusion coefficient, and solvation ability. Current research on the recycling of circuit boards involves the use of supercritical CO₂ and supercritical water, which can be used during the pretreatment and intermediate stages. The supercritical method has numerous advantages; it offers high treatment efficiency and a complete response. In addition, it is rapid

Table 6 Bioleaching of e-scrap based on various published reports

Source of waste	Used amount of chemicals	Medium conditions	Recovery (%)	References
PCB	Brønsted acidic ionic liquid	particle size of 0.1–0.25 mm, 25 mL 80% (v/v) ionic liquid, 10 mL 30% H ₂ O ₂ , S/L of 1/25, 70°C, 2 h	99% Cu	[63]
PCB	[BSO ₄ HPy]HSO ₄ , [BSO ₃ HMIIm]HSO ₄ [MIIm]HSO ₄ [BSO ₃ HMIIm]OTf [BSO ₃ HPy]OTf	particle size of 0.1–0.25 mm, 10%–80% (v/v) ionic liquid, 30 wt.% H ₂ O ₂ , S/L of 1/1–1/15, 40°C–70°C, 0–2 h	100% Cu	[64]
PCB	[BSO ₃ HMIIm]OTf [BSO ₃ HPy]OTf	particle size of 0.5–1.0 mm, 10%–80% (v/v) ionic liquid 10 mL 30% H ₂ O ₂ , S/L of 1/1–1/15, 40°C–70°C, 0–8 h	30% Pb	[65]

and can be used to oxidize and degrade harmful organic matter. Furthermore, it will not result in the formation of secondary pollutants. However, this method has not been directly studied with regard to the recovery of precious metals from waste PCBs. The resultant products of the heavy metals require further refinement.

Supercritical CO₂ fluid can be used to decompose and dissolve the resin layers of a circuit board, which results in the separation of the copper foil layer and glass fiber layer. This process is similar to pyrolysis, but unlike pyrolysis, the surface of the circuit board does not produce light and heavy naphtha or other liquids because high temperatures are not used. In addition, this process is more conducive to material layer separation and enhances the purity of the material. Initially, the supercritical CO₂ extraction of metal ions occurs, and subsequently, a complexing agent is added to generate a neutral complex. This is then combined with a polar modifier to enhance the solubility. Sanyal et al. [84] applied supercritical CO₂ as solvent with an additional small amount of water to separate the PCB components into copper foil, glass fiber and polymer. Calgaro et al. [85] realized copper recovery from waste PCBs using supercritical carbon dioxide with H₂SO₄ and H₂O₂ as co-solvents. Results showed that supercritical extraction was very fast and with high copper recovery rate. Supercritical CO₂ extraction was confirmed to be a promising technology for PCBs recycling. Xiu and Zhang [86] used supercritical methanol as solvent to simultaneously recover polymers and metals from waste printed circuit boards. Following pretreatment with supercritical water, Xiu et al. [87,88] succeeded in the leaching of precious metals by iodine. Subsequently, the separated solid-phase product with concentrated metal contents was subjected to an acid leaching process for metal recovery. In addition, they conducted an investigation on the effect of two supercritical water (SCW) methods, namely supercritical water oxidation (SCWO) and supercritical water depolymerization (SCWD) pre-treatments, on the recovery of various metals from waste PCBs. The results indicated that the SCWO and SCWD pre-treatments had a significant effect on the recovery of the various metals. The SCWO pre-treatment was highly efficient and enhanced the recovery

of copper and lead, where respective leaching rates of 99.8% and 80% were achieved at 420°C. In addition, the recovery of all the studied metals was enhanced by the SCWD pre-treatment; the recovery rates increased as the pre-treatment temperature increased. Up to 90% of the tin, zinc, chromium, cadmium, and manganese within the PCB could be recovered when a SCWD pre-treatment was applied at 440°C.

3 Reduction of precious metals via hydrometallurgical methods

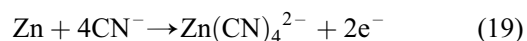
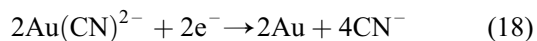
In this process, the precious metals are reduced to a simple substance using a leachant. Many methods are used, such as displacement precipitation, solvent extraction, ion exchange, activated carbon adsorption, and electrolytic refining. This process represents the final step used to recover precious metals from waste PCBs, and is also one of the most important steps. At present, the main issues associated with this process are related to the economic recycling of the precious metals.

3.1 Displacement precipitation

Precious metals often exhibit relatively weak activity, and therefore, it is relatively easy to recover precious metals via the replacement of the base metals. Commonly, base metals, such as iron, aluminum, and zinc, are used to replace the precious metal. In this process, leaching and replacement occur simultaneously. In addition, solid-liquid separation is not necessary during this process. Therefore, the duration of the process can be shortened, which preserves equipment and reduces costs. Therefore, this method is widely used in industry. Compared with aluminum powder replacement, iron and zinc powder replacement are more feasible and established procedures. However, the use of iron and zinc also has disadvantages. The zinc dust replacement system will release hydrogen, and will result in the consumption of acid and zinc. The iron-replacement precipitation method usually employs an iron plate. In addition, severe acid corrosion occurs, and

this greatly increases the costs involved. In addition, the holes that are formed because of acid corrosion negatively influence the gold recovery.

Since the 1890s, zinc has been used to recover gold from cyanide solutions worldwide. Fleming et al. [89] stated that the major reactions of the zinc cementation process are the cathodic deposition of gold and anodic corrosion of zinc, which occur at the surface of zinc particles. And he stated that the cementation of gold is practically constant over the pH range 8–11.



3.2 Solvent extraction

Extraction is a method that is employed to extract a substance from an immiscible liquid phase using an organic solvent. The principle of this method concerns the distribution and dissolution of the substance in the water and organic phases. During the chemical treatment, metals enter the aqueous solution in the form of ions. The extraction agent and metal ions exhibit complexation, association, chelation, and other functions based on the selectivity of the extraction agent. Furthermore, the metal ions and impurities can be separated and enriched by adjusting the reaction conditions.

The solvent extraction method has many advantages; it offers good selectivity, mild reaction conditions, and requires a short process. However, high consumption rates are typical, and at the end of the extraction, a reverse extraction process must occur, which consequently generates high costs. Therefore, the solvent extraction of precious metals could be used for a wide range of applications in industry; to achieve this, we must vigorously develop new types of extraction agents while developing relevant extraction technologies.

In laboratory, the extractants, such as organophosphorus derivations, guanidine derivations, and mixture of amines-organophosphorus derivations, are used extensively. For example, Kumari et al. [61] recovery the copper from the loaded LIX 84IC using 10% (v/v) sulfuric acid by maintaining at O/A of 3 containing 61.23 g·L⁻¹ Cu and 0.0037 g·L⁻¹ Ni. Then 1% (v/v) LIX 84IC diluted in kerosene was used to extract nickel from the concentrate leach liquor. Cui and Zhang [17] made a comparison of extractants on the aurocyanide complex extraction. They stated clearly that the LIX-79 extractant allowed gold extraction from alkaline cyanide media.

3.3 Activated carbon adsorption

The activated carbon adsorption method offers a rapid gold adsorption rate. The activated carbon has a large adsorp-

tion capacity. Therefore, the activated carbon adsorption method is considered a good method for the recovery of gold from gold solutions. The results of a previous investigation show that the maximum adsorption capacity of carbon is 26.5 kg·t⁻¹ when the concentrations of activated carbon and gold are 2g·L⁻¹ and 30mg·L⁻¹, respectively. High gold adsorption and recovery rates were achieved when 4g·L⁻¹ of activated carbon was employed over an adsorption period of 2 h; an adsorption rate of up to 99% was achieved. An effective desorption effect can be achieved when ethanol and sodium hydroxide are used as desorption agents. The equilibrium and kinetics for the adsorption of gold onto activated carbon from acidic thiourea solutions have been studied by Zhang et al. [90]. The result showed that Ag⁺ and Cu²⁺ ions significantly reduce the rate of adsorption of gold, because they strongly compete for the surface sites. And a high concentration of Fe³⁺ (5 g·L⁻¹) also substantially reduces the rate of adsorption of gold.

However, when gold is recovered using activated carbon, many problems can occur; owing to its small grains, the activated carbon can get lost with the pulp. Moreover, when the activated carbon adsorbs the gold, other impurities will also be adsorbed. This is not conducive to the gold recovery. In addition, this process requires high dosages of activated carbon, which renders it relatively uneconomical.

3.4 Ion exchange

Ion exchange adsorption is a very attractive gold recovery method. Compared with the activated carbon adsorption method, it offers higher adsorption and gold recovery rates; in addition, desorption and regeneration can be conducted under ambient temperatures and pressures. Moreover, the mechanical strength, breakage rate, and abrasion resistance of the resin used are significantly lower than those of activated carbon. Therefore, many researchers recover the gold from leach liquors by ion exchange [89,91–94].

Many resins have been studied by researchers; among others, resins such as the 732, OO1A, D61, DJ52CL-P204, and styrene series cation exchange resins exhibit good adsorption effects. Following desorption by a desorption agent, an essence of the extract can be regenerated. Among others, HCl, HCl-NaClO₃, HCl-Br₂, Na₂S₂O₃, and NaCN-NaOH are commonly used as desorption agent. However, resins that offer good selectivity, high adsorption capacity, and are not easily damaged should be further explored and developed. In addition, much work is required to identify desorption agents that are non-toxic, non-corrosive, and offer good desorption effects.

Zhang and Dreisinger [94] carried out that in the absence of copper, gold can be loaded onto strongly basic ion exchange resin from thiosulfate solutions rapidly and to high loading concentration. Thomas et al. [95] claimed to have achieved almost full recovery of gold and silver using

strong base resins. The gold-bearing lixiviant and gold residue were subjected to resin-in-pulp (RIP) or resin-in-leach (RIL) which recovers both copper and gold. Thomas et al. [95] also found that higher gold recoveries were obtained by using very dilute thiosulfate solutions at 45°C–55°C and adding the resin to the pregnant solution containing the solid residue rather than adding it to the pregnant solution after a liquid/solid separation step.

3.5 Electrochemical process

This method uses an electrode to generate a direct current in a solution containing precious metals, so that the precious metals can be immediately electrolytically deposited onto a plate electrode. Compared with the replacement method, it offers better selectivity and high product purity. Moreover, the addition of other metals or chemical reagents is not required. Therefore, this method is worthy of further research. Currently, this method is widely used in industry. In this method, the electrolytic apparatus is considered the most important aspect of the process. Specifically, the recovery of precious metals by electrochemical process is considered a suitable process. Some researchers have paid more attention and done substantial work on this promising method. Fe³⁺/Fe²⁺ redox system was applied to extract copper from waste printed circuit boards [94]. Gold and copper were recovered from waste electrical and electronic equipment by electro-deposition method [97,98]. Lister et al. [99] proposed a process of recovery of critical and value metals from mobile electronics enabled by electrochemical processing. This process includes two stages. The first stage uses electro-generated Fe³⁺ in acidic sulfate media to dissolve Fe, Ni, Sn, Cu, Ag and rare earth elements (REEs). Ag and Cu will be preferentially reduced at the cathode. After most of these metals are dissolved and captured, a HCl solution can be introduced where Cl₂ is electro-generated at the anode to dissolve Au and Pd in the second stage.

4 Conclusions

With increasing quantities of e-waste, researchers need to develop effective and environmentally-friendly methods for its disposal and recycling. Owing to the high content of precious metals in e-waste, their recovery has always been an important research topic for researchers. However, many researchers are attracted to the use of hydrometallurgy methods for the recovery of precious metals from e-waste because they are less expensive and offer high recovery rates. The hydrometallurgy method can be divided into four steps; the first step involves a physical pretreatment (including dismantling, crushing, and sorting). The second step involves the separation of the precious metals and base metals by nitric acid or sulfuric acid. The third step involves the leaching of precious

metals via chemical leaching or bioleaching. The fourth step involves the reduction of the precious metals.

Research on the recovery of precious metals from e-waste has achieved great success in the laboratory. However, few studies have focused on the implementation of these techniques in industry. Therefore, the development of environmentally friendly and efficient methods of applying these techniques in industry will be the focus of our future research. In the future, there will be new breakthroughs with regard to the disposal of e-waste.

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