

Review

Metallurgical recovery of metals from electronic waste: A review

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Received 13 December 2007; received in revised form 1 February 2008; accepted 4 February 2008
Available online 8 February 2008

Abstract

Waste electric and electronic equipment, or electronic waste, has been taken into consideration not only by the government but also by the public due to their hazardous material contents. In the detailed literature survey, value distributions for different electronic waste samples were calculated. It is showed that the major economic driver for recycling of electronic waste is from the recovery of precious metals. The state of the art in recovery of precious metals from electronic waste by pyrometallurgical processing, hydrometallurgical processing, and biometallurgical processing are highlighted in the paper.

Pyrometallurgical processing has been a traditional technology for recovery of precious metals from waste electronic equipment. However, state-of-the-art smelters are highly depended on investments. Recent research on recovery of energy from PC waste gives an example for using plastics in this waste stream. It indicates that thermal processing provides a feasible approach for recovery of energy from electronic waste if a comprehensive emission control system is installed. In the last decade, attentions have been removed from pyrometallurgical process to hydrometallurgical process for recovery of metals from electronic waste. In the paper, hydrometallurgical processing techniques including cyanide leaching, halide leaching, thiourea leaching, and thiosulfate leaching of precious metals are detailed. In order to develop an environmentally friendly technique for recovery of precious metals from electronic scrap, a critical comparison of main leaching methods is analyzed for both economic feasibility and environmental impact.

It is believed that biotechnology has been one of the most promising technologies in metallurgical processing. Bioleaching has been used for recovery of precious metals and copper from ores for many years. However, limited research was carried out on the bioleaching of metals from electronic waste. In the review, initial researches on the topic are presented. In addition, mechanisms and models of biosorption of precious metal ions from solutions are discussed.

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Keywords: Electronic waste; Metal recovery; Metallurgical process; Bioleaching; Biosorption; Precious metals

Contents

1. Introduction	229
2. Recovery of metals from electronic waste by pyrometallurgical processing	231
2.1. Pyrometallurgical recovery of metals from e-waste in practice	231
2.2. New developments on pyrometallurgical recovery of metals from e-waste	232
2.3. Perspectives on pyrometallurgical recovery of metals from e-waste	235
3. Recovery of metals from electronic waste by hydrometallurgical processing	235
3.1. Leaching of precious metals	235
3.1.1. Cyanide leaching	235
3.1.2. Halide leaching	235

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3.1.3.	Thiourea leaching	236
3.1.4.	Thiosulfate leaching	237
3.2.	Recovery of precious metals from leachate	237
3.2.1.	Recovery of precious metals from solutions by cementation	237
3.2.2.	Recovery of precious metals from solutions by solvent extraction	238
3.2.3.	Recovery of precious metals from solutions by activated carbon	238
3.2.4.	Recovery of precious metals from solutions by ion exchange	239
3.3.	Techniques for hydrometallurgical recovery of metals from e-waste	239
4.	Recovery of metals from electronic waste by biometallurgy	243
4.1.	Biorecovery	243
4.1.1.	Mechanisms of bacterial metal sulfide oxidation	243
4.1.2.	Practical applications of biorecovery	244
4.1.3.	Biorecovery of metals from electronic waste	244
4.2.	Biosorption	246
4.2.1.	Biomass used for recovery of precious metals	246
4.2.2.	Mechanisms of biosorption of precious metals	246
4.2.3.	Models of biosorption of precious metals	249
4.2.4.	Recovery of precious metals from electronic waste by biosorption	250
5.	Conclusions	251
	Acknowledgment	252
	References	252

1. Introduction

Waste electric and electronic equipment (WEEE), or electronic waste (e-waste), has been taken into consideration not only by the government but also by the public due to their hazardous material contents [1–5]. Currently, the main options for the treatment of electronic waste are involved in reuse, remanufacturing, and recycling, as well as incineration & landfilling. In many cases, electronic equipment which is no longer useful to the original purchaser still has value for others. In this case, equipment can be resold or donated to schools or charities without any modification. Reuse of end-of-life (EOL) electronic equipment has first priority on the management of electronic waste since the usable lifespan of equipment is extended on a secondary market, resulting a reducing of the volume of treated waste stream. Remanufacturing is a production-batch process where used products or cores, are disassembled, cleaned, repaired or refurbished, reassembled and tested to produce new or like-new equipments [6]. Recycling means the reprocessing in a production of the waste materials for the original purpose or for other purposes. Recycling of electronic waste involves disassembly and/or destruction of the EOL equipment in order to recover materials.

Incineration of electronic waste by traditional incinerator for municipal solid waste is also dangerous. For example, copper is a catalyst for dioxin formation when flame-retardants are incinerated. This is of particular concern as the incineration of brominated flame retardants (BFRs) at low temperature. It was estimated that emissions from waste incineration account for 36 tonnes per year of mercury and 16 tonnes per year of cadmium in the EU Community [1]. The hierarchy of treatment of e-waste encourages reuse the whole equipment first, remanufacturing, then recovery of materials by recycling

techniques, and as a last resort, disposal by incineration and landfilling.

Recycling of electronic waste is an important subject not only from the point of waste treatment but also from the recovery aspect of valuable materials. The US Environmental Protection Agency (EPA) has identified seven major benefits, such as saving in energy and reduction in pollutions when scrap iron and steel are used instead of virgin materials. Using recycled materials in place of virgin materials results in significant energy savings [2,7].

From the point of material composition, electronic waste can be defined as a mixture of various metals, particularly copper, aluminum, and steel, attached to, covered with, or mixed with various types of plastics and ceramics [8]. Precious metals have a wide application in the manufacture of electronic appliances, serving as contact materials due to their high chemical stability and their good conducting properties. Platinum group metals are used among other things in switching contacts (relays, switches) or as sensors to ascertain the electrical measurand as a function of the temperature [9].

Table 1 gives examples of the metal composition of different electronic scraps from literatures. It is clear that electronic waste varies considerably with its age, origin and manufacturer. There is no average scrap composition, even the values given as typical averages actually only represent scrap of a certain age and manufacturer. Additionally, non-ferrous metals and precious metals contents have gradually decreased in concentration in scrap. This is due to the falling power consumption of modern switching circuits and the rising clock frequency (surface conduction). While the contact layer thickness in the '80s was in the region of 1–2.5 μm , in modern appliances today it is between 300 and 600 nm (gold wafer) [9].

The value distributions V_i for different electronic scrap samples (as shown in Table 2) were calculated by using the following

Table 1
Weight composition of metals for different electronic scrap samples from literatures

Electronic waste	Weight (%)					Weight (ppm)			Refs.
	Fe	Cu	Al	Pb	Ni	Ag	Au	Pd	
TV board scrap	28	10	10	1.0	0.3	280	20	10	[10]
PC board scrap	7	20	5	1.5	1	1000	250	110	[10]
Mobile phone scrap	5	13	1	0.3	0.1	1380	350	210	[10]
Portable audio scrap	23	21	1	0.14	0.03	150	10	4	[10]
DVD player scrap	62	5	2	0.3	0.05	115	15	4	[10]
Calculator scrap	4	3	5	0.1	0.5	260	50	5	[10]
PC mainboard scrap	4.5	14.3	2.8	2.2	1.1	639	566	124	[11]
Printed circuit boards scrap	12	10	7	1.2	0.85	280	110	–	[12]
TV scrap (CRTs removed)	–	3.4	1.2	0.2	0.038	20	<10	<10	[13]
Electronic scrap	8.3	8.5	0.71	3.15	2.0	29	12	–	[14]
PC scrap	20	7	14	6	0.85	189	16	3	[15]
Typical electronic scrap	8	20	2	2	2	2000	1000	50	[16]
E-scrap sample 1	37.4	18.2	19	1.6	–	6	12	–	[17]
E-scrap sample 2	27.3	16.4	11.0	1.4	–	210	150	20	[17]
Printed circuit boards	5.3	26.8	1.9	–	0.47	3300	80	–	[18]
E-scrap (1972 sample)	26.2	18.6	–	–	–	1800	220	30	[8]
E-waste mixture	36	4.1	4.9	0.29	1.0	–	–	–	[19]

Note that “–” denotes not reported.

equation:

$$V_i = \frac{100W_t Pr_i}{\sum W_t Pr_i} \quad (1')$$

where W_t is the weight percent of metal i in the electronic scrap sample (as shown in Table 1), Pr_i is the current price of metal i . The metal price data are from London Metal Exchange (LME) official prices for cash seller and settlement on the 24 October 2007.

It can be seen that for cell phones, calculators, and printed circuit board scraps, the precious metals make up more than 70% of the value, for TV boards and the DVD player they still contribute to about 40%. This indicates that the major economic driver for recycling of electronic waste in industry is from the

recovery of precious metals. Behind the precious metals come copper and zinc, while Al, Pb, and Fe have less value.

Currently, recycling of e-waste can be broadly divided into three major steps [2]: (a) disassembly: selectively disassembly, targeting on singling out hazardous or valuable components for special treatment, is an indispensable process in recycling of e-waste; (b) upgrading: using mechanical processing and/or metallurgical processing to up-grade desirable materials content, i.e. preparing materials for refining process; (c) refining: in the last step, recovered materials are retreated or purified by using chemical (metallurgical) processing so as to be acceptable for their original using.

Mechanical process and disassembly are mainly used for the pre-treatment of e-waste for upgrading the valuable materi-

Table 2
Calculated value distribution for different electronic scrap samples

Electronic waste	Value-share (%)								
	Fe	Cu	Al	Pb	Ni	Ag	Au	Pd	Sum of precious metals
Prices ^a (\$/tonne)	300	7736	2475	3580	31150	430000	24490000	11660000	
TV board scrap	4	39	13	2	5	6	25	6	37
PC board scrap	0	16	1	1	3	4	62	13	79
Mobile phone scrap	0	8	0	0	0	5	67	19	91
Portable audio scrap	3	78	1	0	0	3	12	2	17
DVD player scrap	17	35	4	1	1	4	33	4	42
Calculator scrap	1	12	6	0	8	6	64	3	73
PC mainboard scrap	0	6	0	0	2	2	81	8	91
Printed circuit boards scrap	1	19	4	1	6	3	66	–	69
TV scrap (CRTs removed)	–	82	9	2	4	3	–	–	3
Electronic scrap	1	38	1	6	36	1	17	0	18
PC scrap	3	28	18	11	14	4	20	2	26
Typical electronic scrap	0	5	0	0	2	3	87	2	92
E-scrap sample 1	5	60	20	2	–	–	13	–	13
E-scrap sample 2	1	22	5	1	–	2	65	4	70
Printed circuit boards	0	37	1	–	3	25	35	0	60
E-scrap (1972 sample)	1	19	–	–	–	9	66	5	80

^a The metal price data are from London Metal Exchange (LME) official prices for cash seller and settlement on the 24th October, 2007.

als content. Mechanical recycling of electronic waste has been extensively reviewed by Cui and Forssberg in 2003 [2], and has been investigated by different researchers [13,20–24]. However, mechanical recycling cannot efficiently recover precious metals.

In the last refining step, recovered metals are melted or dissolved by using metallurgical techniques, including pyrometallurgical processing and hydrometallurgical processing for removal of impurities. A series of chemical reactions are involved in this step. The objective of this paper is to offer a comprehensive literature survey on metallurgical recovery of metals from electronic waste, so as to provide a detailed research status for a further investigation.

Although few studies exist on recovery of metals from electronic waste by biometallurgical process, there are other fields dealing with similar processes, such as: recovery of metals from gold ores in mineral processing, and biosorption of heavy metals from waste waters [25–30]. It should be stated, however, that applying results from the field of mineral processing to the treatment of electronic waste has limitations: the size of particles involved and material contents are quite different in the two systems. At this stage, however, it is believed that some techniques used in mineral processing and waste water treatment provide alternatives for recovery of metals from electronic waste.

2. Recovery of metals from electronic waste by pyrometallurgical processing

Pyrometallurgical processing, including incineration, smelting in a plasma arc furnace or blast furnace, dressing, sintering, melting and reactions in a gas phase at high temperatures [8,16,31] has become a traditional method to recover non-ferrous

metals as well as precious metals from electronic waste in the past two decades. In the process, the crushed scraps are burned in a furnace or in a molten bath to remove plastics, and the refractory oxides form a slag phase together with some metal oxides.

2.1. Pyrometallurgical recovery of metals from e-waste in practice

Veldhuizen and Sippel [32] reported the Noranda process at Quebec, Canada (as shown in Fig. 1). The smelter recycles about 100,000 tonnes of used electronics per year, representing 14% of total throughput (the balance being mostly mined copper concentrates). Materials entering the reactor are immersed in a molten metal bath (1250 °C), which is churned by a mixture of supercharged air (up to 39% oxygen). Energy cost is reduced by combustion of plastics and other flammable materials in the feeding. The resulting of agitated oxidation zone converts impurities including iron, lead and zinc into oxides which become fixed in a silica-based slag. The slag is cooled and milled to recover more metals before disposal. The copper matte containing precious metals is removed and transferred to the converters. After an upgrading in the converters, liquid blister copper is refined in anode furnaces and cast into anodes with purity of 99.1%. The remaining 0.9% contains the precious metals, including gold, silver, platinum and palladium, along with other recoverable metals, such as selenium, tellurium, and nickel. Subsequently, electrorefining of the anodes recovers these marketable metals.

Another application for pyrometallurgical process to recover metals from e-waste is practiced at the Boliden Ltd. Rönnskår

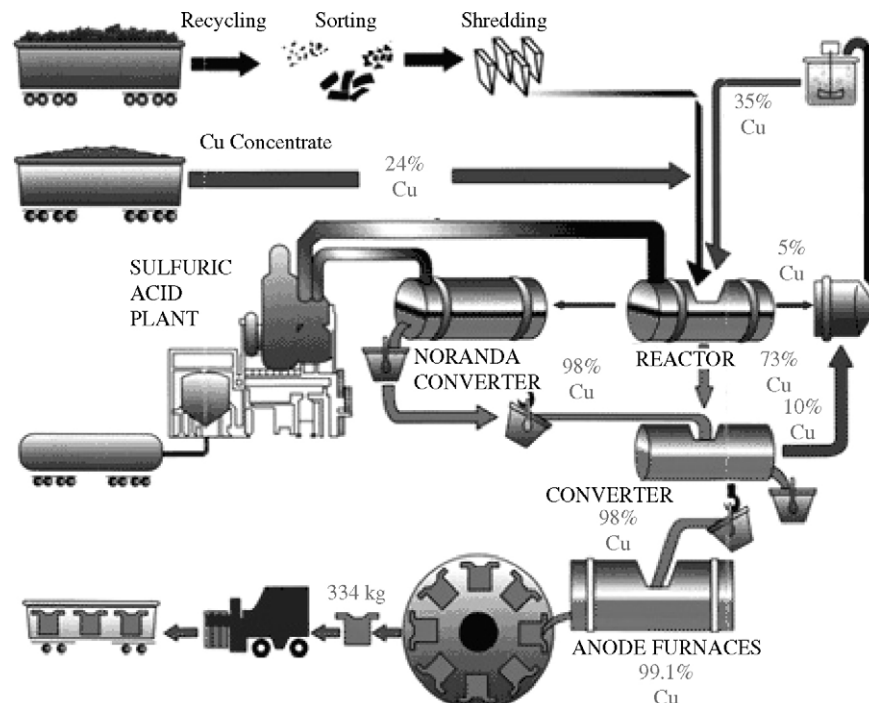


Fig. 1. Schematic diagram for the Noranda Smelting Processing [32].

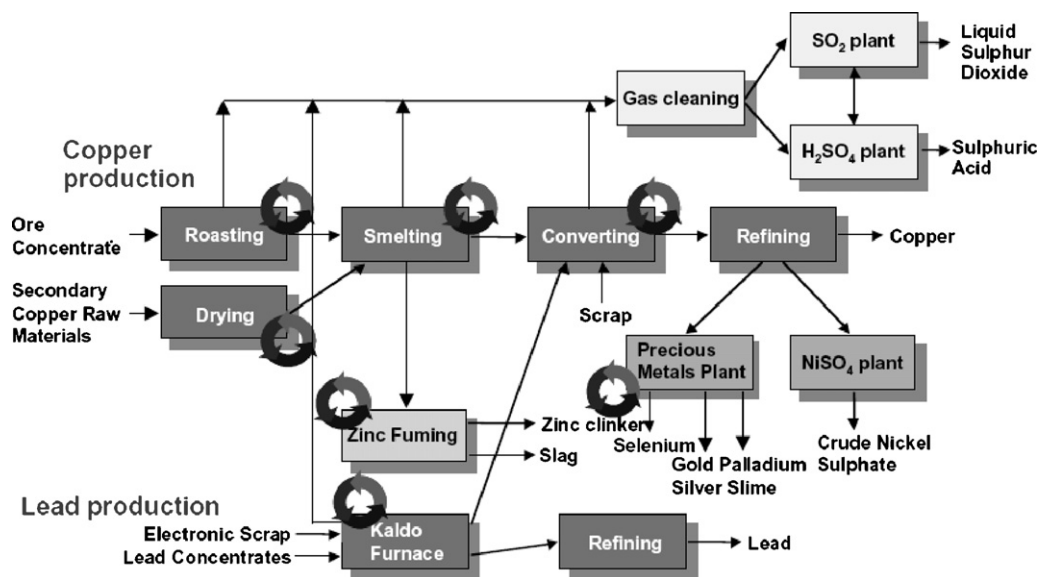


Fig. 2. Schematic diagram for the Rönnskär Smelter [35].

Smelter, Sweden [18,33,34]. As shown in Fig. 2 [35], scraps can be fed into the process in different steps depending on their purities. High copper containing scrap is fed into Converting process directly, but low grade e-waste is fed into Kaldo Furnace. It was reported [35] that 100,000 tonnes of scrap including waste from electronics is fed into Kaldo Furnace every year. In the patented [36] Kaldo reactor, blended feed material with e-waste and lead concentrates is charged by skip hoist. An oxygen lance supplies the needed O₂ for combustion with an oil-oxygen burner. Off-gases are subjected to additional combustion air at around 1200 °C in post-combustion. A standard gas handling system recovers thermal energy by a steam network. The Kaldo Furnace produces a mixed copper alloy that is sent to the copper converting for recovery of metals (Cu, Ag, Au, Pd, Ni, Se, and Zn) and the dusts (containing Pb, Sb, In and Cd) are sent to other operations for metal recovery. However, a detailed discussion on environmental issues, such as emissions to the air and water is lacking in the publications.

In the recent years, Umicore published [10,37–40] his precious metals refining process at Hoboken, Belgium, which is mainly focused on recovery of precious metals from e-waste. Various industrial wastes and by-products from other non-ferrous industries (e.g. drosses, mattes, speiss, anode slimes), precious metals sweeps and bullions, spent industrial catalysts, as well as consumer recyclables such as car exhaust catalysts or printed circuit boards are acceptable for the integrated metals smelter and refinery process. The plant treats 2,50,000 tonnes of different wastes per annual, from which electronic waste presently covers up to 10% of the feed [40]. The first step in the precious metals operations (PMO) is smelting by using an IsaSmelt furnace. Plastics or other organic substances that are contained in the feed partially substitute the coke as reducing agent and energy source. The smelter separates precious metals in a copper bullion from mostly all other metals concentrated in a lead slag, which is further treated at the Base Metals Operations (BMO). The copper bullion is then treated by copper-leaching

and electrowinning and precious metals refinery for copper and precious metals recovery.

The Base Metals Operations process by-products from the PMO. The main processing steps are lead blast furnace, lead refinery and special metals plant. The lead blast furnace reduces the oxidized lead slag from the IsaSmelt together with high lead containing third party raw materials and transforms them into impure lead bullion, nickel speiss, copper matte and depleted slag. The impure lead bullion, collecting most of the non-precious metals, is further treated in the lead refinery (Harris process). Special metals (indium, selenium, tellurium) residues were reported [40] to be generated in the lead refining process. Consequently, pure metals are recovered in a special metals refinery. In the Umicore's plant, complex flowsheet with several steps including pyrometallurgical techniques, hydrometallurgical process, and electrochemical technology are employed in recovery of base metals, precious metals, as well as platinum group metals and special metals [37].

An emission control system is installed at Umicore's IsaSmelt process (as shown in Fig. 3). Hygienic gases and process gases are cooled with energy recovery and cleaned using some techniques, such as bag house filters, electrofilters, and scrubbers. Sulfur is converted into SO₂, which is transformed to sulfuric acid in the "contact" plant. On the stack, SO₂ and NO_x are continuously monitored with a direct display of the measured value in the control rooms, so that the operators can react immediately. Diffuse emissions from stockyards and roads are abated by intensive sprinkling, using either fixed sprinkling systems or watering carts. According to the report by Hageluken [37], emissions from the plant are well below the European limits.

2.2. New developments on pyrometallurgical recovery of metals from e-waste

In a research [35], sponsored by Boliden Minerals AB, Association of Plastics Manufacturers Europe (APME), and

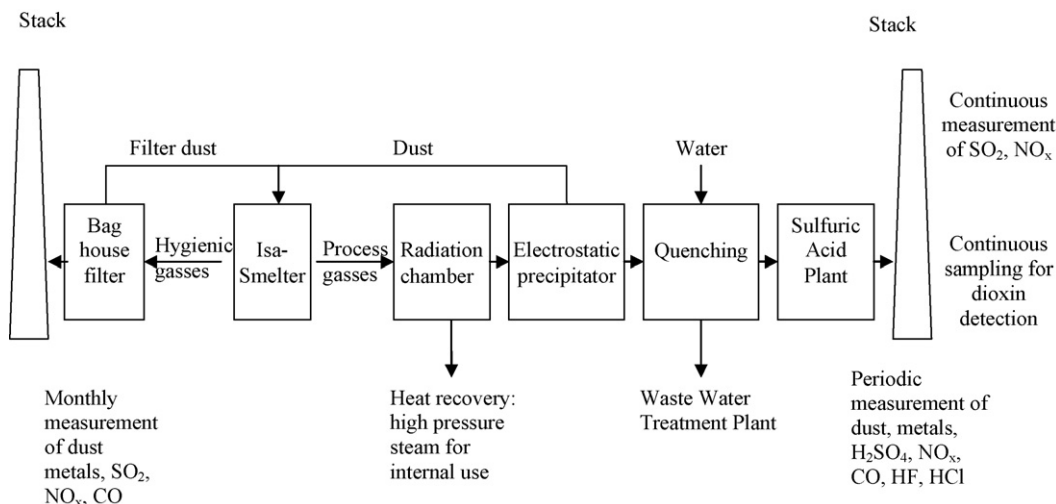


Fig. 3. Offgas emission control installations at the IsaSmelt furnace [37].

American Plastics Council (APC), the use of personal computer (PC) scrap in the Zinc Fuming furnace feed was investigated (Fig. 2). In the study, the Zinc Fuming process was chosen for PC waste because it uses fossil fuel both as a reducing agent and as fuel to recover zinc from slags.

The PC scrap was collected from various sources within Scandinavia. After a removing of Hg-containing pieces by dismantling, the scrap was shredded and pre-treatment by utilizing a hammer mill and magnetic iron separator, respectively. The shredded scrap with particle size ~ 30 mm was mixed with crushed revert slag in a 50:50 mixture to optimize bulk handling and silo feeding, avoiding blockage during feeding. The plastics contained in the PC scrap worked with added coal fines to facilitate the fuming of zinc, lead, arsenic, and related metals in addition to the contained halogens. Copper and precious metals from the e-waste follow the copper collector to be recovered to the copper smelter.

According to the report from APME [35], almost complete recovery of the copper and precious metals from the e-waste can be obtained in this step. The test gave a successful example for recovery of energy and metals from PC waste. However, it should be pointed out that the possible influence of an increased halogen load on the corrosion of gas cleaning equipment much be assessed in a long-term performance test.

A full scale trial was reported [38] to be carried out in September 2004 at Umicore's plant to investigate the feasibility of using mixed plastics-rich material from WEEE to replace coke as a reducing agent and energy source for the IsaSmelt furnace. Two hundred fifty tonnes of waste was fed into the smelter and a comparison was carried out between operation with zero plastics input plus 4.5% coke, compared to 6% WEEE plastics and 1% coke. The result showed that the smelter operation and its performance, such as metal recovery rates and operating stability, are not negatively affected by the treatment of the plastics.

Researches on the recovery of copper and precious metals from electronic scraps by pyrometallurgical processing also involved some patents [36,41–45].

A process for the recovery of precious metal values as essentially pure gold from gold scraps like electronic scrap was described by Dunn et al. [41]. The gold scrap reacted with chlorine at a temperature with the range of about 300–700 °C to form a mixture containing metallic gold, silver chloride, and other metal chlorides. The mixture was washed with air-sparged hydrochloric acid to dissolve the impurity-metal chlorides other than silver chloride forming a metallic gold/silver chloride mixture. Then ammonium hydroxide and nitric acid were used respectively for washing the metallic gold/silver chloride mixture to dissolve the silver chloride and the traces of metallic silver from the metallic gold. Gold with 99.9% purity was recovered from gold scraps. It should be pointed out that Dunn's processing is developed for refining high grade gold materials that contain more than 80% of gold.

Day [42] reported a process for the recovery of precious metals from refractory ceramic materials. The scrap was charged to a plasma arc furnace at a temperature of at least 1400 °C to produce a molten metallic phase containing a substantial proportion of the precious metals and collector metal, as well as a slag phase containing ceramic residues. Suitable collector metals if needed are silver or copper in divided form. A SiO₂ containing flux with 7–10% by weight in the charge is useful for lowering the melting point. 38.13 kg electronic scrap, containing barium titanate was treated as a sample. After the treatment in a plasma arc for 15 min, platinum and palladium were recovered with recovery of 80.3% and 94.2%, respectively.

Patent by Aleksandrovich et al. [44] described a method for recovery of PGM and gold from electronic scraps. The method includes fusing together of scraps based on chalcogenides of base metals with carbon reducer. After the settling and cooling of melted materials, solidification and separation of solidified product are carried out by formed phase boundaries. Separated bottom product is ground into powder which is processed as refining concentrate. In processing of matte-like light alloys, recovery of noble metals into desired product is increased.

Table 3
A summary of typical pyrometallurgical methods for recovery of metals from electronic waste

Techniques	Metals Recovered	Main process features	Main results	Refs.
Noranda process at Quebec, Canada	Cu, Au, Ag, Pt, Pd, Se, Te, Ni	Feeding to copper smelter with copper concentration (14% of the total throughput); Upgrading in converter and anode furnaces; Electrorefining for metal recovery	High recovery for both copper and precious metals.	[32]
Boliden Rönnskår Smelter, Sweden	Cu, Ag, Au, Pd, Ni, Se, Zn, Pb	Feeding to Kaldo reactor with lead concentrates (totally 100,000 tonnes every year); Upgrading in copper converter and refining; Precious metals refining for recovery	High recovery of copper and precious metals.	[18,33]
Test at Rönnskår Smelter	Copper and precious metals	PC scrap feeding to Zinc Fuming process (1:1 mixture with crushed revert slag); Plastics was tested as reducing agent and fuel; Copper and precious metals following the copper collector to be recovered to the copper smelter.	Almost complete recovery of copper and precious metals in the Zinc Fuming process.	[35]
Umicore's precious metal refining process at Hoboken, Belgium	Base metals, precious metals, Platinum group metals and Selenium, Tellurium, Indium	IsaSmelt, copper leaching & electro-winning and precious metal refinery for Precious Metals Operation (PMO); E-waste cover up to 10% of the feed (250,000 tonnes of different wastes per annual); Plastics partially substitute the coke as reducing agent and fuel in IsaSmelt. Base Metals Operations process by-products from the PMO, including Lead blast furnace, lead refinery and special metals plant. Offgas emission control system is installed at the IsaSmelt furnace.	Recovering both base metals, precious metals and special metals such as Sb, Bi, Sn, Se, Te, In.	[10,37,40]
Full scale trial at Umicore's smelter	Metals in electronic scrap	Plastics-rich materials from WEEE were tested to replace coke as a reducing agent and energy source for the IsaSmelt.	The smelter operation and metal recovery are not negatively affected by using 6% WEEE plastics and 1% of coke to replace 4.5% coke.	[38]
Dunn's patent for gold refining	Gold	Gold scrap reacted with chlorine at 300 °C to 700 °C; Hydrochloric acid washing to dissolve the impurity-metal chlorides; Ammonium hydroxide and nitric acid washing respectively to dissolve the silver chloride; Samples should contain more than 80% of gold.	Gold with 99.9% purity was recovered from gold scraps.	[41]
Day's patent for refractory ceramic precious metals scraps	Precious metals such as platinum and palladium	The scrap was charged to a plasma arc furnace at a temperature of at least 1400 °C; A molten metallic phase containing precious metals and collector metal was produced; Ceramic residues went into a slag phase; Silver and copper are suitable collector metals in the process.	For an electronic scrap, platinum and palladium were recovered with recovery of 80.3% and 94.2%, respectively.	[42]
Aleksandrovich's Patent for recovery of PGM and gold from electronic scraps	PGM and gold	Fusing together of scraps based on chalcogenides of base metals with carbon reducer; After the settling and cooling of melted materials, solidification and separation of solidified product are carried out by formed phase boundaries.	PGM and gold were recovered.	[44]

2.3. Perspectives on pyrometallurgical recovery of metals from e-waste

Table 3 gives a summary of typical pyrometallurgical methods for recovery of metals from electronic waste. It is clear that the traditional technology, pyrometallurgy has been used for recovery of precious metals from waste electronic equipment in practice for years. However, most methods involving pyrometallurgical processing of electronic waste give rise to the following limits [10,16,46–49]:

1. Integrated smelters cannot recover aluminum and iron as metals, they are transferred into the slag. Unfortunately, aluminum has influences on the slag properties which are in most cases not wanted.
2. The presence of halogenated flame retardants (HFR) in the smelter feed can lead to the formation of dioxins unless special installations and measures are present. Traditional smelters designed for the treatment of mining concentrates or simple copper scrap encounter some challenges for electronic waste treatment. However, state-of-the-art smelters are highly depended on investments.
3. Ceramic components and glass in the e-waste increase the amount of slag from blast furnaces, which thereby increases the loss of precious metals and base metals from the scrap.
4. Energy recovery and utilizing of organic constituents as a reducing agent are only on its beginning.
5. Only partial separation of metals can be achieved using pyrometallurgy, resulting in a limited upgrading of the metal value. Furthermore, hydrometallurgical techniques and/or electrochemical processing are subsequently necessary.
6. Precious metals stay for a long time in the pyrometallurgical process and are obtained at the very end of the process.

Recent research on recovery of energy from PC waste gives an example for using of plastics in electronic waste. It indicates that thermal processing of e-waste provides a feasible approach for recovery of energy from e-waste if a comprehensive emission control system is installed.

3. Recovery of metals from electronic waste by hydrometallurgical processing

As discussed above, precious metals contribute the most value in electronic scraps. From an economic point of view, recovery of precious metals from e-waste is most attractive. In the past two decades, the most active research area on recovery of metals from electronic scraps is recovering precious metals by hydrometallurgical techniques [50–58]. Comparing with the pyrometallurgical processing, hydrometallurgical method is more exact, more predictable, and more easily controlled [59].

The main steps in hydrometallurgical processing consist of a series of acid or caustic leaches of solid material. The solutions are then subjected to separation and purification procedures such as precipitation of impurities, solvent extraction, adsorption and ion-exchange to isolate and concentrate the metals of interest. Consequently, the solutions are treated by electrorefining pro-

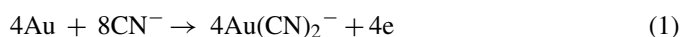
cess, chemical reduction, or crystallization for metal recovery [16,60–64].

3.1. Leaching of precious metals

Leaching is the process of extracting a soluble constituent from a solid by means of a solvent, which is the initial step in a hydrometallurgical process. The most common leaching agents used in recovery of precious metals include cyanide, halide, thiourea, and thiosulfate [53,54,65,66].

3.1.1. Cyanide leaching

Cyanide as lixiviant for gold has been utilized in the mining industries for more than one century [67]. The mechanism of gold dissolution in cyanide solution is essentially an electrochemical process. The overall reactions are shown in Reactions (1) and (2) [68].



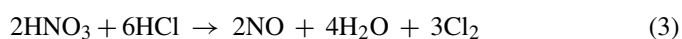
The effect of pH on dissolution rate for the noble metals (gold, silver, palladium, and platinum) investigated by Dorin and Woods [68]. The results showed that a maximum dissolution of gold, silver, palladium, and platinum in cyanide solution can be obtained at pH 10–10.5. The order of activity for noble metals is $\text{Au} > \text{Ag} > \text{Pd} > \text{Pt}$.

A series of environmental accidents at various gold mines that caused severe contamination of rivers and groundwater, has precipitated widespread concern over the use of cyanide as a leach reagent [67]. Several substitutes have been proposed (as shown in Table 4), but generally, the non-cyanide lixiviants thiourea, and thiosulfate are regarded as being the most realistic substitutes.

3.1.2. Halide leaching

The use of halide (fluorine, chlorine, bromine, iodine and astatine) systems for gold dissolution pre-dates cyanidation [69]. With the exceptions of fluorine and astatine, all halogens have been tested and/or used for the extraction of gold [67]. Gold forms both Au(I) and Au(III) complexes with chloride, bromide and iodide depending on the solution chemistry conditions. However, of the halides, only chlorine/chloride has been applied industrially on a significant scale [70]. Chlorination rates are favored by low pH, high chloride and chlorine levels, increased temperatures, and high surface areas.

The traditional medium for dissolving gold (and the platinum group metals) is aqua regia, a mixture of three parts concentrated hydrochloric to one part concentrated nitric acid. The reactions involved in the aqua regia leaching are as Reactions (3) and (4) [65].



Several investigations have been undertaken to determine the effectiveness of chlorine [71–75]. However, chloride leaching

Table 4
Suggested alternatives for leaching of gold to cyanide [67]

Reagent type	Concentration range	pH range	Basic chemistry	Research level	Extent of commercialization
Ammonia	High	8–10	Simple	Low	Pilot tests + 100 °C
Ammonia/cyanide	Low	9–11	Simple	Extensive	Applied to Cu/Au ores
Ammonium thiosulfate	High	8.5–9.5	Complex	Extensive	Semi-commercial
Slurry CN-electrolysis	Low	9–11	Simple	Historical	Limited historical
Sodium sulfide	High	8–10	Simple	Low	Geological interest only
Alpha-hydroxynitriles	Moderate	7–8	Fairly simple	Fairly popular	None
Malononitrile	Moderate	8–9	Fairly complex	Low	None
Alkali cyanoform	Poorly defined	~9	Poorly defined	Low	None
Calcium cyanide	Poorly defined	~9	Poorly defined	Low	None
Alkaline polysulfides	High	8–9	Poorly defined	Low	None
Hypochlorite/chloride	High chloride	6–6.5	Well defined	Extensive	Historical and modern
Bromocyanide	High	6–7	Poorly defined	Historical	Historical
Iodine	High	3–10	Poorly defined	Low	None
Bisulfate/sulfur dioxide	High	4–5	Fairly simple	Low	None
Bacteria	High	7–10	Fairly complex	Low, growing	None
Natural organic acids	High	5–6	Fairly complex	Low	None
DMSO, DMF	Poorly defined	7	Poorly defined	Very low	None
Bromine/bromide	High	1–3	Well defined	Low	Historical
Thiourea	High	1–2	Well defined	Fairly popular	Some concentrates
Thiocyanate	Low	1–3	Well defined	Low	None
Aqua regia	High	Below 1	Well defined	Low	Analytical and refining
Acid ferric chloride	High	Below 1	Well defined	Low	Electrolytic Cu slimes
Ethylene thiourea	High	1–2	Poorly defined	Very low	None
Haber process	Poorly defined		Proprietary	One entity	None
“Bio-D leachant”	Poorly defined		Proprietary	One entity	None
High temperature chlorination	High	6–7	Simple	Historical	Historical

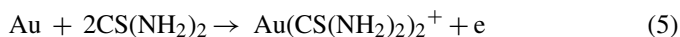
of gold is more difficult to apply than cyanide extraction for two major reasons:

- special stainless steel and rubber-lined equipment is required to resist the highly corrosive acidic and oxidizing conditions;
- chlorine gas is highly poisonous and must be controlled to avoid any health risk.

3.1.3. Thiourea leaching

The research on using of thiourea ((NH₂)₂CS) as a gold extraction agent has shown considerable promise [76,77] in recovery of gold from ores. In acidic conditions, thiourea dissolves gold, forming a cationic complex; the reaction is rapid and gold extractions of up to 99% can be achieved [67]. The

anodic reaction follows the Reaction (5):



Pyper and Hendrix [78] summarized that: (a) the rate of leaching is contingent upon thiourea and oxidant concentrations; (b) the use of ferric ion in sulfuric acid is the most effective system; (c) the ferric ion ties up thiourea in iron–thiourea complexes; and (d) the rate of gold dissolution is strongly determined by pH.

A comparison of cyanidation and thiourea leaching process in gold recovery from refractory ore was investigated by Gönen et al. [79]. As shown in Table 5, only 75% leaching extent and high thiourea and ferric sulfate consumptions are important disadvantages in economic point of view. For this reason, the direct

Table 5
Results of leaching processes [79]

	Cyanidation			Thiourea leaching	
	Leach	Roasting and leach		Leach	CIL
Roasting temp.	–	550 °C	Active carbon (kg/ton ore)	–	50
S/L ratio (g/mL)	1/1.5	1/1.5	S/L ratio (g/mL)	1/2	1/2
NaCN (kg/ton ore)	6.2	4.6	TU ^a (kg/ton ore)	15.2	15.2
Ca(OH) ₂ (kg/ton ore)	8.2	2.9	FS ^b (kg/ton ore)	140.9	140.9
pH	10.5	10.5	SA ^c (kg/ton ore)	46.2	46.2
			pH	1.5	1.5
Leaching time (h)	48	48	Leaching time (h)	5	5
Gold extent (%)	66.7	79.8	Gold extent (%)	66.8	74.9

^a Thiourea.

^b Ferric sulfate.

^c Sulfuric acid.

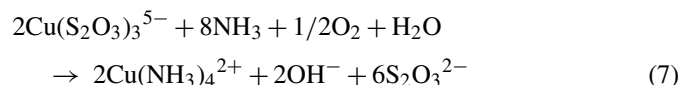
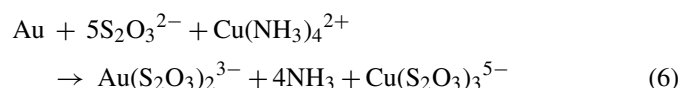
application of carbon-in-leach (CIL) process in gold recovery for refractory ores, as well as direct cyanidation method, are not adequate.

Despite the proven effectiveness of thiourea as a gold leach reagent, there are still few full-scale operations in existence. Its commercial application has been hindered by the following three factors [69,80]: (1) it is more expensive than cyanide; (2) its consumption in gold processing is high because thiourea is readily oxidized in solution; and (3) the gold recovery step requires more development. However, it was implied [80] that the high costs attached to leaching are likely due to the thiourea process still being in an infancy stage.

3.1.4. Thiosulfate leaching

Thiosulfate ($S_2O_3^{2-}$), a chemical used widely in photography and in the pharmaceutical industries, has also been proposed as a substitute for cyanide by many researchers [81–97].

It has been believed that gold dissolution in ammoniacal thiosulfate solution is an electrochemical reaction catalyzed by the presence of cupric ions. The electrochemical-catalytic mechanism of gold leaching by ammoniacal thiosulfate was investigated by Aylmore and Muir [98]. It was proposed that $Cu(NH_3)_4^{2+}$ species present in solution acquires electrons on the cathodic portion of the gold surface and is directly reduced to $Cu(NH_3)_2^+$. 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 $Au(NH_3)_2^+$ or $Au(S_2O_3)_2^{3-}$. Depending on the concentration of $S_2O_3^{2-}$, $Cu(NH_3)_2^+$ converts to $Cu(S_2O_3)_3^{5-}$ ions, and likewise for $Au(NH_3)_2^+$. Both the $Cu(S_2O_3)_3^{5-}$ species and the $Cu(NH_3)_2^+$ species in solution are then oxidized to $Cu(NH_3)_4^{2+}$ with oxygen. The predominant cathodic reaction will depend on the relative concentrations of the species in solution. The role of copper(II) ions in the oxidation of metallic gold to aurous Au^+ ion can be simplified as:



Several promising experimental investigations [84–86,88,89,99–103] have been undertaken. The stability constants for thiosulfate in comparison with various other gold complexes are shown in Table 6. It can be seen that the gold thiosulfate complex is fairly stable once it has formed. However, alkaline conditions are necessary to prevent thiosulfate decomposition by acid [69]. The pH range is dictated by the ammonia/ammonium buffer point (9.25 at 25 °C) since the presence of ammonia has to be ensured to solubilize copper as Cu(II)-ammonia complex. The thiosulfate stability will decrease at higher temperature and low pH values. Therefore, a pH of 9–10 is generally preferred at ambient temperature because thiosulfate appears to be less prone to degradation in this region and Cu(II)-ammonia complex is also stable [101,103,104].

Table 6
Stability constants for gold complexes

Gold species	Stability log K^a	Refs.
$Au(CN)_2^-$	38.3	[105]
$Au(SCN)_2^-$	16.98	[105]
$Au(SCN)_4^-$	10	[105]
$AuCl_4^-$	25.6	[106]
$Au(NH_3)_2^+$	26	[106]
	13 ^b	[107]
$Au(S_2O_3)_2^{3-}$	26.5	[108]
	28	[109]

^a Constant $K = [AuL_n]/[Au^{2+}][L]^n$ for the reaction $Au^{2+} + nL = AuL_n$ at temperature 25 °C.

^b Calculated from linear free energy relationship, ionic strength = 1.0.

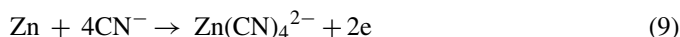
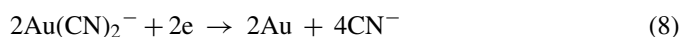
The principal problem with thiosulfate leaching is the high consumption of reagent during extraction. Zipperian et al. [103] reported a loss of up to 50% of thiosulfate in ammoniacal thiosulfate solutions containing copper. Moreover, the process is generally slow, although acceptable leaching rates can be achieved in the presence of ammonia using copper(II) as an oxidant. Nevertheless, high reagent consumption renders most thiosulfate systems uneconomical overall, in spite of their potential environmental benefits. At present, no simple and affordable method for recovering gold from thiosulfate leach solutions exists.

3.2. Recovery of precious metals from leachate

To recover the precious metals from these different solutions, a variety of methods are found in literatures. These methods include cementation [110–112], solvent extraction [113–117], adsorption on activated carbon [118–120], and ion exchange [121–126].

3.2.1. Recovery of precious metals from solutions by cementation

Since the 1890s, zinc cementation has been used to recover gold from cyanide solutions on a commercial scale. The process actually employed is called the “Merrell-Crowe process” and it has been used worldwide [119]. 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 [110].



In practice, if the cyanide concentration is reduced too much, a passivating layer of zinc hydroxide may form on the surface of the zinc particles. It was reported [110] that cementation of gold is practically constant over the pH range 8–11. However, impurities such as lead, copper, nickel, arsenic, antimony, and sulfur are most deleterious for gold cementation.

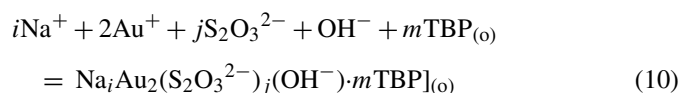
Recovery of gold from thiourea, thiosulfate, or thiocyanate solutions by reduction-precipitation with a stabilized form of sodium borohydride (SBH) was reported by Awadalla and Ritcey [127]. Sodium borohydride was used as stabilized aque-

ous solution containing 12% by weight NaBH₄ and 40% NaOH. The results showed that gold ion can be reduced effectively to metallic gold from acidic solutions of thiourea by the addition of SBH even at ambient temperature. This reaction can be carried out from very dilute solutions as well as from more concentrated liquors. This result indicates that thiourea can be used as not only an alternative leachant for gold bearing materials but also a stripping agent for gold from loaded solvents and resins. It was also been concluded [127] that gold can be recovered selectively from mixtures of foreign ions with Au-thiourea acidic solution by carefully controlling the amount of reagent added.

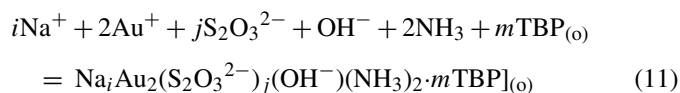
3.2.2. Recovery of precious metals from solutions by solvent extraction

Solvent extraction has been studied to meet gold-extraction requirements. A number of extraction systems have been investigated [113,114,116,128–131], including organophosphorus derivatives, guanidine derivations, and mixture of amines-organophosphorous derivatives. Table 7 gives a comparison of extractants on the aurocyanide complex extraction. It is clear that the LIX-79 extractant allowed gold extraction from alkaline cyanide media. The aurocyanide complex is extracted preferentially over the metal-cyano complexes at alkaline pH values. Gold stripping was investigated using NaOH or NaCN solutions [117], and the efficiency of stripping slightly increases with an increase in the reagent concentration. Cyanex 921 is used to extract gold cyanide over the entire pH range [130]. The presence of the Li⁺ ion enhances the extraction. From chloride media, this reagent is also capable of extracting gold throughout entire acid concentration range. In this case, the extractant concentrations required are much lower than needed in cyanide media. The stripping can be performed efficiently with water or KCN.

Extraction of gold from thiosulfate solutions with alkyl phosphorus esters was studied by Zhao et al. [132]. It was observed that the addition of ammonia has a strong influence on the extraction of gold from thiosulfate solutions with alkyl phosphorus esters. The extraction mechanism in the presence or absence of ammonia should be considered separately. For the system with no ammonia, the extraction reaction was proposed to be expressed as [132]:



While with the addition of ammonia into thiosulfate solutions, the extraction reaction was proposed to be expressed as [132]:



where i ($i = 3-5$) varies with j ($j = 2-3$), and the TBP coefficients m in the two equations are in the ranges of 1.5–2.5 and 6–9, respectively.

3.2.3. Recovery of precious metals from solutions by activated carbon

The first new technique for the recovery of Au and Ag cyanide complexes on activated carbon was patented by McQuiston and Chapman in 1946 [133]. Since that time, new development has been introduced to this process and now carbon-in-pulp (CIP) and carbon-in-leach (CIL) are commercially used for gold recovery from cyanide solutions [79,122,126,134].

Mechanism and kinetic of adsorption of gold from solutions onto activated carbon have been investigated by many researchers [135–145].

For solid/liquid adsorption processes, two isothermal expressions are well known. One is the Langmuir isotherm [146].

$$Q = \frac{Q_{\max}bC}{(1 + bC)} \quad (2')$$

where Q is the quantity of solute adsorbed per unit weight of carbon, Q_{\max} is the maximum sorption capacity, C is the equilibrium concentration of the adsorbate in solution and b is the adsorption equilibrium constant. In a multicomponent system ($i = 1, 2, \dots, k$), Langmuir isotherm equation can be expressed as:

$$Q_i = \frac{b_{i0}C_i}{\left(1 + \sum_{j=1}^k b_jC_j\right)} \quad (3')$$

in which Q_i is the amount of solute i , adsorbed per unit weight of carbon at equilibrium concentration C_i in a solution containing k solutes, $b_{i0} = Q_{\max i} \cdot b_i$, b_i is the adsorption equilibrium constant for solute i .

Another expression is the Freundlich isotherm [147,148]:

$$Q = KC^n \quad (4')$$

Table 7
Comparison of extractants on the aurocyanide complex extraction

Extractant	Type	Concentration	Diluent	[Au] (mmol/L)	[pH ₅₀]	Refs.
Primene JMT	Primary amine	10% (v/v)	Xylene	0.25	7.65	[116]
Primene 81R	Primary amine	10% (v/v)	Xylene	0.25	7.85	[116]
Adogen 283	Secondary amine	2.2% (v/v)	Xylene	5	7.05	[131]
TBP	Phosphoric ester	Undiluted	–	5	<99% (pH 1–13)	[128]
DBBP	Phosphonic ester	Undiluted	–	5	5.0	[128]
Cyanex 921	Phosphine oxide	20% (w/v)	Xylene	0.25	<99% (pH 2–11.5)	[130]
Primene JMT + Cyanex 923	Primary amine + phosphine oxide	10 + 10% (v/v)	Kerosene	0.10	<90% (pH 2–12)	[113]
Hostarex S2706	Quaternary ammonium salt	0.02% (v/v)	Escaid 100	0.10	<90% (pH 2–12)	[117]
LIX 79	Guanidine derivative	8%	Cumene	0.5	10.60	[117]

where K and n ($0 < n < 1$) are Freundlich constants. In this case, a linear relationship is expected between $\ln Q$ and $\ln C$.

A Freundlich-type multicomponent isotherm was developed by Sheindorf et al. [148] as:

$$Q_i = K_i C_i \left(\sum_{j=1}^k a_{ij} C_j \right)^{n_i-1} \quad (5')$$

where a_{ij} is defined as competition coefficient ($a_{ii} = 1$). $K_i = q_{mi} A_i$ and K_i can be determined from the monocomponent system.

The theoretical basis of Freundlich's equation was explained in 1916 by Langmuir as follows [147]: adsorption is achieved when the rate at which gas molecules are held to the surface equals the rate of their evaporation from the surface.

Fritz and Schlunder [149] proposed a general empirical equation for calculating the adsorption equilibria of organic solutes in aqueous solution:

$$Q_i = \frac{b_{i0} C_i^{k_{i0}}}{D_i + \sum_{j=1}^k b_{ij} C_j^{k_{ij}}} \quad (6')$$

For $k_{i0} = k_{ij} = D_i = 1$, Eq. (6') becomes the Langmuir model for multisolute systems (Eq. (3')).

Kinetics studies of activated carbon adsorption of gold from thiourea solutions carried out by Juarez and Oliveira [150] showed a good agreement of the experimental kinetics data with the La Brooy model that was proposed for batch tests of gold adsorption from cyanide solutions. The model is represented by the following equation:

$$\Delta Q = k_e C t^n \quad (7')$$

where: ΔQ : increase of gold adsorbed onto activated carbon, k_e and n : empirical constants, C : gold concentration in the solution, t : time.

3.2.4. Recovery of precious metals from solutions by ion exchange

Gold can be recovered from leach liquors using ion exchange resins [81,87,151–156]. Commercial IEX resins employing small quaternary ammonium moieties (strong base resins) have been successful in recovering gold from thiosulfate liquors.

The recovery of gold from ammoniacal thiosulfate solutions containing copper using ion exchange columns was carried out by Zhang and Dreisinger [154]. The resins involved in the work, including Dowex G51, Dowex 21K and amberlite IRA-410, were selected from a group of resins. These resins are all of gel type, with a polystyrene divinylbenzene matrix and quaternary ammonium functional groups. Zhang's research showed 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. In the presence of copper, effective ion exchange operation can only be performed under limited conditions due to the instability of the thiosulfate solution and the possible formation of poisoning polythionates.

Thomas et al. [157] 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. [157] found that higher gold recoveries were obtained by using very dilute thiosulfate solutions at 45–55 °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. The presence of the resin in contact with both the pregnant solution and solid residue reduces degradation of gold thiosulfate and thiosulfate reagent and reduces the adsorption of gold on the solids. The pulp and barren lixiviant exiting during the final RIP stage are sent to tailings for further treatment and reclaim. The loaded resin is sent to an elution stage where copper is eluted from the loaded resin by washing with ammonia salt or a mixture containing 100–200 g/L of ammonium thiosulfate solution. The eluate containing ammonium thiosulfate and copper (500–1500 ppm) together with about 10% of the gold on the resin is then recycled to the leaching circuit. After copper elution, a thiocyanate solution (100–200 g/L) is used to elute gold from the resin. The eluate is passed to a gold recovery process such as electro-winning whilst the resin is recycled to the RIP circuit. Because the resin is returned in its SCN^- form, it is not clear whether gold is taken up on to the resin as the $\text{Au}(\text{SCN})_2^-$ complex.

3.3. Techniques for hydrometallurgical recovery of metals from e-waste

Before the 1990s, the activities on recovery of metals from e-waste were summarized by Sum [16]. It was shown that in the 1970s and early to mid-1980s, the predominant method of recycling of electronic scrap was blast furnace smelting in conjunction with secondary copper or lead smelters. Since the mid-1980s, the trend has shifted toward the hydrometallurgical processing.

Aqua regia leaching was selected by Sheng and Etsell [65] for recovery of gold from computer chips due to its flexibility, ease and low capital requirement. In Sheng's study, gold leaching involved three stages. During stage I, computer chips were separated from the printed circuit boards by leaching. Stage I leaching was conducted in nitric acid systems, in which the effects of acid concentration, temperature, pulp density and retention time were investigated. After stage I leaching, the computer chips and coagulated epoxy resin were mechanically crushed. Stage II leaching used the optimized parameters from stage I. The third stage leach dissolved metallic gold with aqua regia from the second stage leach computer chip residue. The parameters, such as temperature, pulp density, and retention time, were studied. It was concluded [65] that higher temperatures tend to give faster leaching rates of gold. The amount of aqua regia required for complete immersion of the computer chips was approximately 2 ml per gram of computer chips. Increasing aqua regia beyond this ratio did not increase the leaching rate of gold. Agitation was unnecessary for gold leaching in the aqua regia solution. The self-induced agitation brought about by the release of nitrous oxide and chlorine vapors caused bubbling and frothing of the aqua regia solution.

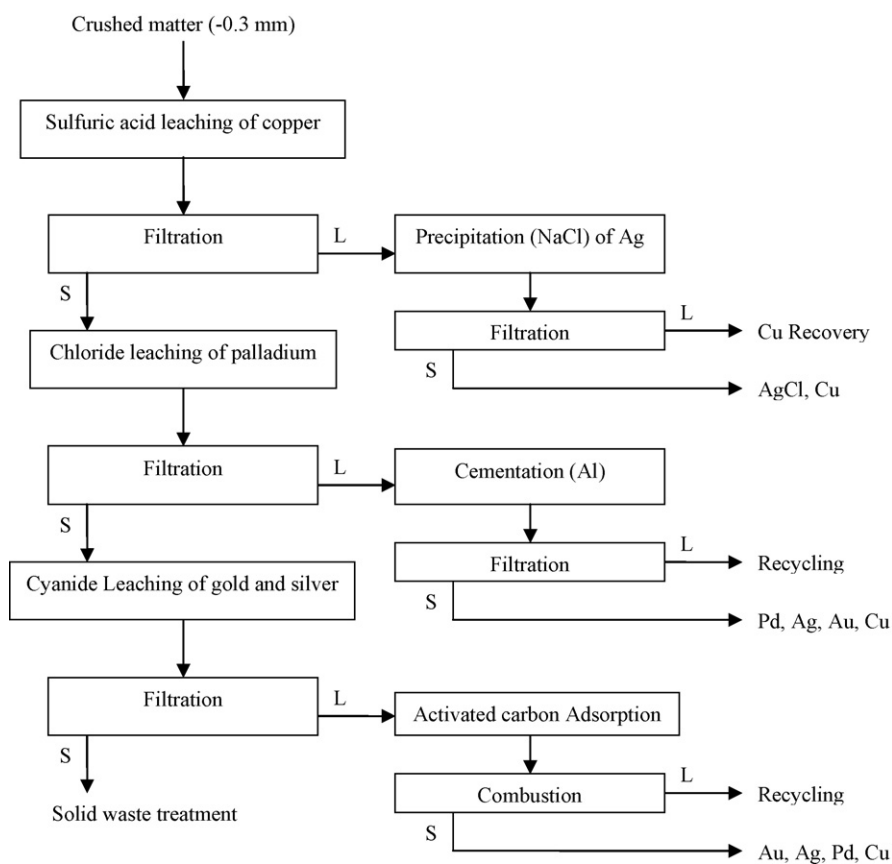


Fig. 4. Proposed flowsheet for the recovery of precious metals from electronic scrap by Quinet et al. [54].

Quinet et al. [54] carried out their bench-scale extraction study on the applicability of economically feasible hydrometallurgical processing routes to recover precious metals from waste mobile phones. The starting material contained 27.37% copper, 0.52% silver, 0.06% gold and 0.04% palladium. This material was crushed with a Retsch heavy-duty cutting mill, and the crushed matter was separated into four groups with particle size as: +1.168 mm, $-1.168 + 0.6$ mm, $-0.6 + 0.3$ mm, and -0.3 mm. The smallest size portion was researched by a series of hydrometallurgical processing routes, such as sulfuric acid leaching, chloride leaching, thiourea leaching, cyanide leaching, cementation, precipitation, ion exchange, and activated carbon adsorption. The proposed flowsheet by Quinet et al. is summarized in Fig. 4. This flowsheet permits the recovery of 93% of the silver, 95% of the gold and 99% of the palladium. The amounts of each reagent needed for one metric tonne of starting material are listed in Table 8.

Chmielewski et al. [66] reported their process for recovery of gold from solid wastes generated in the electronic and jewellery industries. As shown in Fig. 5, the hydrometallurgical process consists of the following steps: (a) low-temperature carbonization and roasting of the wastes; (b) leaching with nitric acid solution to remove silver and other metals; (c) leaching with aqua regia; (d) selective solvent extraction of gold with diethyl malonate; (e) separation of metallic gold from the organic phase by reduction.

In the purification step, various extractants were investigated [66] including hexanol, methyl-*iso*-butyl ketone, di-*n*-butyl ketone, diethyl malonate, dibutyl ether, ethylene glycol, *n*-amyl ether, iso-amyl ether, 2,2-dichloroethyl ether, TBP, and several natural oil fractions. The main properties taken into account by the researchers were: selectivity, possible loading with gold, resistance to contact with aqua regia, organic-aqueous phase disengagement, and price of the extractant. On the basis of results obtained, diethyl malonate was selected by as the best extractant among those investigated for industrial applications. It showed very high extraction coefficient values under proper conditions and the highest saturation capacity with gold of 140 g/l, as well as a good selectivity.

Table 8
Amount of each reagent needed for one metric tonne of starting material [54]

Reagent	Quantity
H ₂ SO ₄ (kg)	470
Fe ₂ (SO ₄) ₃ (kg)	12
O ₂ (L)	36×10^4
H ₂ O ₂ (kg)	74
NaCN (kg)	19
HCl (kg)	165
Al (kg)	0.3
NaCl (kg)	1.7
Activated carbon (kg)	94
NaOH (kg)	53

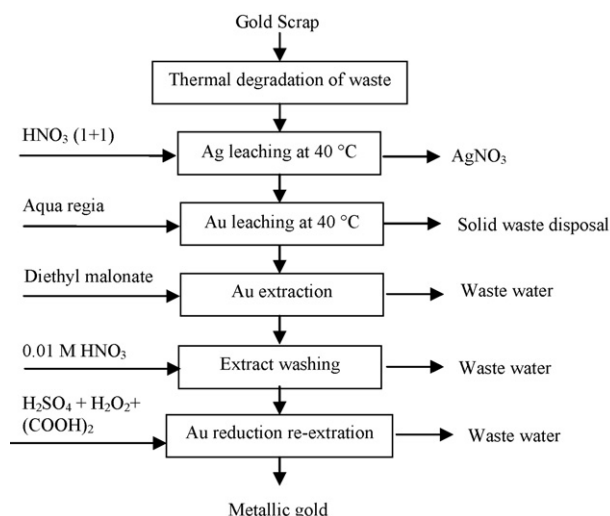


Fig. 5. Diagram of hydrometallurgical process for Au recovery [66].

A Chinese patent by Zhou et al. [158] described a process for recovering precious metals (Ag, Au, Pd) from electronic waste containing plastics. The scrap was heated at 400–500 °C for 8–12 h to burn off the plastics, and the crude metal residue was treated with HCl or H₂SO₄ at 90 °C to dissolve base metals. After a filtration, the residue was leached in dilute HNO₃ with a solid/liquid ratio of 1:2 at 60 °C to dissolve silver. Finally, HCl and NaClO₃ solution was used for gold and palladium leaching. It was reported that the recovery of precious metals can be up to more than 92%.

Kogan [159] recently patented a hydrometallurgical technique for recovering precious metals from waste electronic equipment. The scrap was added to hydrochloric solution containing 180 g/L HCl and 250 g/L MgCl₂ for 3 h at temperature 80–95 °C. During this period 98% of aluminum, 94% of tin, 96% of lead and 94% of zinc were extracted in solution. To recover copper, the solid residue was treated with hydrosulfuric acid solution containing 50 g/L H₂SO₄ and 200 g/L MgCl₂ for 2.5 h at a temperature of 80 °C. The redox-potential of the leach system near 550 mV was adjusted by adding to the stirred pulp a solution of 50% hydrogen peroxide. In result more than 96% of copper and 98% of nickel were dissolved by this procedure. After a filtration and washing, the solid residue was added to an acidic sodium bromide solution containing 30 g/L HCl and 180 g/L bromide-ions in order to combine recovering of precious metals. To the obtained pulp were added 100 mL of 10% solution of triisobutylphosphinesulfoxide in tributylphosphate and kerosene during intensive stirring of this pulp. In addition, the leaching system was further treated by 50% hydrogen peroxide solution providing redox-potential of the system at the level near 850 mV and the temperature not more than 60 °C. The pulp was stirred for 3 h where more than 98% of gold, 84% of silver, 96% of palladium and 92% of platinum were extracted by organic solvent. The metals were extracted from the organic solution by precipitation using zinc powder in an acidic medium.

Veit et al. [20] published their research on recovery of copper from printed circuit boards (PCBs) scraps by mechanical pro-

cessing and electrometallurgy. In the electrowinning processing, two different solutions were used for recovery of copper: aqua regia and sulfuric acid. It was shown that the copper content in solution decayed quickly in all the tests. For the samples dissolved with sulfuric acid, this decline happened in a time range smaller than for the samples dissolved with aqua regia. This phenomenon was explained by the presence of the ion NO₃ in aqua regia solution that can act as an oxidizing agent, decreasing the efficiency of electrowinning processing.

Recovery of base metals, including copper, lead and tin from scrap printed circuit boards by leaching and electrochemical processing was reported by Mecucci and Scott [160]. Fig. 6 gives the schematic diagram of the process for recovering metals. It was pointed out that size reduction of the PCBs scraps is essential due to the fact that multilayer boards restricts access of the stripping solution to the internal layers. The results showed that the efficient recovery of both copper and lead was highly dependent upon pH. At 0.5 M HNO₃ a maximum of 43% CE (current efficient) was obtained at a current density of 20 mA cm⁻². The efficiency fell both with decreasing current density and increasing acid concentration and reached approximately 5% at 5 M HNO₃. The low efficiency for copper and lead depositions at high nitric acid concentration was mainly due to re-dissolution of copper and lead. An alternative to the recovery of lead and copper as metal was also studied [160] using a simulated leaching solution of lead and copper nitrate in nitric acid. An undivided rotating cylinder electrode reactor (RCER), operating in batch mode, was employed for electrodeposition from an aqueous binary mixture of 0.1 M Cu(NO₃)₂ and 0.025 M of Pb(NO₃)₂ in 0.5 M HNO₃. This investigation showed a possible recovery of copper at the cathode and deposition of lead dioxide at the anode.

Korean researchers investigated recovery of nickel, copper, tin and lead from waste multi-layer ceramic capacitors (MLCC) or spent nitric etching solutions of printed circuit board [161,162]. It was resulted that the leaching rate of nickel from MLCC in HNO₃ solution was found to be much higher than that obtained with HCl and H₂SO₄ solutions. Nickel extraction was 97% with 1 M HNO₃ at 90 °C, 90 min reaction time, and 5 g/L pulp density.

A summary of new developments on the recovery of metals from electronic waste by hydrometallurgical techniques is listed in Table 9. It can be seen that most of the hydrometallurgical techniques for recovery of metals from electronic waste are involved in acid leaching and/or halide leaching. This is due to the fact that acid leaching is a feasible approach for removing of base metals so as to free the surface of precious metals. However, in order to develop an environment-friendly technique for recovery of precious metals from e-waste, we should pay more attention on evaluating the environmental impact of techniques. Table 10 gives a critical comparison of four main leaching methods based on an analysis for both economic feasibility and environmental impact. It can be seen that cyanide leaching provides the best economic feasibility for recovery of precious metals from electronic waste. However, cyanide leaching and thiourea leaching obtain same final result if the toxicity of reagent is considered. It should be mentioned here, thiourea

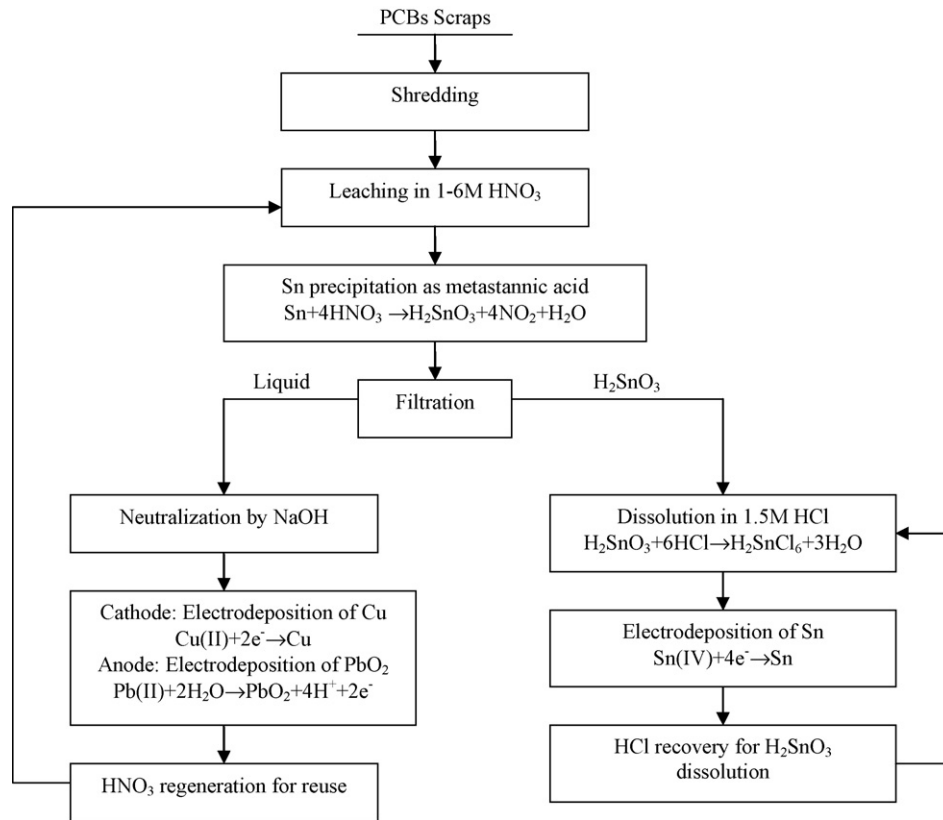


Fig. 6. Schematic diagram of the hydrometallurgical recovery of base metals by Mecucci and Scott [160].

Table 9

New developments on the recovery of metals from electronic waste by hydrometallurgical techniques

Metals recovered	Main process features	Main product	Year	Refs.
Au	Computer chips were treated in nitric acid to dissolve base metals; the residue was leached with aqua regia; ferrous sulfate precipitation was used for gold recovery.	Gold flakes	2007	[65]
Au and Ag	E-waste with size -0.5 mm was treated with combination of KI and I_2 or NaCl and bleaching powder; solvent extraction was used for gold and silver recovery.	Au and Ag	2007	[163]
Ni	Leaching of nickel from waste multi-layer ceramic capacitors was performed by using 1 M HNO_3 at $90^\circ C$, 90 min reaction time, and 5 g/L pulp density.	Ni in solution	2007	[161]
Au (98%), Pd (96%), Pt (92%), Ag (84%) Cu (98%)	H_2SO_4 and $MgCl_2$ for dissolution of base metals; HCl and bromide-ions was used to dissolve precious metals; cementation of gold by zinc powder. Copper was dissolved by Sulphuric acid or aqua regia; electrowinning was performed for copper recovery.	Au and PGMs powders Cu	2006 2006	[159] [20]
Cu, Ag (93%), Pd (99%), Au (95%)	Sulfuric acid leaching of copper, chloride leaching of palladium, thiourea or cyanide leaching of gold and silver, activated carbon adsorption of gold, silver and palladium.	AgCl, Cu, Pd, Au	2005	[54]
92% for Au, Ag, Pd	HCl or H_2SO_4 for dissolution of base metals, leaching of silver and palladium by, leaching of gold and palladium by HCl and $NaClO_3$; precipitation of Au by $FeCl_2$	Gold sponge	2005	[158]
Au	E-scrap was treated with a leaching solution based on NaCl, $CuCO_3$, and HCl.	Gold residue	2004	[164]
Sn, Pb	Solder was dissolved with a solution comprising Ti(IV) and an acid. Tin and lead were recovered by electrowinning.	Sn and Pb	2003	[165]
Cu, Pb, and Sn	HNO_3 leaching of PCBs, electrodeposition recovery of base metals.	Cu, Pb and Sn	2002	[160]
Au	Thermal treatment, HNO_3 leaching and aqua regia leaching for gold dissolution, solvent extraction of gold by diethyl malonate, ferrous sulfate solution was used for gold precipitation.	Metallic gold	1997	[66]
Au	Treatment with an alkali solution in a autoclave at $80-190^\circ C$ to remove aluminum, treatment with a sulfuric acid solution in another autoclave under surplus oxygen pressure for removing non-ferrous metals	Enriched concentrate of precious metal	1993	[166]
Au and Ni	Leaching of base metals by sulfuric acid and oxidant (ferric sulfate) and aqua regia leaching of precious metals	Ni and Au in solution	1992	[167]

Table 10
Comparison of leaching methods for recovery of precious metals from e-waste

Leaching method	Leaching rate	Leaching kinetics	Reagent cost	Corrosive	Economic feasibility*	Toxicity	Final results	Research level
Cyanide	++++	++	--	0	++++	-----	—	Extensive
Aqua regia	+++++	+++	-----	-----	—	—	----	Fairly popular
Thiourea	+++	++++	-----	--	0	—	—	Low
Thiosulfate	++	+	-----	0	--	—	----	Low

Note that “0”, “—”, and “+” denote base, negative and positive, respectively. (*) Summary of the score from “leaching rate”, “leaching kinetics”, “reagent cost”, and “Corrosive”.

leaching of precious metals from wastes is currently at a low research level. It may be expected that thiourea leaching will be economic feasible following an extensive research.

4. Recovery of metals from electronic waste by biometallurgy

In the last decade, recovery of metals by biotechnology has been one of the most promising technologies [14,55,168–175]. Biometallurgy has the potential for a major technology breakthrough for the materials and minerals industry due to the great interest shown by major international companies for this new technology. The understanding of the biochemical processes involved in the treatments of metals has been subject to growing investigations for the last 20 years. At present, research and development is in progress for a number of metals such as copper, nickel, cobalt, zinc, gold, and silver [176]. However, for recovery of gold and silver, the activity of leaching bacteria is applied only to remove interfering metal sulfides from ores bearing the precious metals prior to cyanidation treatment [177].

All microbes employ metal species for structural functions and/or catalytic functions. The way microbes interact with metals depends in part on whether the organisms are prokaryotic or eukaryotic [174]. Both types of microbes have the ability to bind metal ions present in the external environment at the cell surface or to transport them into the cell for various intracellular functions. This metal/microbes interaction provides possibility or promotes selective or non-selective in recovery of metals.

There are two main areas of biometallurgy for recovery of metals, namely bioleaching and biosorption. Bioleaching has been successfully applied in recovery of metals from metallic sulfides, which are the major bearing minerals for many base and precious metals, by the use of bacterially assisted reactions [176]. The extraction of metals such as Co, Mo, Ni, Pb, and Zn from sulfidic ores by bioleaching is technically feasible [174]. However, today only copper and gold are the metals that are industrially produced in significant proportions by this way [176].

Biosorption process is a passive physico-chemical interaction between the charged surface groups of micro-organisms and ions in solution, in which living as well as dead organisms can be used. Numerous micro-organisms including algae [25,27,29,178–180], bacteria [169,181], yeasts [182–184], and fungi [185,186] are known to accumulate heavy metals and precious metals actively. A biosorption-based process offers a number of advantages when compared to the conventional methods used. These include low operating costs, minimization of the

volume of chemical and/or biological sludge to be handled and high efficiency in detoxifying effluents [28,30,187–189].

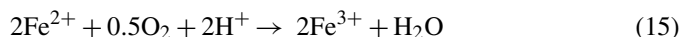
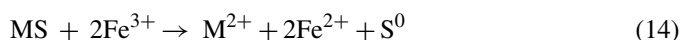
4.1. Bioleaching

4.1.1. Mechanisms of bacterial metal sulfide oxidation

The mechanism of bacterial leaching of metal sulfides has been discussed for a long time [190–193]. Generally, there are two possible mechanisms whereby microorganisms can increase the leaching rate of metals from mineral ores. In direct action mechanism, microorganisms will directly oxidize minerals and solubilize metals, the reactions can be simplified as [194]:



In indirect action mechanism, ferric ion (Fe^{3+}) is the oxidizing agent for minerals and the role of organisms is simply regeneration of Fe^{3+} from Fe^{2+} . It can be simplified as [194]:

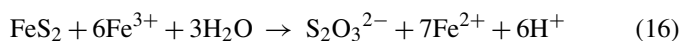


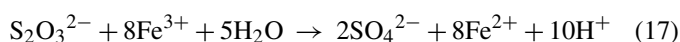
It was concluded that [194] in the actual microbial leaching of metals, both direct and indirect leaching as well as physico-chemical reactions can contribute.

Mechanisms of bacterial metal sulfides by indirect leaching were proposed by Sand and co-workers [177,192,193,195–198]. According to their research, metal sulfides are leached via two different reaction mechanisms: the thiosulfate and the polysulfide pathways. In general, dissolution is achieved by a combination of proton attack and oxidation processes. The reaction pathway is determined by the mineral species [195]. However, the crystal structure (e.g., monosulfide or disulfide structure) does not control the pathway of dissolution. The reactivity of metal sulfides with protons (acid solubility) is the relevant criterion. The latter property is determined by the electronic configuration [197].

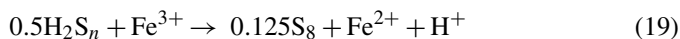
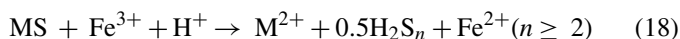
4.1.1.1. Acid-insoluble metal sulfides: thiosulfate pathway.

The thiosulfate mechanism is exclusively based on the oxidative attack of iron(III) ions on the acid-insoluble metal sulfides FeS_2 , MoS_2 , and WS_2 . Here, the main sulfur intermediate is thiosulfate. The thiosulfate mechanism can be simplified by the following equations [197]:





4.1.1.2. Acid-soluble metal sulfides: polysulfide pathway. The polysulfide mechanism allows for a dissolution by an attack of iron(III) ions and/or by protons. In this case, the main sulfur intermediate is polysulfide (and consequently elemental sulfur). The two mechanisms can be simplified by the following equations [197]:



Consequently, bioleaching of metal sulfides means that the bacterial function is to generate sulfuric acid biologically to supply protons for hydrolysis attack and/or to keep the iron ions in an oxidized state [as iron(III) ions] for an oxidative attack.

In both pathways, the main role of leaching bacteria consists of regeneration of iron(III) ions – the most important oxidants in acidic biotopes. Thus, the acidophilic iron(II) ion oxidizers control the redox potential in their environment, which is determined mainly by the iron(III)/iron(II) ratio in leaching solutions. It is the iron-oxidizing microorganisms, mesophilic or thermophilic, that increase the redox potential resulting in metal sulfide biooxidation [196,197].

4.1.2. Practical applications of bioleaching

Heap or dump leaching and stirred-tank leaching are the ways of applying bioleaching treatment for the recovery of precious and base metals. Heap or dump leaching has been applied as a controlled process to low-grade copper ores containing secondary minerals such as covellite and chalcocite for about 40 years. The static bioleaching techniques are based on the principle of circulating water and air through heaps of ore coarsely fragmented to activate the growth of microorganisms that amplify the oxidation of the sulfidic minerals. Stirred-tank bioleaching at industrial scale has been applied for 20 years. Most of the current stirred-tank bioleaching operations are applied to refractory gold arsenopyrite-pyrite flotation concentrates, where the gold trapped in the sulfides is liberated by means of biooxidation of the host minerals and then recovered by conventional treatment [176].

Bioheap leaching for recovery of copper has now become a common practice in the industry [199]. Since 1980 at least 13 copper bioleach operations have been commissioned (Table 11).

The copper bioleach plants listed in Table 11 are for recovery of copper from the mineral chalcocite (Cu_2S). Copper is leached from chalcocite by acid, forming covellite (CuS), or by ferric iron formed from microbial oxidation of ferrous iron, as shown in the following reactions [199]:

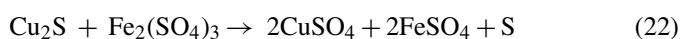
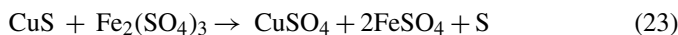


Table 11
Commercial copper bioheap leach plants [199]

Plant and location	Size: tonnes ore/day	Years in operation
Lo Aguirre, Chile	16,000	1980–1996
Gunpowder's Mammoth Mine, Australia	In situ ^a	1991–present
Mt. Leyshon, Australia	1,370	1992–1997
Cerro Colorado, Chile	16,000	1993–present
Girilambone, Australia	2,000	1993–in closure
Ivan-Zar, Chile	1,500	1994–present
Quebrada Blanca, Chile	17,300	1994–present
Andacollo, Chile	10,000	1996–present
Dos Amigos, Chile	3,000	1996–present
Cerro Verde, Peru	32,000	1996–present
Zaldivar, Chile	~20,000	1998–present
S&K Copper, Myanmar	18,000	1998–present
Equatorial Tonopah, USA	24,500	2000–2001

^a ~1.2 million t ore body.

The mineral covellite is subsequently also leached by ferric iron:



Chalcocite leaching generally considered a two-step process (as shown in Reactions (21) and (23)).

Bioleaching of refractory gold ores, which contain finely disseminated gold particles associated with sulfide minerals including arsenopyrite, pyrite and pyrrhotite, has been developed to an industrial application and several tank leaching operation are being run in South Africa, Brazil and Australia [200]. Refractory gold ores are recalcitrant to direct cyanidation processes and decomposition of the mineral sulfide matrix is required before the gold can be extracted. Bioleaching provides a new, low-energy approach for the treatment of refractory ores. Without pretreatment usually less than 50% of the gold is recovered by cyanidation. After bioleaching more than 95% of the gold is extracted depending on the mineral composition of the ore and extend of pretreatment.

The first commercial stirred-tank bioleach plant was commissioned in 1986 to pretreat a sulfidic gold concentrate to enhance gold recovery [199]. Typically, refractory gold plants operate with a 15–20% slurry density. The slurry is fed continuously to a primary reactor. Most of the microbial growth occurs in the primary reactor, which has a typical slurry residence time of 2–2.5 days. The primary reactor overflows to a series of smaller secondary reactors connected in series. This design increases the efficiency of sulfide oxidation by reducing short-circuiting of sulfide particles. Total residence time in the circuit is about 4–6 days.

It was reported [201] that Newmont Mining Corporation commissioned the first biooxidation heap facility for pretreatment of refractory gold or in 1999. Gold recovery was 30–39% before biooxidation, increasing to 49–61% after biooxidation.

4.1.3. Bioleaching of metals from electronic waste

Faramarzi et al. [171] reported their preliminary investigation on the feasibility of recovery of gold from printed circuit boards by bioleaching process. Gold containing pieces

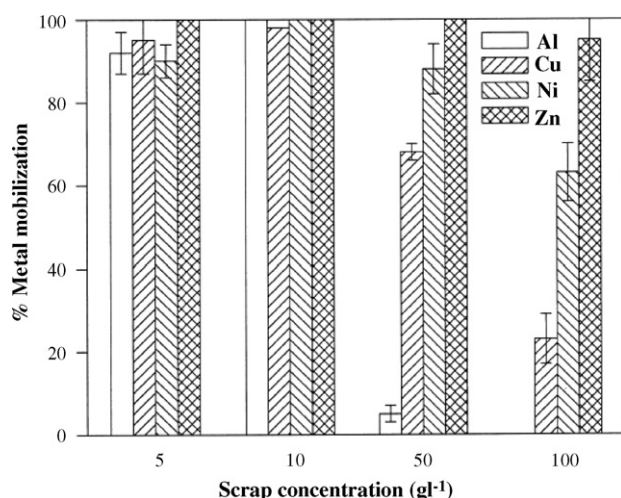


Fig. 7. Mobilization of Al, Cu, Ni, and Zn from different concentrations of electronic scrap at 30 °C in a two-step process [172]: A mixed culture of *T. ferrooxidans* and *T. thiooxidans* was previously grown for 7 days in the absence of electronic scrap. Scrap was added and the culture was grown for an additional period of 10 days. Bars represent mean values \pm standard errors of duplicate experiments.

(5 mm \times 10 mm) were obtained by manually cutting printed circuit boards followed by manual sorting. Each piece contained approximately 10 mg of gold. Using *C. violaceum*, it is demonstrated that gold can be microbially solubilized from printed circuit boards. The maximum dicyanoaurate [$\text{Au}(\text{CN})_2^-$] measured corresponds to a 14.9% dissolution of the initially gold added.

Microbiological processes, applied to mobilize metals from electronic waste materials were carried out by Brandl et al. [172]. Dust collected from shredding processes of electronic scrap was used in the investigation. The leaching experiments by using a mixed culture of *Thiobacillus ferrooxidans* and *T. thiooxidans* on electronic scrap showed that the addition of elevated amounts of scrap led to an increase of the initial pH due to the alkalinity of electronic scrap. In order to reduce toxic effects on the microorganisms, a two-step process was introduced. In the first stage, biomass was produced in the absence of electronic scrap. Subsequently, electronic scrap was added in different concentrations and the cultures were incubated for an additional time period.

The leaching results showed (Fig. 7) that at scrap concentrations of 5 and 10 g/L, respectively, *Thiobacilli* were able to leach more than 90% of the available Al, Cu, Ni, and Zn. At higher concentration, metal mobilization was reduced, especially for Al and Cu. Ni and Zn showed much better results with mobilization of 60% and 95%, respectively. In all cultures, Pb and Sn were not detected in the leachate. It is proposed that Pb precipitated as PbSO_4 , and Sn precipitated probably as SnO. That was confirmed by applying a computer program named MICROQL to model the speciation of dissolved components under the given conditions [172]. An Atomic Absorption Spectroscopy (AAS) study [14] of this kind of precipitates formed during the bioleaching of electronic scrap by *S. thermosulfidooxidans* confirmed the presence of lead and Tin in the precipitates (Table 12).

Table 12

Concentrations of various metals in the precipitates formed during bioleaching of electronic scrap as determined by atomic absorption spectroscopy [14]

Element	Content (%)
Al	0.7 ± 0.05
Cu	2.0 ± 0.08
Fe	2.0 ± 0.07
Pb	20.0 ± 0.08
Ni	0.25 ± 0.005
Sn	6.9 ± 0.05
Zn	0.09 ± 0.006

The feasibility for using fungi (*A. niger* and *P. simplicissimum*) to leach metals from electronic scrap by a two-step process was also investigated by Brandl et al. [172]. The one-step leaching experiments by fungi demonstrated that at a concentration of >10 g/L of scrap in the medium, microbial growth was inhibited. In a two-step leaching, however, concentrations of up to 100 g/L electronic scrap could be easily treated resulting in almost complete solubilization of the available Cu, Pb, Sn, and Zn (Table 13). The two-step leaching process was demonstrated using a commercial gluconic acid (NaglusolTM, 2.5 M) produced by *A. niger*.

The two-step process has been suggested by Brandl and co-workers [202,203] for metal mobilization from fly ash using both bacteria and fungi with the following advantages: (a) biomass is not in direct contact with metal-containing waste and might be recycled; (b) waste material is not contaminated by microbial biomass; (c) acid formation can be optimized in the absence of waste material; (d) higher waste concentrations can be applied as compared to the one-step process resulting in increased metal yields.

The bioleaching mechanism of copper from printed circuit boards shreds by *A. ferrooxidans* has been suggested to be similar to that of metal sulfide [204]. In the leaching process, $\text{Fe}_2(\text{SO}_4)_3$ formed by *A. ferrooxidans* oxidizes the elemental copper contained in PCBs to cupric ion following the Reaction (24).



Metal precipitation was observed by several researchers [14,172,204] during microbial leaching process of electronic

Table 13

Percentages of metal mobilized and metal content of leachates from different concentration of electronic scrap when NaglusolTM (four-fold diluted) was used as leaching agent [172]

Element	Scrap concentration (g/L)							
	Metal mobilization (%)				Metal content in leachates (g/L)			
	1	10	50	100	1	10	50	100
Al	62	57	42	43	0.15	1.28	4.98	10.2
Cu	85	86	70	8	0.07	0.69	2.8	0.6
Pb	100	92	99	97	0.02	0.18	0.99	1.9
Ni	100	100	100	100	0.02	0.15	0.75	1.5
Sn	100	100	100	100	0.02	0.23	1.15	2.3
Zn	100	100	100	100	0.02	0.26	1.3	2.6

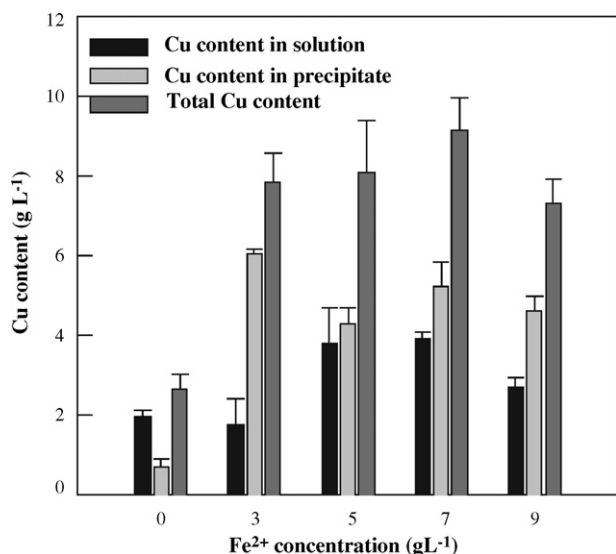


Fig. 8. Variation of the contents of copper in solution and precipitate with the initial addition of ferrous ion [204].

waste. Fig. 8 shows the variation of the copper contents in solution and precipitates with the initial concentration of ferrous ion studied by Choi et al. [204]. It is clear that in the conditions of the initial addition of Fe²⁺ ion, the contents of copper in the precipitates were even higher than those remaining in solution. Therefore, after the bioleaching of PCBs shreds by *A. ferrooxidans*, subsequent treatment of reaction precipitates in a proper way should be sought in an effort to develop a more efficient method for recovery of copper in the practical processes. Based on the total amount of copper both in solution and precipitate, the optimal addition of ferrous ion for the leaching of copper was proposed around 7 g/L, and the recovery efficiency of copper against the input was 24%.

To increase the solubility of copper and improve the efficiency of this bioleaching process, addition of a complexing agent was attempted by Choi et al. [204]. When citric acid was not added, only about 37 wt% of the total leached copper remained dissolved; however, it increased to greater than 80 wt% in the existence of citric acid. This indicates that the addition of a complexing agent like citric acid to the bioleaching solution can raise the solubility of the leached metal ions, which enables subsequent recovery processes, including solvent extraction, to be carried out more efficiently.

4.2. Biosorption

4.2.1. Biomass used for recovery of precious metals

Biosorbents are prepared from the naturally abundant and/or waste biomass of algae, fungi or bacteria. The type of biomass used for biosorption of precious metal ions is varied. Table 14 gives a list of adsorbents used for precious metal ions recovery. The following conclusions can be summed from the table:

(a) Acid condition favors the biosorption of precious metals from solution, especially for the adsorption on bacteria and derivatives of chitosan.

- (b) The adsorption capacities (Q_{\max}) of precious metals on different types of biomass vary from 0.003 to 40 mmol/g (dry biomass). This indicates that much more work should be done to select a perfect biomass from the billions of microorganisms and their derivatives.
- (c) Researches on biosorption of precious metals mainly focused on gold. More attentions should be taken into biosorption of silver from solutions.
- (d) Few researches have been reported on recovery of precious metals from multi-elemental solutions. A statistical review of biosorption with algae showed that only 10% of references belong to multi-metallic systems [29].
- (e) The biomass may be used in its “natural state” or modified, e.g. by cross-linking to improve biosorption efficiency.
- (f) Biosorption by chitosan derivatives provides an alternative for recovery of precious metals from solution due to the fact that relatively higher adsorption capacities have been obtained for Au³⁺, Pt⁴⁺, and Pd²⁺.

Chitosan is a deacetylated derivative of chitin, the second most abundant biopolymer on earth after cellulose. The major advantage of using chitosan for precious metal sorption is that the amino sites of chitosan are easily protonated in acid media, accentuating the electrostatic forces often implicated in the initial stages of sorption. Chitosan can be easily modified by grafting new functional groups onto the polymer backbone to increase its range of properties and functionalities [30].

Freely suspended microbial biomass has disadvantages that include small particle size, low mechanical strength and difficult biomass/effluent separation. Immobilized biomass particles in packed- or fluidized-bed reactors minimize these disadvantages [223,224]. Living or dead biomass of all groups has been immobilized by encapsulation or cross-linking [211,224]. Supports include agar, cellulose, alginates, cross-linked ethyl acrylate-ethylene glycol dimethylacrylate, polyacrylamide, silica gel and the cross-linking reagents toluene diisocyanate and glutaraldehyde [208,211,217,219–221,225].

Fungal biomass was immobilized with polyvinyl alcohol (PVA) by Khoo and Ting [208], as well as Ariga et al. [225]. Scanning electron microscopy (SEM) analysis revealed that PVA beads loaded with fungi showed a dense distribution of filamentous biomass tightly packed within the PVA matrix, while the surface of the blank PVA bead was undulating, with numerous folds and pores [208]. Chemical stability of the immobilized PVA beads was investigated to evaluate its suitability for industrial application. The result revealed that PVA beads were very stable over the pH range 1–13. The stability of the beads was also investigated using other chemical solutions. PVA gels showed remarkable stability with no loss in mass in urea and the solutions containing various sodium salts [208].

4.2.2. Mechanisms of biosorption of precious metals

Biosorption is a very complex process, in which there is physical or chemical adsorption onto the cell walls, cell-associated materials, or alternatively biosorption can be related to cell metabolism [181,223]. Physico-chemical mechanisms such as ion-exchange, complexation, coordination and chelation

Table 14
Adsorbents used for precious metal biosorption

Adsorbents	Metal	pH	Q_{\max}^a (mmol/g)	Refs.
Bacteria				
<i>Streptomyces erythraeus</i>	Au ³⁺	4.0	0.03	[205]
<i>Spirulina platensis</i>	Au ³⁺	4.0	0.026	[205]
<i>Desulfovibrio desulfuricans</i>	Pd ²⁺	2.0	1.2	[181]
<i>Desulfovibrio fructosivorans</i>	Pd ²⁺	2.0	1.2	[181]
<i>Desulfovibrio vulgaris</i>	Pd ²⁺	2.0	1.0	[181]
<i>Desulfovibrio desulfuricans</i>	Pt ⁴⁺	2.0	0.32	[181]
<i>Desulfovibrio fructosivorans</i>	Pt ⁴⁺	2.0	0.17	[181]
<i>Desulfovibrio vulgaris</i>	Pt ⁴⁺	2.0	0.17	[181]
<i>Penicillium chrysogenum</i>	Au(CN) ₂ ⁻	2.0	0.0072	[186]
<i>Bacillus subtilis</i>	Au(CN) ₂ ⁻	2.0	0.008	[186]
Fungi				
<i>Saccharomyces cerevisiae</i>	Au ³⁺	5.0	0.026	[205]
<i>Cladosporium cladosporioides</i>	Au ³⁺	4.0	0.5	[189]
<i>Cladosporium cladosporioides</i>	Au, waste water	4.0	0.18	[189]
<i>Cladosporium cladosporioides</i> Strain 1	Au ³⁺	4.0	0.4	[206]
<i>Cladosporium cladosporioides</i> Strain 2	Au ³⁺	4.0	0.5	[206]
<i>Cladosporium cladosporioides</i> Strain 1	Ag ⁺	4.0	0.4	[206]
<i>Cladosporium cladosporioides</i> Strain 2	Ag ⁺	4.0	0.12	[206]
<i>Aspergillus niger</i>	Au ³⁺	2.5	1.0	[207]
<i>Rhizopus arrhizus</i>	Au ³⁺	2.5	0.8	[207]
PVA-immobilized biomass (<i>Fomitopsis carnea</i>)	Au ³⁺	1–13	0.48	[208]
<i>Aspergillus niger</i>	Ag ⁺	5–7	0.9	[209]
<i>Neurospora crassa</i>	Ag ⁺	5–7	0.6	[209]
<i>Fusarium oxysporium</i>	Ag ⁺	5–7	0.5	[209]
Algae				
<i>Chlorella vulgaris</i>	Ag ⁺	6.7	0.5	[210]
<i>Chlorella vulgaris</i>	Au ³⁺	2	0.5	[178]
<i>Sargassum natans</i>	Au ³⁺	2.5	2.1	[207]
<i>Ascophyllum nodosum</i>	Au ³⁺	2.5	0.15	[207]
<i>Sargassum fluitans</i>	Au(CN) ₂ ⁻	2.0	0.0032	[186]
Alginate cross-linked with CaCl ₂	Au ³⁺	2.0	1.47	[211]
Alginate cross-linked with Ca(OH) ₂	Au ³⁺	2.0	0.34	[211]
Dealginated Seaweed Waste	Au ³⁺	3	0.4	[212]
Proteins				
Hen eggshell membrane (ESM)	Au(CN) ₂ ⁻	3	0.67	[213]
Hen eggshell membrane (ESM)	AuCl ₄ ⁻	3	3.1 ^c	[213]
Lysozyme	Au ³⁺ , Pd ²⁺ , Pt ⁴⁺	–	–	[214]
Bovine serum albumin (BSA)	Au ³⁺ , Pd ²⁺ , Pt ⁴⁺	–	–	[214]
Ovalbumin	Au ³⁺ , Pd ²⁺ , Pt ⁴⁺	–	–	[214]
Alfalfa				
Condensed-tannin gel	Au ³⁺	5.0	0.18 ^d	[215]
Condensed-tannin gel	Pd ²⁺	2.0	1.0 ^e	[216]
Condensed-tannin gel	Au ³⁺	2.0	40 ^e	[57]
Bayberry tannin immobilized collagen fiber (BTICF) membrane	Pt ⁴⁺	3.0	0.23	[217]
Bayberry tannin immobilized collagen fiber (BTICF) membrane	Pd ²⁺	4.0	0.32	[217]
Acid-washed <i>Ucides cordatus</i> (waste crab shells)	Au(CN) ₂ ⁻	3.4	0.17	[218]
Glutaraldehyde crosslinked chitosan (GCC)	Au ³⁺	1.6	2.9	[219]
Sulfur derivative of chitosan (RADC)	Au ³⁺	3.2	3.2	[219]
Glutaraldehyde crosslinked chitosan (GCC)	Pd ²⁺	2.0	2.44	[220]
Thiourea derivative of chitosan (TGC)	Pd ²⁺	2.0	2.54	[220]
Rubeanic acid derivative of chitosan (RADC)	Pd ²⁺	2.0	3.24	[220]
Thiourea derivative of chitosan (TGC)	Pt ⁴⁺	2.0	2.0	[221]
Glutaraldehyde crosslinked chitosan (GC)	Pt ⁴⁺	2.0	1.6	[221]
Chitosan derivatives	Pd ²⁺	2.0	3.5	[222]
Chitosan derivatives	Pt ⁴⁺	2.0	3.2	[222]

^a At ambient temperature, except for special statement. (b)[–] means not reported.

^c Temperature 65 °C.

^d In a multi-elemental solutions containing Au(III), Cd(II), Cu(II), Cr(III), Pb(II), Ni(II), and Zn(II) at 0.3 mM for each element.

^e Initial pH 2.0, pCl 2.0, and temperature 60 °C.

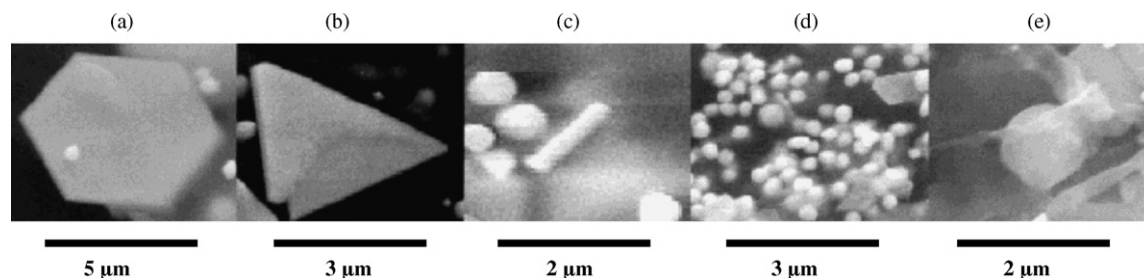


Fig. 9. Detail of the types of gold particles observed: (a) hexagonal platelets, (b) tetrahedral, (c) rods, (d) irregular shaped, and (e) decahedral [212].

between metal ions and ligands, depend on the specific properties of the biomass (alive, or dead, or as a derived product). Other metal-removal mechanisms dependent on metabolism include metal precipitation as sulfides or phosphates, sequestration by metal-binding proteins, peptides or siderophores, transport and internal compartmentalization [224].

Biosorption of precious metals from solutions can be simplified as chemical sorption mechanisms and physical sorption mechanisms. Chemical sorption mechanisms include complexation, chelation, microprecipitation, and microbial reduction, while physical sorption mechanisms generally involve electrostatic forces and ion exchange [188,207].

Physical sorption mechanism was proposed [213] for the sorption of dicyanoaurate(I) by eggshell membrane (ESM) since the gold(I) sorption reaction by ESM is exothermic. In contrast, the biosorption of gold(III) on ESM was assumed to be complex chemical reaction involving the dissociation of Au^{3+} from tetrachloroaurate(III).

X-ray photoelectron (XPS) and Fourier transform infra-red spectroscopy (FT-IR) were used by Pethkar et al. [206] for the elucidation of binding mechanisms involved in the adsorption of gold and silver ions to two strains of a fungus, *Cladosporium cladosporioides*. These methods confirmed that no chemical change to the biosorbent took place after metal loading, suggesting that the acidic conditions merely favored electrostatic interaction between gold anions (AuCl_4^-) and protonated biomass.

More recently, more and more studies propose chemical adsorption mechanisms [25,57,178,180,212,216,226,227]. A detailed determination of gold binding in an Algal biomass using EXAFS and XANES was carried out in 1980 by Watkins II, Greene and co-workers [25,180]. It was proposed that the mechanism of tetrachloroaurate(III) interaction with *Chlorella vulgaris* involves rapid reduction of gold(III) to gold(I), followed by a slow reduction to gold(0). It was believed that ligand-exchange reactions leading to formation of bonds between Au(I) and sulfur and/or nitrogen contained in the algae.

Spectroscopic studies of the biosorption of gold(III) by dealginated seaweed waste was carried out by Romero-González et al. [212]. It was reported that colloidal Au formed on the surface of dealginated seaweed by reduction of Au(III) to Au(0) was observed using ESEM and four different types of particles were clearly identified (Fig. 9). EXAFS measurements showed that colloidal Au is present on the surface of the biosorbent. Evidence of gold reduction from Au(III) to Au(I) and Au(0) was also confirmed by the measured bond distances characteristic of the

metal. The coordination number obtained by EXAFS indicated that approximately 75% of the Au on the sample was present in the colloidal form and the remaining Au was bound to S as nearest neighbor. The proposed mechanisms for Au removal from solution are reduction of Au species by components on the surface of the biosorbent to form colloidal metal followed by retention of the ionic Au(I) species at the sulfur containing sites.

Adsorption mechanism of gold and palladium by redox within condensed-tannin gel was reported by Nakano and co-workers [57,216,227]. Tannin gel particles that adsorbed palladium were sampled for XRD analysis to find out the chemical form of the adsorbed palladium. Fig. 10 shows the XRD pattern of the sample. The diffraction peaks corresponded to those of crystalline metallic palladium at $2\theta = 40^\circ$, 46.6° , 68° , 82° and 86.5° with 196 Å diameter of crystalline particle (estimated by Williamson-Hall plot), which means the crystallization of reduced Pd(0) on tannin gel network. The presence of metallic palladium on the tannin gel particles confirms that the palladium(II) can be reduced to palladium(0), while the hydroxyl groups of tannin gel are oxidized by redox-reaction during the adsorption.

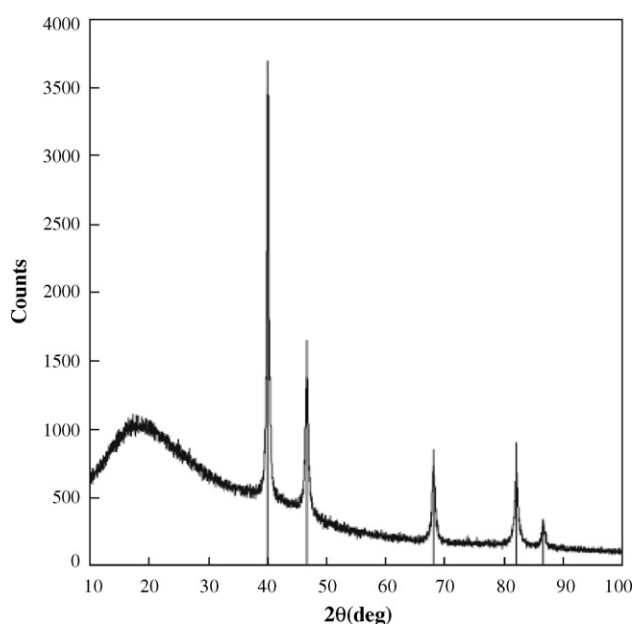
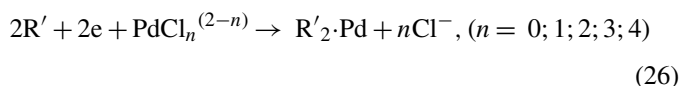
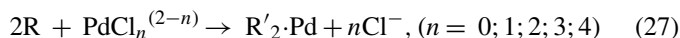


Fig. 10. XRD pattern of the palladium adsorbed onto condensed-tannin gel particles [216].

Based on the research, the following reaction pathways are proposed by Kim and Nakano [216]:



From the above reactions,



where R representing the hydroxyl group of tannin gel is oxidized to R' and reduces palladium(II) to metallic palladium simultaneously, forming R'2·Pd with metallic palladium.

It was pointed out [216] that the adsorption mechanism of palladium by condensed-tannin gel is more complicated, because palladium exists as various chemical forms, by which the adsorption rate is affected.

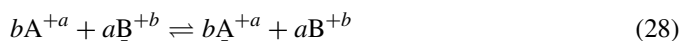
4.2.3. Models of biosorption of precious metals

The two most widely used adsorption isotherms are the Langmuir (Eq. (2')) and Freundlich isotherms (Eq. (4')). The Langmuir isotherm assumes a surface with homogeneous binding sites, equivalent sorption energies, and no interaction between sorbed species. The Freundlich isotherm is an empirical equation based on an exponential distribution of sorption sites and energies [208].

Table 15 gives a part of biosorption isothermal constants for Langmuir model and Freundlich model reported in the references. It can be seen that Langmuir isotherm model is being widely used. However, both the isothermal models do not correspond to the ion-exchange phenomena apparently playing an

important role in biosorption [188]. An ion-exchange isotherms model was developed by Schiewer and Volesky in McGill University, Montreal, Canada [188,228–230].

In an ion exchange mechanism, ion exchange was supposed to be the predominant metal-ion-binding mechanism. The classical ion-exchange concept based on exchange equilibrium constants and separation factors can thus be applied to this case. For a generalized ion-exchange reaction (Reaction (28)) for dissolved species A (of valence +a) exchanging for a bound species B (of valence +b), with underlining representing the bound species,



the equilibrium constant K_{AB} and the separation factor r_{AB} are defined in Eqs. (8') and (9'), respectively, for the case of ideal behavior of the exchanging species (1:1 ion exchange, activity = 1) in both of the phases [188]:

$$K_{AB} = \frac{q_A^b C_{Bf}^a}{C_{Af}^b q_B^a} = \left(\frac{y_A^b x_B^a}{x_A^b y_B^a} \right) \frac{C_0^{a-b}}{Q^{a-b}} \tag{8'}$$

$$r_{AB} = \left(\frac{y_A x_B}{x_A y_B} \right) \tag{9'}$$

where: q_A, q_B : uptake of species A or B (mmol/g); C_{Af}, C_{Bf} : equilibrium final concentration of species A or B in liquid phase (mmol/L); x_A, x_B : equivalent fractions of species A and B, respectively, in liquid phase; y_A, y_B : equivalent fractions of species A and B, respectively, in solid phase; C_0 : normality of the solution (meq/L); Q : equilibrium uptake of A and B.

Biosorbents can also be prepared in different ionic forms, and the sorption analysis is often reduced to considering a series of simple binary ionexchange systems. For a binary ion-exchange

Table 15
Isothermal constants of Langmuir model and Freundlich model for precious metal biosorption

Adsorbents	Metal	Langmuir model			Freundlich model			Refs.
		Q_{max} (mg/g)	b (L/mg)	R^2	K	n	R^2	
<i>Desulfovibrio desulfuricans</i>	Pd ²⁺	128.2	0.9	6.20 ^a	65.5	0.224	11.23 ^a	[181]
<i>Desulfovibrio fructosivorans</i>	Pd ²⁺	126.5	0.17	8.44 ^a	22.8	0.321	13.51 ^a	[181]
<i>Desulfovibrio vulgaris</i>	Pd ²⁺	108.6	0.56	7.16 ^a	38.0	0.275	6.06 ^a	[181]
<i>Desulfovibrio desulfuricans</i>	Pt ⁴⁺	62.5	0.50	2.27 ^a	24.2	0.292	2.66 ^a	[181]
<i>Desulfovibrio fructosivorans</i>	Pt ⁴⁺	32.3	1.17	2.66 ^a	20.3	0.140	1.95 ^a	[181]
<i>Desulfovibrio vulgaris</i>	Pt ⁴⁺	32.1	0.42	3.39 ^a	16.8	0.169	3.71 ^a	[181]
<i>Streptomyces erythraeus</i>	Au ³⁺	6.00	0.00472	– ^b				[205]
<i>Spirulina platensis</i>	Au ³⁺	5.55	0.0129	–				[205]
PVA-immobilized fungal biomass	Au ³⁺	94.34	0.1125	0.9466	37.174	0.182	0.9158	[208]
<i>Saccharomyces cerevisiae</i>	Au ³⁺	5.55	0.00259	–				[205]
Bayberry tannin immobilized collagen fiber (BTICF) membrane	Pt ⁴⁺	45.8	0.21	0.991				[217]
Bayberry tannin immobilized collagen fiber (BTICF) membrane	Pd ²⁺	33.4	0.16	0.992				[217]
Eggshell membrane	Au ⁺	132	0.0146	0.997				[213]
Eggshell membrane	Au ³⁺	226	0.2213	0.976				[213]
Eggshell membrane ^c	Au ³⁺	618	0.0634	0.918				[213]

^a Sum residuals according to: $MSR = \sqrt{\sum_{i=1}^n [F \exp(C_i) - F_{cal}(C_i)]^2 / n}$ [181].

^b “–” means not reported.

^c Temperature 65 °C.

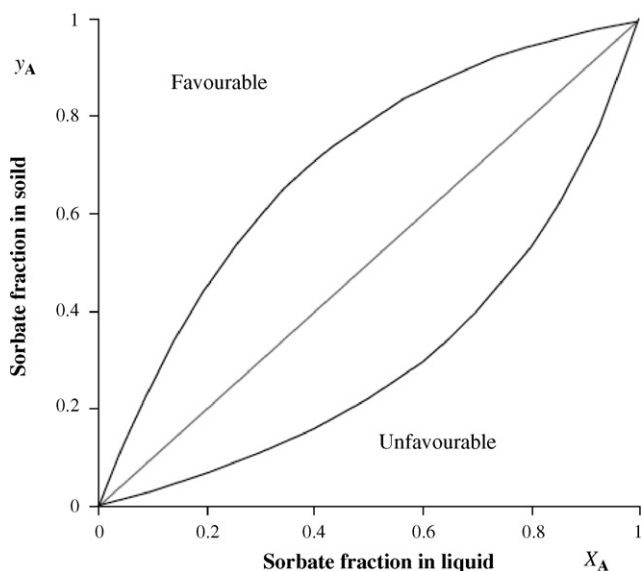


Fig. 11. Ion-exchange equilibrium isotherm becomes relevant when two ions exchange at one active binding site. A favorable isotherm gives a higher fraction of the bound ion A than that remaining in the liquid phase [188].

system, the value of the equilibrium constant K_{AB} can be determined from the slope of the plot of q_A/q_B versus C_A/C_B . By eliminating q_B through substitutions ($Q = q_A + q_B$), a useful expression using dimensionless forms of the uptake and concentration (q_A/Q) can be obtained:

$$\frac{q_A}{Q} = \frac{1}{1 + C_B/K_{AB}C_A} = \frac{1}{1 + k'C_B} \quad (10')$$

where

$$k' = \frac{1}{K_{AB}C_A} \quad (11')$$

Because q_A/Q represents the fraction of the binding sites occupied by A, Eq. (10') may be used to evaluate the decrease of the equilibrium uptake of the species A by the biosorbent caused by the presence of species B. It also shows that, when $C_B = 0$, $q_A/Q \approx 1$, regardless of the absolute value of the final concentration of A, C_A . This distinguishes ion exchange from chemisorption and/or physical sorption, which are known to occur on activated carbon.

Furthermore, Eq. (10') shows that, for a fixed value of C_A , q_A/Q is a hyperbolic function of C_B that may also be described using simple dimensionless concentration fractions as variables [188]:

$$x_A = \frac{C_A}{C_0}; x_B = \frac{C_B}{C_0}; y_A = \frac{q_A}{Q}; \quad (12')$$

yielding Eq. (13'), which represents an ion-exchange isotherm for a binary sorption system:

$$y_A = \frac{1}{1 + x_B/K_{AB}x_A} \quad (13')$$

As y_A , x_B and K_{AB} are all dimensionless variables, Eq. (13') represents the most generalized description of the ion-exchange sorption equilibrium for binary systems (Fig. 11).

4.2.4. Recovery of precious metals from electronic waste by biosorption

Biotechnological approaches that are designed to recover heavy metals from waste waters have received great deal of attention in the recent years [27,174,184,231]. However, recovery of precious metals from electronic waste is only beginning. The only reference that can be found from the databases is the research by Macaskie' group in the University of Birmingham, UK [55,232].

The studies on recovery of precious metal recovery from electronic scrap leachates by *Desulfovibrio desulfuricans* was reported by Creamer et al. [232]. Samples of electronic and WEEE scrap were obtained from Sims Group UK (shredded printed circuit board fragments from a commercial plant) and Midex Europe Ltd. (granulated electronic scrap with the iron and aluminum content previously reduced). The approximate contents of the metals of interest were: Cu: 20–25 wt% (Sims) 43 wt% (Midex); Au: 60–113 ppm (Sims); 35–55 mg/L (Midex); Pd: up to ~30 mg/L. (i.e. approximately equimolar Au and Pd). The tin/lead (solder) and copper were selectively leached out hydrometallurgically (virtually complete tin/lead removal and ~40% copper removal by this step). The solubilized copper, and also the tin/lead solder components were recovered electrochemically prior to use and the solder- and copper-depleted scrap was treated with aqua regia (e.g. 90% v/v HNO₃/10% HCl). In the test, the gold and palladium contents were supplemented with NaAu(III)Cl₄ or Na₂Pd(II)Cl₄ [232].

A columnar electrobioreactor (2 L) was constructed which supplied either nitrogen (from a bottle) or hydrogen via an external electrochemical cell through the bottom of the vessel via a glass fritted gas diffuser, to provide H₂ reductant and also gas-lift mixing of the vessel contents. Precipitated material was collected under gravity in a cone at the bottom of the vessel. Leachate (~2 L) was introduced and contacted with native biomass (for Au removal) or palladized biomass (for Pd removal), initially under N₂ to provide anaerobiosis and then under H₂, provided electrochemically, for 30 min. For demonstration of Au recovery a solution of CuCl₂ (10 g/L; 0.5%; pH 2; 2 L) was supplemented with 55 mg NaAuCl₄/L and 165 mg dry wt washed cells/L; H₂ was sparged for 30 min and precipitation proceeded under gravity for 24 h. For demonstration of Pd recovery the CuCl₂ solution (as above; 2 L) was supplemented with 106 mg Pd(II)/L and 317 mg dry wt palladized cells/L (Pd content was ~10% of the dry weight: see above). H₂ was sparged for 30 min and precipitation was followed over 45 min and left to go to completion over 24 h under gravity. The precious metal-depleted solutions were then treated using biogas from broth-grown cultures of *Klebsiella pneumoniae* [232].

It was reported [232] that addition of *D. desulfuricans* biomass and bubbling of H₂ through the WEEE leachate samples or WEEE leachate samples supplemented with Pd(II) to 2 mM did not promote deposition of Pd(0). It was proposed that copper inhibits hydrogenase activity and the presence of Cu²⁺ in the leachate would be problematic for Pd(II) recovery. Tests were done to evaluate the effect of Cu²⁺ on the removal of Pd(II) and Au(III) from test solutions and leachate. The results

Table 16

Palladium and gold recovery from solution and leachate by *D. desulfuricans*, and the effect of copper [232]

Au recovery	Native biomass	With 'bio-Pd(0)*'
2 mM NaAu(III)Cl ₄	+	+
2 mM NaAu(III)Cl ₄ + 2% CuSO ₄	+	+
2 mM NaAu(III)Cl ₄ + 5% CuSO ₄	+	+
2 mM NaAu(III)Cl ₄ + 7% CuSO ₄	+	+
2 mM NaAu(III)Cl ₄ + 10% CuSO ₄	+	+
Leachate	–	–
Leachate + 1 mM Au(III)	+	+
Pd recovery	Native biomass	With 'bio-Pd(0)*'
2 mM Na ₂ Pd(II)Cl ₄	+	+
2 mM Na ₂ Pd(II)Cl ₄ + 2% CuSO ₄	–	+
2 mM Na ₂ Pd(II)Cl ₄ + 5% CuSO ₄	–	+
2 mM Na ₂ Pd(II)Cl ₄ + 7% CuSO ₄	–	+
2 mM Na ₂ Pd(II)Cl ₄ + 10% CuSO ₄	–	+
Leachate + 1 mM Pd(II)	–	+

*For testing the leachates were supplemented with 2 mM Au(III) or Pd(II) as shown. A positive result in the case of palladium indicates a heavy black deposit over and above that of the Bio-Pd(0) alone. The background copper content of the leachate was 2039 ± 193 ppm (mean ± S.E.M.; three determinations).

showed that Cu²⁺ inhibited the removal of Pd(II), but not Au(III) (as shown in Table 16). It was also observed [232] that native biomass and bio-Pd(0), catalyzed Au(III) removal (Table 16), resulting in, respectively, a gold precipitate and a gold precipitate flecked with black. Similar results were obtained using Au-supplemented leachate (copper concentration was ~2,000 mg/l; Table 16). In order to visualize the reaction more clearly a second series of tests used pre-palladized cells where the Pd(0) loading was only ~10% of the dry cell mass. Similar results were obtained to those shown in Table 16. Hence, pre-polarization resulted in the production of a bio-inorganic catalyst for Pd(II) (and Au(III)) removal in the presence of Cu²⁺. In contrast to the test solutions, no gold was removed from the leachate using either fresh or pre-palladized biomass but Au(III) was removed (by visualization of gold precipitate) when the leachate solution was freshly supplemented with additional Au(III) (Table 16).

It was concluded [232] that a bioseparation method is feasible for Au(III), Pd(II) and Cu(II). A 3-step process was proposed (Fig. 12) for platinum group metal (PGM) recovery from WEEE leachate, and removal of Cu²⁺. In the process fresh biomass would be used to selectively remove Au(III) (with inhibition of Pd(II) removal by the Cu²⁺ also present). Supplementation with palladized biomass then catalyses the removal of Pd(II)

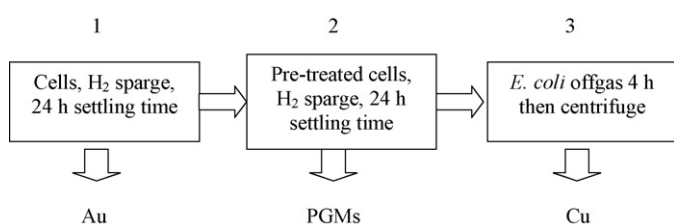


Fig. 12. Diagrammatic representation of proposed 3-step process for platinum group metal (PGM) recovery from WEEE leachate, and removal of Cu²⁺. Pre-treatment of cells refers to pre-polarization in order to facilitate recovery of more Pd from the aggressive solution autocatalytically [232].

autocatalytically and the Cu²⁺ is finally recovered by a bioprecipitation method using bacterial off-gas. It should be noted that pre-palladized cells of *E. coli* can remove metals in the same way as described for *D. desulfuricans* (Mabbett et al. 2005) and the biomass grown for off-gas generation could then be recycled for metal recovery.

5. Conclusions

Recycling of electronic waste is an important subject not only from the point of waste treatment but also from the recovery of valuable metals. The value distribution for different electronic scrap samples shows that for cell phones, calculators, and printed circuit board scraps, the precious metals make up more than 70% of the value, for TV boards and the DVD player they still contribute to about 40%. This indicates that the major economic driver for recycling of electronic waste is from the recovery of precious metals. Behind the precious metals come copper and zinc.

Traditional technology, pyrometallurgy has been used for recovery of precious metals from waste electronic equipment. However, it has encountered some challenges from environmental considerations. Consequently, state-of-the-art smelters are highly depended on investments. Recent research on recovery of energy from PC waste gives an example for using of plastics in electronic waste. It reveals that thermal processing of e-waste provides an approach for recovery of energy from e-waste if a comprehensive emission control system is installed.

In the last decade, attentions have been removed to hydrometallurgical process for recovery of metals from e-waste. Cyanide leaching of gold has been used by the mining industries for more than 100 years. However, a series of environmental accidents at various gold mines around the world has precipitated widespread concern over the use of cyanide. Based on a critical comparison of various leaching methods from the points of view economic feasibility and environmental impact, it is concluded that leaching of gold by thiourea may be the most realistic substitute. Leaching of gold by thiourea should be taken into consideration due to a rapid reaction with gold, as well as less environmental impact comparing with cyanide.

It is believed that biotechnology has been one of the most promising technologies in metallurgical processing. Bioleaching has been used for recovery of precious metals and copper from ores for many years. However, limited researches were carried out on the bioleaching of metals from electronic waste. Biosorption of precious metals from solutions has received great deal of attention in the recent years. Compared with the conventional methods, a biosorption-based process offers a number of advantages including low operating costs, minimization of the volume of chemical and/or biological sludge to be handled and high efficiency in detoxifying effluents.

It was reported that living or dead biomass including bacteria, fungi, yeast, and algae has been investigated for recovery of precious metals from waste water. It should be pointed out here that biomass of all groups has been immobilized by encapsulation or cross-linking to improve the stability and other

physical/chemical properties. Further work should be done for seeking and modifying a biomass to have a high uptake capacity and good biosorption characteristics.

Acknowledgment

The author is grateful for financial support for the research on Recovery of Metals from Electronic Waste from the Research Council of Norway (RCN).

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