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Recovery technologies for indium, gallium, and germanium from end-of-life products (electronic waste) – A review

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Abstract

Advanced high-tech applications for communication, renewable energy, and display, heavily rely on technology critical elements (TCEs) such as indium, gallium, and germanium. Ensuring their sustainable supply is a pressing concern due to their high economic value and supply risks in the European Union. Recovering these elements from end-of-life (EoL) products (electronic waste: e-waste) offers a potential solution to address TCEs shortages. The review highlights recent advances in pre-treatment and hydrometallurgical and biohydrometallurgical methods for indium, gallium, and germanium recovery from EoL products, including spent liquid crystal displays (LCDs), light emitting diodes (LEDs), photovoltaics (PVs), and optical fibers (OFs). Leaching methods, including strong mineral and organic acids, and bioleaching, achieve over 95% indium recovery from spent LCDs. Recovery methods emphasize solvent extraction, chemical precipitation, and cementation. However, challenges persist in separating indium from other non-target elements like Al, Fe, Zn, and Sn. Promising purification involves solid-phase extraction, electrochemical separation, and supercritical fluid extraction. Gallium recovery from spent GaN and GaAs LEDs achieves 99% yield via leaching with HCl after annealing and HNO₃, respectively. Sustainable gallium purification techniques include solvent extraction, ionic liquid extraction, and nanofiltration. Indium and gallium recovery from spent CIGS PVs achieves over 90% extraction yields via H₂SO₄ with citric acid-H₂O₂ and alkali. Although bioleaching is slower than chemical leaching (several days versus several hours), indirect bioleaching shows potential, achieving 70% gallium extraction yield. Solvent extraction and electrolysis exhibit promise for pure gallium recovery. HF or alkali roasting leaches germanium with a high yield of 98% from spent OFs. Solvent extraction achieves over 90% germanium recovery with minimal silicon co-extraction. Solid-phase extraction offers selective germanium recovery. Advancements in optimizing and implementing these e-waste recovery protocols will enhance the circularity of these TCEs.

Keywords: Technology critical elements recovery, pre-treatment methods, hydrometallurgy, biohydrometallurgy, e-waste recycling

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1 Introduction

The ongoing development of novel high-tech applications for communications, renewable energy production, and display purposes strongly depends on technology critical elements (TCEs) such as indium, gallium, and germanium. These elements play important roles in the functionality of liquid crystal displays (LCDs), light emitting diodes (LEDs), photovoltaics (PVs), and optical fibers (OFs). However, the sustainable supply of these elements is a major concern, as their supply to the European Union (EU) manufacturing industry is not secured due to increasing demand and export controls from resource-rich countries (Licht et al., 2015). European Commission has classified these TCEs on the main list of critical raw materials (CRMs: total 30 materials) in view of their high importance to the EU economy and because of the high risk associated with their supply from 2011 to the present (European Commission, 2020).

The EU proposed a circular economy with efficient energy use, low carbon emissions, efficient resource recovery, and a competitive economy in 2011 (European Commission, 2011). The EU Green Deal Communiqué also adopted a proposal in 2019 to achieve carbon neutrality by 2050. As a result, EU members are continuously working to develop sustainable and efficient processes to recover TCEs needed for electronic applications, therefore contributing to the sustainable supply of these elements. According to the International Telecommunication Union News in 2020, approximately 53.6 million metric tonnes (Mt) of global electronic waste (e-waste) (excluding PV panels) were generated in 2019, and this figure is expected to increase to 74 Mt by 2030 (Forti et al., 2050). Moreover, according to the International Renewable Energy Agency (IRENA), End-of-life (EoL) PVs were projected to reach 1.7-8 Mt in 2030 and 70 Mt in 2050 (Stephanie et al., 2016). Global e-waste generation is increasing at an alarming rate of almost 2 Mt per year (Forti et al., 2050).

Furthermore, according to the Platform for Accelerating the Circular Economy report, if current trends continue, the amount of global e-waste will double to 120 Mt per year by 2050. Also, Elshkaki and Graedel (2013) reported that the demand for indium, gallium, and germanium will increase by 225%, 224%, and 2,130%, respectively, in 2050 compared to 2010. In addition, production losses account for 70% of total losses for indium and more than 95% for gallium and germanium in the global production processes (Charpentier Poncelet et al., 2022). The recovery of these TCEs from EoL products is seen as a sustainable approach to overcome the foreseeable supply shortages of indium, gallium, and germanium.

In contrast to existing reviews, which primarily focus on single TCE type and its recovery from primary resources or pyrometallurgical industry waste streams, this review paper provides a comprehensive exploration of contemporary methodologies dedicated to the recovery of indium, gallium, and germanium from EoL products, such as LCDs, LEDs, PVs, and OFs. In addition, the reliance on energy-intensive pyrometallurgical methods such as thermal decomposition for TCEs recovery hindered by environmental and economic concerns has not been reviewed in the present paper but is discussed elsewhere (Akcil et al., 2019; Fontana et al., 2020; Pradhan et al., 2018; Schaeffer et al., 2017; Zhang et al., 2015). Consequently, the present study encompasses an overview of the above-mentioned TCEs content and distribution in EoL products, as well as a detailed discussion of the full electronic waste treatment chain, including the pre-treatment, and both hydrometallurgical and biohydrometallurgical TCE recovery processes. Further details regarding the methodology for literature selection can be found in Supplementary Material Text S1. This paper presents a complete perspective covering diverse TCEs recovery routes from various types of EoL products and emphasizes recent advances in hydrometallurgical and biohydrometallurgical approaches, contributing to a comprehensive understanding of current research and providing valuable insights for future research.

1.1 Indium

Indium is a silvery white metal. The oxidation states of indium are +1 and +3, but the most stable oxidation state is In(III) (Alfantazi and Moskalyk, 2003; Gunn, 2014; Zhang et al., 2017). Its specific properties, including ductility, scalability, electrical conductivity, and optical transparency, make it attractive for high-tech applications (Ciacci et al., 2019). Indium is used in manufacturing industries to produce a variety of applications to improve the quality of human life, such as flat panel displays (FPDs), PVs, LEDs, batteries, and more (Lokanc et al., 2015). Additionally, the considerable economic value and irreplaceable nature of indium solidify its importance within technological domains (Harper et al., 2015).

The scarcity of indium in rocks is obvious by its average crustal abundance of 0.072 mg/kg in oceanic crust and 0.05 mg/kg in continental crust (Gunn, 2014). It is most commonly found in higher concentrations in zinc (sphalerite), copper sulphide (chalcopyrite), and tin ores, often as a by-product of the extraction of elements like Zn, Cu, Pb, and Sn (Ciacci et al., 2019; Mejías et al., 2023). Despite this, its concentration in zinc ores usually remains below 20 mg/kg (Takahashi et al., 2009).

Given the limited availability and growing demand, the global indium supply faces challenges. The world produced approximately 900 tons of indium, about 7% less than in 2021, possibly

due to global COVID-19 pandemic restrictions (USGS, 2022, 2023). The United States, for instance, relied on a 100% net import from countries such as China (31% in 2017-2020) and the Republic of Korea (32% in 2018-2021), leading to fluctuations in supply (USGS, 2022, 2023). This increasing demand has contributed to a rise in the price of indium, reaching \$395 (99.99% purity) per kilogram by 2020 (Křištofová et al., 2016; Zhang et al., 2017; USGS, 2023). Owing to its high economic importance ($EI \geq 2.8$) and supply risk ($SR \geq 1$), indium ($EI: 3.3$ and $SR: 1.8$) has been classified on the CRMs list by the EU commission from 2011 to 2020 (European Commission, 2020).

To counteract indium supply shortages, recovering indium from EoL products presents a viable solution (Lokanc et al., 2015). While past indium recovery rates were limited ($< 1\%$) due to technological and economic barriers, the production losses of indium were relatively high (70%) in the global production process (Charpentier Poncelet et al., 2022; Ylä-Mella & Pongrácz, 2016). However, efficient indium recovery technologies have been explored for waste electrical and electronic equipment (WEEE) containing significant concentrations of TCEs (Danilo Fontana et al., 2015). In this context, hydrometallurgical and biohydrometallurgical methods stand out, offering lower energy consumption, reduced operating costs, and improved environmental friendliness compared to pyrometallurgical routes (Mejías et al., 2023; Sethurajan et al., 2018, 2019).

1.2 Gallium

Gallium is silvery-white in appearance and a relatively soft metal (Gunn, 2014). It has two valence states of +1 and +3, with Ga(III) being the predominant stable state. The benefits of electronic, optoelectronic, and thermal conductivity properties attract the attention of high-tech industries (Gunn, 2014; USGS, 2018). Gallium is used in electronic circuits, semiconductors, laser diodes, transistors, PVs, and LEDs due to its unique physical and chemical properties, compared to conventional semiconductor materials like silicon (Chen et al., 2018a; Licht et al., 2015; Maarefvand et al., 2020). Therefore, gallium is important in high-tech industries.

Gallium usually occurs in trace amounts in nature, although it has an average crustal abundance of 19 mg/kg, similar to other well-known metals, such as lead (10 mg/kg) and tin (2 mg/kg). Not occurring naturally as a pure mineral, gallium replaces similar elements in minerals like iron (Gunn, 2014). Extracted primarily as a by-product of aluminum from bauxite, zinc production from sphalerite (ZnS), and coal, gallium is highly dependent on the production of primary commodities (Licht et al., 2015; Lu et al., 2017). While around 90% of primary gallium production is related to aluminum refining, less than 5% (438 tonnes) can be recuperated from

Bayer liquor generated in aluminum refining (Licht et al., 2015). Growing technological needs have increased demand, predicted a more than 200% increase by 2050 from 2010 (Elshkaki and Graedel, 2013). However, as of 2022, global gallium production has already reached 550 tonnes per year, a 127% increase from 2021 (USGS, 2023). Dependency on 100% net imports (2017 to 2021), particularly from China (53%), along with the price increase of low-purity gallium to \$420 per kg in 202, may be caused by the pandemic restriction, highlights the global competition driven by limited resources and heaving demand (USGS, 2023). The irreplaceability of gallium drives competition in such dynamics (Frenzel et al., 2017). This explains why the European Commission has identified this element as critical (EI: 3.5 and SR: 3.9) (European Commission, 2023).

In addition, the growing market for wireless communications and mobile technologies is driving the need to develop gallium recovery from related EoL products (Swain et al., 2015a). Despite this, less than 1% of gallium is recycled from EoL products, and the production loss exceeds 95% in the global production process (Charpentier Poncelet et al., 2022; Chen et al., 2018a). EoL products, such as LEDs and PVs, contain significant amounts of gallium, which is predicted to see over a 12-fold demand increase by 2050 (Ueberschaar et al., 2017). Therefore, hydrometallurgical and biohydrometallurgical approaches are developing as promising routes to recover gallium from EoL products (Chen et al., 2018a; Maarefvand et al., 2020; Nagy et al., 2017; Swain et al., 2015a).

1.3 Germanium

Germanium is greyish-white and brittle semi-metal (Gunn, 2014; Rosenberg, 2009). It has two main valence states, +2 and +4, with Ge(IV) as the stable redox state. It appears as compounds like GeO_2 and GeS_2 , and substitutes silicon in silicate minerals due to similar ionic radii (Ge^{4+} 0.53 Å versus Si^{4+} 0.40 Å) and similar covalent radii (Ge^{4+} 1.22 Å versus Si^{4+} 1.17 Å) (Höll et al., 2007). The unique electrical properties of germanium, its high refractive index in transmission, and its low dispersion to avoid chromatic aberrations, make it essential in various applications, such as optical fibers, infrared optics, electronics, and PVs. (Bumba et al., 2018; Licht et al., 2015; Rosenberg, 2009). With escalating semiconductor and optical industry demands, germanium use is projected to increase by 2,130% in 2050 compared to 2010 (Elshkaki and Graedel, 2013).

Germanium is a rare element in rocks, with an average abundance of 13.8 mg/kg on the earth (1.5 mg/kg for the oceanic crust and 1.6 mg/kg for the continental crust). It does not occur as a free metal in nature, and is found in trace amounts within various rocks, including oxidic and sulfide metalliferous deposits (zinc-copper-lead-gold-silver ores), and non-ferrous metal

deposits, such as coal combustion by-products (coal fly ash and flue dust) (Gunn, 2014; Höll et al., 2007; Rosenberg, 2009; USGS, 2022). Global refinery production increased by 113% to 140 tonnes in 2021 compared to 2018 (USGS, 2018, 2022). However, net imports, mainly from China (53%) and Russia (9%), are vulnerable to geopolitical factors (i.e. the conflict in Ukraine) (Kot-Niewiadomska et al., 2022). The price of germanium metal was high (\$1,315 per kg of 99.999% purity) in 2021 (USGS, 2022). Despite these, germanium supply is scarce and is unable to meet the rising manufacturing demand (Chen et al., 2018b). Consequently, the EU Commission listed germanium as a CRM with an EI value of 3.5 and an SR value of 1.8, emphasizing the urgency for alternative supply solutions (European Commission, 2023).

In recent years, around 30% of germanium recovery comes from recycled materials (Charpentier Poncelet et al., 2022), with global production losses exceeding 95% (Chen et al., 2018b; USGS, 2022) (Charpentier Poncelet et al., 2022; Chen et al., 2018b; USGS, 2022). The growing popularity of optics with the development of 5G networks presents an opportunity to recycle EoL fiber optics (Chen et al., 2020). Fiber optics account for 40% of total germanium usage and can assistance in germanium recycling (Chen et al., 2017; Chen et al., 2018b). This emphasizes the importance of EoL products recovery to mitigate germanium supply pressure.

1.4 The aqueous chemistry of indium, gallium, and germanium

The ionic radii of In(III), Ga(III), and Ge(IV) play a role in their behavior (

Table 1), together with those of Fe(III), Al(III), and Si(IV). These metals often replace elements with similar ionic radii and charges in various ores, and emerge as by-products, including sphalerite, bauxite, and chalcopyrite (Gunn, 2014). In addition, higher oxidation states and ionic radii lead to the formation of stable complexes with oxygen-bound organic ligands (Hofmann et al., 2020; Höll et al., 2007; Wood & Samson, 2006). Thus, the stability of these metals with organic ligand complexes follows the following order: $\text{In(III)} < \text{Fe(III)} \approx \text{Ga(III)} \approx \text{Al(III)}$ and $\text{Ge(IV)} < \text{Si(IV)}$. The above information contributes to utilizing insights from the recovery methods of Fe, Al, and Si and applying them to the recovery of In, Ga, and Ge from EoL products.

In aqueous solutions, In(III) and Ga(III) are mainly present in their hydrated forms with octahedral coordination formed by six bonds, while Ge(IV) has tetrahedral coordination formed by four bonds (Lu et al., 2017; Nguyen & Lee, 2019; Höll et al., 2007; Wood & Samson, 2006) (

165 Table 1). These metals have a full set of 10 d-orbitals in their electronic configuration, enabling
166 stronger covalent bonding with ligands and forming stable complexes.
167

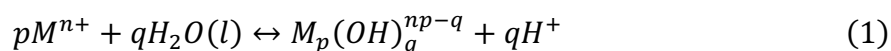
168 Table 1 Ionic radii of metal ions

Metal ion	Al ³⁺	Ga ³⁺	Fe ³⁺	In ³⁺	Si ⁴⁺	Ge ⁴⁺
Radius (Å)	0.54	0.62	0.65	0.80	0.26	0.39
Coordination site	Octahedral	Octahedral	Octahedral	Octahedral	Tetrahedral	Tetrahedral

169 Notes: GaCl₄⁻ and InCl₄⁻ belong to the tetrahedral coordination site. Modified from Amthauer et al.
 170 (1982) and Wood & Samson (2006).

171
 172 For a better understanding of the metal reaction in aqueous solution, the reaction for hydrolysis
 173 and complexation with ligands is shown below:

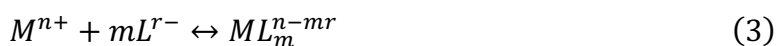
174 1) The hydrolysis reaction of these elements in aqueous medium is defined as:



176 And the equilibrium constant (K_a) is expressed as:

$$177 \quad K_a = \frac{[M_p(OH)_q^{np-q}][H^+]^q}{[M^{n+}]^p[H_2O]^q} \quad (2)$$

178 2) Except for hydroxide complexes, these elements also have different stabilities in
 179 combination with other inorganic ligands, such as fluoride, sulphate and phosphate,
 180 chloride, and bisulphide (Lu et al., 2017; Wood & Samson, 2006). The complex
 181 reaction of these elements with ligands could be written as:



183 And the equilibrium constant (K_b) is expressed as:

$$184 \quad K_b = \frac{[ML_m^{n-mr}]}{[M^{n+}][L^{r-}]^m} \quad (4)$$

185 Where M is metal, n is the relative metal ion charge ($n = 3$ for indium and gallium, $n = 4$ for
 186 germanium), and any ligand of L with ion charge of r .

187 Ionic charges and radii play an important role in metal-ligand complexation (Hofmann et al.,
 188 2020; Höll et al., 2007; Wood & Samson, 2006). Ga(III) ions form stable complexes with hard
 189 ligands such as hydroxide, fluoride, sulphate and phosphate, whereas they form weak
 190 complexes with soft ligands such as chloride and bisulphide (Supplementary Material Table
 191 S1). However, In(III) ion shows an affinity for both hard and soft ligands (hydroxide, fluoride,
 192 sulphate and phosphate, nitrate, chloride and bisulphide). Ge(IV) ion form stable complexes
 193 with hydroxide and fluoride, but limited experimental data for interactions with other ligands

due to limiting thermodynamic information and redox chemistry (Filella & May, 2023; Wood & Samson, 2006). However, the well-characterized Ge(IV) acid-base chemistry and the solubility of GeO₂ polymorphs provide insights into its reactivity, interactions, and potential applications (Filella & May, 2023).

In aquatic systems, indium, gallium, and germanium are present at exceedingly low concentrations (0.1 to 72 µg/L for gallium and 0.5 to 130 µg/L for germanium in continental and oceanic geothermal systems) (Wood & Samson, 2006). Their low solubility and difficulty in dissolving pose challenges for recovery methods. The hydrometallurgical and biohydrometallurgical routes for their recovery from WEEE face significant challenges due to their low solubility and the complex environment of non-target metals with high concentrations, such as aluminum, iron, and calcium.

2 End-of-life products as a secondary source for indium, gallium, and germanium

2.1 End-of-life products as a secondary source of indium

EoL products are considered to be a promising secondary source of indium (Lokanc et al., 2015). In the EU, total indium consumption is estimated at 64 tonnes per year from 2012 to 2016, with 60% of the total indium used in FPDs, mainly in the form of indium tin oxide (ITO). In addition, 11% and 9% of the consumption is used in solders and PVs, respectively, while the remaining 20% is used in thermal interface materials, batteries, alloys/compounds, and semiconductors & LEDs (Figure 1) (European Commission, 2020). This highlights the importance of considering EoL electronic products as a viable source of indium, particularly for FPDs.

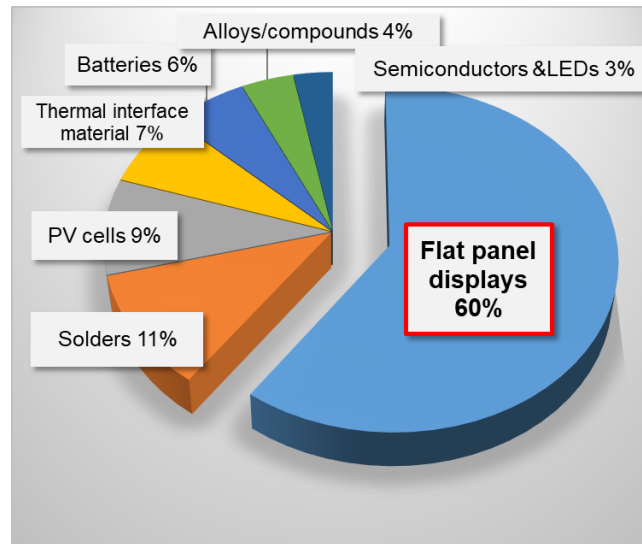


Figure 1 Main uses of indium in the EU. Modified from Critical Raw Materials Factsheets (European Commission, 2020).

Table 2 describes the various EoL products that could be used as secondary sources of indium. As mentioned above, indium is mainly used in FPDs containing ITO thin films. The ITO film consists of 80-90% indium oxide (In_2O_3) and 10-20% tin oxide (SnO_2) by weight (Fontana et al., 2015; Silveira et al., 2015). Ylä-Mella and Pongrácz (2016) reported that up to 80% of total global indium consumption is accounted for by ITO products, which are used in electronic devices such as smartphones, tablets, and televisions (Assefi et al., 2018). LCDs have the highest market share among FPDs and are gradually replacing the old cathode ray tube (CRT) devices because they are lighter and thinner than CRT devices (Zhang et al., 2017). The increasing use of LCDs and the frequent replacement of devices due to their relatively short lifespan (less than 10 years) has resulted in the generation of a significant amount of e-waste, which is typically disposed of in landfills (Lokanc et al., 2015). This is an issue of concern as spent LCDs contain a significant amount of indium, which is a valuable resource. Savvilotidou et al. (2015) reported that the concentration of indium in spent LCDs can reach up to 530 mg/kg. Therefore, collection and recycling of spent LCDs is essential for the recovery of indium. This approach could significantly reduce the reliance on primary sources of indium and help to mitigate the environmental impact of electronic waste.

Indium and gallium are key semiconductors required in the manufacture of photovoltaic systems used to generate electricity. Second-generation PV copper indium gallium selenide (CIGS) is a thin-film solar cell based on the copper indium selenide (CIS) family of chalcopyrite semiconductors. This technology is gaining popularity and replacing conventional

crystalline silicon modules due to their lower costs of materials, lower energy consumption, and thinner and higher stability (Licht et al., 2015).

Although the contribution of PV systems to the global indium demand is less than 2%, the output of the global production capacity of CIGS thin-film solar cell systems is expected to cover almost 30% of the total electricity demand (Bleiwas, 2010; Lv et al., 2019). Indium accumulation will start in 2035 and grow, reaching 1,500 tonnes in 2050 in the case of 60 TW scenarios, which is the maximum evaluated by the system for cumulative PV capacity (Gómez et al., 2023). Given this growing demand for indium, the recycling of indium from CIGS thin-film solar cells is expected to be crucial in the future.

The versatile use of indium in various electronic devices demonstrates its importance as a critical element for the electronics industry. Indium can also be found in LEDs in the form of indium gallium nitride (InGaN), indium arsenide (InAs), or indium gallium arsenide (InGaAs) (Ciacci et al., 2019; Zhan et al., 2020). LEDs typically exist as LED semiconductor chips and coloured LED lights (Ciacci et al., 2019). To improve the definition and brightness of LCDs, LED semiconductor chips are also used in the LCDs as screen backlighting, which requires an LED-backlit LCD. Currently, colored LED lights are used as lighting devices in homes, cars, instruments, and street-lighting due to their longer life and lower energy consumption than incandescent lamps (Nagy et al., 2017). Other electronic devices, such as DVDs, laser diodes, and printed circuit boards, also contain indium (Licht et al., 2015; Ylä-Mella and Pongrácz, 2016). With the increasing demand for electronics, the consumption of indium is expected to continue to grow.

In addition to LEDs and LCDs, indium is also found in batteries that contain indium incorporated in indium oxide and have better cyclability and longer cycle life than normal batteries (Nagao et al., 2012; Zhao et al., 2013). It has been reported that the cycle life of batteries with 0.02% In_2O_3 added to the negative active materials is more than four times that of batteries without In_2O_3 (Zhao et al., 2013). The consumption of batteries in the electronics industry is rapidly increasing due to the development of electronic products, such as mobile phones, laptops, recorders, and cameras (Sethurajan et al., 2019). However, the potential for indium recovery from spent batteries has not been fully explored compared to the recovery of other metals (i.e. cobalt and lithium) (Sethurajan et al., 2019; Wang et al., 2016). The recovery of indium could provide additional benefits to the battery recycling industry.

Products	Target metals	EoL products	Advantages
FPDs -LCDs	Indium tin oxide (ITO)	E-books, smartphones, tablets, TVs	Low power consumption, thinness, and light weightiness
PV -thin film solar cell	CuInGaSe (CIGS)/ CuInSe (CIS)	Rooftop and building integrated systems, concentrator photovoltaics, and photodetectors	Thinner, less costly, and highly stable
Semiconductors -LEDs	InGaN, InGaAs, InAs, GaAs, GaN, GaP	LED semiconductor chips on LCDs, LED lamps, and monitors	Longer lifespan and lower energy consumption than incandescent lamps
Semiconductors -Others	InP, InN, InGaN, In ₂ Se	DVDs, laser diodes, printed circuit boards	Higher electron velocity and diffusivity, lower base resistance
Batteries -Lithium-ion batterie	Indium thin film (In ₂ O ₃), GaAs, GaN, and GaTe	Mobile phones, laptops, recorders, cameras, nuclear and solar batteries	Good cyclability and longer cycle life
Integrated circuits	GaAs, GaN	PCBs of printers, mobile phones, and computers	Smaller, faster, and less expensive
Laser diodes	GaAs, GaN	DVD, CD, and Blu-ray players	Lasers produced range from infra-red to the UV spectrum
Optical fibers (OFs)	GeO ₂	Communication networks, sensors, and power transmission	Immune to electromagnetic interference compared with metal wires, lower optical losses with germanium than silicon
Infrared (IR) optics	Ge	Night vision systems, camera lenses, IR spectroscopy, military, active car safety systems, satellite systems, and fire alarms	Higher refractive index, transparency and optical uniformity, and low dispersion
Catalyst	GeO ₂	PET and synthetic textile fibers	Colorless by germanium compared with other catalysts, like titanium and antimony

Semiconductor in electronics and solar applications	Ge	Wireless devices, optical communication systems, hard disk drives, GPS, transistors, rectifiers, lasers, and photovoltaic solar cells	Higher speed and lower energy consumption compared with silicon
Catalysts and others	Ge	Catalysts in fluorescent lamps, diodes, transistors, and crystals of X-ray detectors	Germanium detectors are thicker than silicon detectors

2.1.1 LCDs as a secondary source of indium

In an LCD module, electrically conductive electrodes are located between two glass panels. These electrodes are mainly made of ITO. More specifically, the LCD unit is made up of 86.52 wt% glass, 12.81 wt% organic materials and approximately 0.02 wt% indium. Indium is located in the ITO layer, which is sandwiched between the two glass substrates (Ma and Xu, 2013). According to Savvilotidou et al. (2015), the thickness of the ITO layer is consistent and stable at approximately 150 nm, and the indium content is estimated to be more than 100 mg/kg. The lamination structure of the ITO layer of the LCD panel is shown in Figure 2.

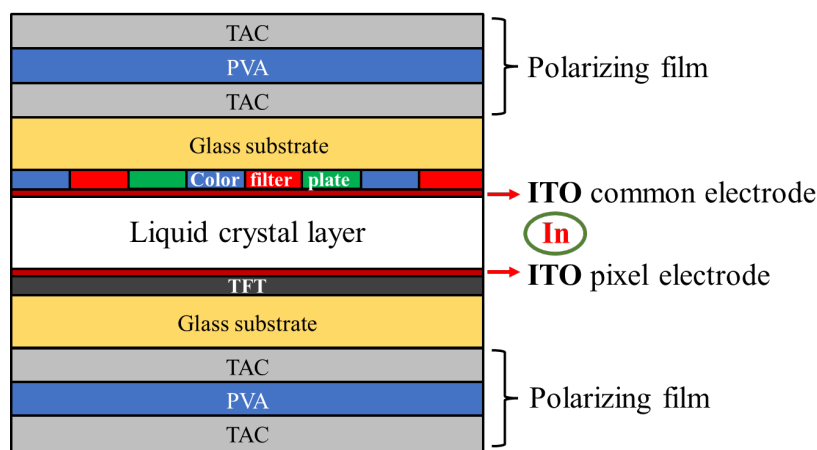


Figure 2 Lamination structure of the ITO layer from LCD panel. TAC: cellulose triacetate; PVA: polyvinyl alcohol; TFT: thin-film transistor; ITO: indium tin oxide. Modified from Dodson et al. (2012) and Křištofová et al. (2016).

2.2 End-of-life products as a secondary source of gallium

Although gallium is reported to be used in GaAs, InGaN, GaP, GaN, and GaSb semiconductors, the major consumption of gallium is reported for GaAs and GaN. GaAs has higher signal transmittance speed and semiconducting property. It also has higher saturation electron velocity and better radiation hardness than silicon due to its energy band structure in the electronics industry (Chen et al., 2011, 2012; Lee and Nam, 1998). The majority of gallium (almost 99%) is consumed in the form of GaAs and GaN, with 92% of gallium used for GaAs and 8% used for GaN in various EoL products such as integrated circuits, LEDs, laser diodes, PVs, and solar cells. In the EU, integrated circuits account for 70% of total gallium consumption, while lighting accounts for 25%, and CIGS solar cells account for almost 5% (Figure 3) (Chancerel et al., 2013; European Commission, 2020; Licht et al., 2015; Ueberschaar et al., 2017).

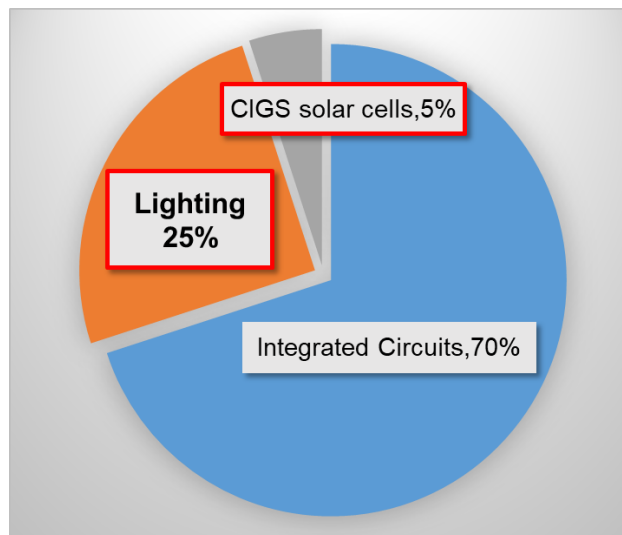


Figure 3 Main gallium used in the EU. Modified from Critical Raw Materials Factsheets (European Commission, 2020).

Table 2 provides information on potential sources of gallium from EoL products. This shows that integrated circuits are a significant source of gallium, as the metal is used in GaAs components, which offer superior performance compared to discrete circuits. Gallium is also present in the printed circuit boards (PCBs) of various electronic devices, including printers, mobile phones, computers, and other applications (Licht et al., 2015). Chancerel et al. (2013) indicate that gallium concentrations in PCBs can range from 2 mg/kg to 140 mg/kg. However,

the recovery of gallium from EoL products is limited due to the complexity of integrated circuit chips (Ueberschaar et al., 2017).

LEDs have become a popular choice in various applications, including lighting products and backlighting systems for televisions, monitors, and other devices, mainly due to their long lifespan and low energy consumption (Tan et al., 2009). The concentration of gallium in LEDs ranges from 248 to 690 mg/kg and is typically assembled as GaAs, GaN, InGaN, or GaP, depending on the type of LED (Chancerel et al., 2013; Nagy et al., 2017). Gallium is also used in the manufacture of laser diodes, with GaN and GaAs being the most commonly used materials. Laser diodes have a wide range of applications, such as in DVD, CD, and Blu-ray players (Chancerel et al., 2013). Gallium is also found in the production of indium photovoltaic systems, as described in Section 2.1, which are used in solar parks and buildings and supplied to consumers with related products (Schmidt et al., 2019).

Gallium compounds (GaTe_x , AsN, GaAs) are used in various batteries, such as secondary lithium batteries, nuclear batteries, and solar batteries (Hoang Huy et al., 2022). For example, gallium can improve the specific capacity, efficiency, cycling, and overcharge resistance of lithium batteries (Nishida et al., 1997; Patil et al., 2015). However, there is a lack of research into the recovery of gallium from lithium batteries.

2.2.1 LEDs as a secondary source of gallium

The LED industry produces various types of LED chips, such as GaN, GaAs, InGaN, and GaP. Waste from these materials contains indium and gallium, which can be recycled as a secondary source for the manufacture of related electrical and electronic equipment. However, LEDs also contain major and hazardous materials, including Fe, Cu, Al, Cr, Ni, Zn, Sn, Pb, Ba, and As (Nagy et al., 2017; Pourhossein & Mousavi, 2018; Swain et al., 2015a and 2015b). Therefore, the recycling process needs to carefully consider these factors.

Four common types of LEDs have been discussed, which offer essential data support that will help us better understand how to pre-treat these devices and find effective ways to concentrate the desired elements in future studies (Figure 4). The first type is a traditional dual in-line package (DIP) LED, also known as a "pill" or "bullet" due to its shape, which can be easily welded onto circuit boards. DIP LEDs are commonly used in accent tube lamps. The typical structure of DIP LEDs is shown in Figure 4 (a). The second type is surface mounted device (SMD) LEDs, which come in various shapes and sizes, such as SMD 3528 (size: 2.8×3.5 mm) and SMD 5050 (size: 5.0×5.0 mm), and are commonly used in strip lights for decoration, advertising, and backlighting. The basic structure of SMD LEDs is shown in Figure 4 (b). The

third type is chip-on-board (COB) LEDs, which consist of multiple diodes in a few individual modules. These LEDs are more advanced than DIP and SMD types and are used in street lighting and mobile phone cameras, as shown in Figure 4 (c). The final type is high-power (HP) LEDs, which can have an operating power of tens of watts (J/s). HP LEDs are designed for specific high lumen applications such as industrial facilities, mines, sports venues, and urban landscapes, as shown in Figure 4 (d).

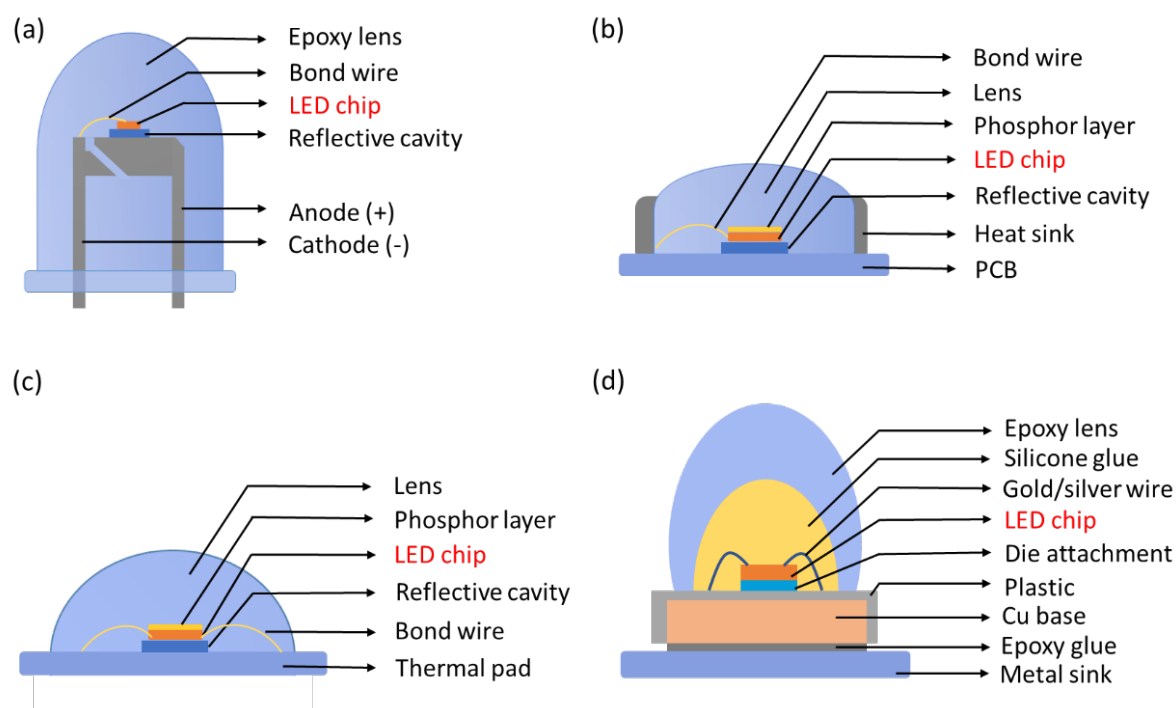


Figure 4 Schematic of four different types of LEDs: (a) DIP LEDs, (b) SMD LEDs, (c) COB LEDs, and (d) HP LEDs. Modified from Hamidnia et al. (2018), Pourhossein & Mousavi, (2018), and Tan et al. (2009).

The critical component of an LED is the LED chip, which is responsible for converting electricity into light with different colors and brightness levels according to the user's needs. The LED chip is made up of three different layers that are connected to two electrodes (anode and cathode) and grown on a substrate, such as sapphire (Al_2O_3), as shown in Supplementary Material Figure S1. The LED chip utilizes materials such as GaN, GaAs, AlGaInP, or InGaN in its layers. These materials facilitate the generation of light emission when combined with electrons and holes (Hamidnia et al., 2018; Pimputkar et al., 2009; Tan et al., 2009; Yam & Hassan, 2005; Zhan et al., 2015).

2.2.2 PVs as a secondary source of gallium

Photovoltaics (PVs), or solar cells, have become increasingly popular due to their low-emission properties in response to the global warming problem (Amato and Beolchini, 2019). Second-generation thin-film photovoltaics, including CIGS ($\text{CuIn}_x\text{Ga}_{(1-x)}\text{Se}_2$) PVs and GaAs PVs, have replaced first-generation Si-based technology due to their superior performance and high efficiency. While second-generation PVs currently account for only 10% of total PV electricity production and 2% of CIGS PVs in 2017, they are expected to grow in popularity (Ma et al., 2020; Schmidt et al., 2019). For example, gallium and indium are predicted to increase to 15-20% and 15%, respectively, in CIGS PVs in the near future, and it has been reported that gallium and indium may contain high concentrations in spent CIGS PVs, 530 mg/kg and 2,900 mg/kg, respectively (Gu et al., 2018). Therefore, from a long-term perspective, it is important to recover these valuable elements from spent PVs, even if the retirement period of PVs has not yet been reached (which is expected to be about 25 years) (Lv et al., 2019; Ma et al., 2020; Savvilotidou and Gidarakos, 2020).

Supplementary Material Figure S2 presents the schematic structure of CIGS PV and GaAs PV. The layers include the back contact layer (often molybdenum), an absorber layer $\text{CuIn}_x\text{Ga}_{(1-x)}\text{Se}_2$ or CuInSe (CIS), a buffer layer (like CdS or emerging materials), and a window layer (primarily ZnO with a multilayer antireflective coating) (Polman et al., 2016; Schmidt et al., 2019; Tang, 2017). GaAs PVs share a similar structure, with n-type GaAs and p-type $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ layers surrounded by AlInP windows for protection (Kim et al., 2022; Polman et al., 2016). This information provides essential insights for dismantling devices and concentrating desired elements in future studies.

2.3 End-of-life products as a secondary source of germanium

EoL products can be a secondary source of germanium, as shown by studies on the global distribution of EoL products in Figure 5. From 2012 to 2016, a total of 122.6 tonnes of germanium was supplied for manufacturing. The EU accounted for 32% of total germanium consumption, with 38.7 tonnes used for three main manufacturing applications: 47% for infrared optics, 40% for optical fibers, and 13% for satellite solar cells (European Commission, 2020). Furthermore, in the United States, optical fibers accounted for 40% of germanium use, followed by 30% in infrared optics, 20% in electronics and solar applications, and 10% in other uses, where germanium is not used in polymerization catalysts (Chen et al., 2018b; Rosenberg, 2009).

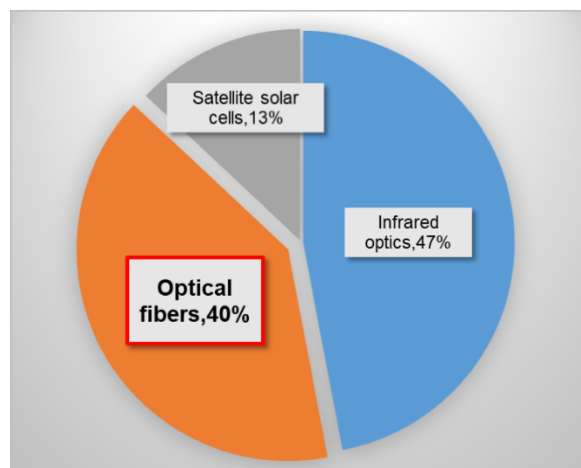


Figure 5 Main uses of germanium in the EU. Modified from Critical Raw Materials Factsheets (European Commission, 2020).

Table 2 shows that the EoL products could be used as a secondary source of germanium. OFs contain various types of flexible and transparent fibers, which typically contain a core surrounded by transparent cladding to transmit the information as light pulses (Rosenberg, 2009). OFs are an important source of germanium because they contain germanium oxide (GeO_2) as a dopant to prevent electromagnetic interference, light absorption, and optical losses. Germanium is used because it has similar atomic and ionic radii compared to SiO_2 , which helps to modify the refractive index and achieve lower optical losses (Licht et al., 2015; Rosenberg, 2009). OFs are used as a medium for communication, sensing, and power transmission (Gunn, 2014). The concentration of germanium in spent OFs can be as high as 1,100 mg/kg (Ruiz et al., 2018).

Infrared (IR) optics also contain germanium due to its higher refractive index, transparency and optical uniformity, and low dispersion (Gunn, 2014; Rosenberg, 2009). GeCl_4 is used in the fields of night vision systems, optical instruments, IR spectroscopy, IR detectors, active vehicle safety systems, satellite systems, and fire alarms (Gunn, 2014; Nguyen & Lee, 2021).

Germanium is also used as a catalyst in polymerization, mainly in the production of polyethylene terephthalate (PET) and synthetic textile fibers production. GeO_2 is incorporated into PET products to produce colourless final product compared to other catalysts, such as titanium and antimony (Gunn, 2014).

In electronics and solar applications, germanium is used as a semiconductor and applied for germanium-based wafers are used in wireless devices, optical communication systems, hard disk drives, GPS, transistors, rectifiers, lasers, and space-based PV solar cells (Gunn, 2014; Licht et al., 2015; Rosenberg, 2009).

Germanium semiconductors have higher speed and lower energy consumption than silicon semiconductors, making them an attractive option for optoelectronic and electronic applications. Germanium is also used as a catalyst in fluorescent lamps, diodes, and transistors, and as a crystal in X-ray detectors, which are thicker and more sensitive than silicon detectors (Gunn, 2014; Rosenberg, 2009).

In summary, OFs, which account for 40% of total germanium consumption in the EU, contain a higher concentration of germanium and are easier to collect and pre-treat than other germanium-containing EoL products. Therefore, several studies have described the recovery of germanium from OFs.

2.3.1 OFs as a secondary source of germanium

Supplementary Material Figure S3 shows the typical structure of OFs, which are a potential source of germanium as they contain a small amount of germanium in their core. The core of OFs consists of pure silica glass with GeO_2 added as a dopant to improve the optical properties (European Commission, 2020; Nguyen & Lee, 2021). OFs consist of fiber bundle tubes, reinforcements, and plastic sheaths, with the fiber bundle tubes consisting of acrylic resin coating and fiber optic (Zhang et al., 2019). X-ray fluorescence (XRF) analyses have shown that OFs contain 99% silicon and less than 1% germanium (Chen et al., 2020; Zhang et al., 2019). However, the concentration of germanium ($> 1000 \text{ mg/kg}$) in OFs can be higher than that in primary sources such as coal and sulfide ores. Therefore, OFs are a potential secondary source of germanium, and several studies have focused on the recovery of germanium from spent OFs (Chen et al., 2017; Ruiz et al., 2018).

3 The recovery of indium, gallium, and germanium from end-of-life products

The recovery of indium, gallium, and germanium from EoL products is currently carried out using different technologies such as pyrometallurgy, hydrometallurgy, and biohydrometallurgy. Pyrometallurgy, which operates at high temperatures and generates high energy costs and toxic gas emissions, is not discussed in this review (Savvilotidou et al., 2015). However, hydrometallurgical and biohydrometallurgical technologies, which are considered to have better performance, have been reviewed in detail.

The hydrometallurgical approach is probably one of the most advanced ways to recover indium, gallium, and germanium from EoL products because this process has the advantages of being versatile, flexible, and highly efficient (Akcil et al., 2019; Sethurajan et al., 2019). In this

process, the target products are leached after e-waste pre-treatment with mineral and organic acids, followed by selective recovery of dissolved TCEs from generated leachates by solvent extraction, solid phase extraction, precipitation, cementation, electrochemical separation/electrowinning, or supercritical fluid extraction. However, due to the stringent conditions generated during leaching, highly complex leaching solutions in terms of elemental composition require multiple purification steps to remove unwanted elements, such as iron, among others prior to any selective recovery of the target elements (Erüst et al., 2013; Nancharaiah et al., 2016; Sethurajan et al., 2018; Yu et al., 2020).

The influencing parameters for indium, gallium, and germanium recovery are discussed in the present paper. In the leaching process, the most important influencing parameters are pH, the selection and concentration of leaching agent(s), the ratio of solid e-waste samples to liquid in the leaching system, the particle size fraction of samples, reaction time, temperature, and agitation rate (Akcil et al., 2019; Chen et al., 2017; de Oliveira et al., 2021; Fontana et al., 2020; Mir et al., 2022; Tao et al., 2021). Thoughtful optimization of these parameters can exert a profound influence on the dissolution and leaching yields of indium, gallium, and germanium. For instance, a more acidic leaching system has been found to achieve higher indium leaching yields. Similarly, smaller particle sizes, higher leachant concentrations, longer reaction times, and elevated temperatures have shown favourable effects. However, it is essential to conduct preliminary tests with complex pre-treated e-waste samples as different parameters may interact differently. The establishment of optimal conditions often requires a combination of various favourable parameters. In contrast, in the recovery process, factors influencing extraction efficiency include the choice of extracting agents, metal ion concentration in the leaching solution, extraction temperature and duration, and the distribution ratio between phases (Akcil et al., 2019; Chen et al., 2017; de Oliveira et al., 2021; Fontana et al., 2020; Mir et al., 2022; Tao et al., 2021). Proper optimization of these factors is also crucial for effectively recovering indium, gallium, and germanium from the leaching solution. The determination of optimal conditions may vary depending on the specific e-waste leachate composition, necessitating also to perform preliminary tests with different parameter combinations.

The biohydrometallurgical approach uses microorganisms to convert insoluble TCEs into their dissolved forms and then selectively recover soluble metal ions from leachates (Nancharaiah et al., 2016). The bioleaching process can take place via the acidolysis, complexolysis, or redoxolysis processes. The biorecovery process, such as bioprecipitation, biosorption, bioreduction, or bioaccumulation, have been widely used to recover target metals from dilute solutions (Nancharaiah et al., 2016; Sethurajan et al., 2018). The key influential parameters include microbial activity and adaptation, environmental conditions (i.e. pH and temperature),

and substrate concentration (i.e. minerals and nutrients). These kinetic factors determine the recovery rates of target metals. In recent years, biohydrometallurgy has been considered as a promising and green technique to recover and recycle TCEs from e-waste due to its superior value of selectivity, friendly environment, cost-effectiveness, and non-toxic reagents (Dodson et al., 2012; Işıldar et al., 2019; Sethurajan et al., 2018). However, the development of biohydrometallurgy protocols to recycle TCEs from EoL products such as LCDs, LEDs, PVs, and OFs is still in its infancy and requires in-depth attention before full-scale implementation.

3.1 Kinetic study

In the process of recovering indium, gallium, and germanium from EoL products, various hydrometallurgical recovery approaches are utilized. These methods include complex chemical reactions and mass transfer processes. This part aims to provide illustrations of leaching and recovery methods to explore their principles and emphasize the significance of kinetic studies. The biohydrometallurgical routes are not addressed here, as specific explanations will be provided in the sections “Indium/Gallium bioleaching” and “Indium/Gallium biorecovery”.

3.1.1 Kinetic studies of the leaching step

Strong acids such as hydrochloric acid, sulfuric acid, and mixed strong acids are commonly utilized for the purpose of dissolving indium, gallium, and germanium from EoL products into solution via an acidolysis process (Chen et al., 2018b; Gabriel et al., 2020; Hu et al., 2014; Maarefvand et al., 2020). Furthermore, the addition of catalysts such as oxidants like MnO_2 and H_2O_2 has been shown to accelerate reactions and enhance dissolution efficiency via a redoxolysis process (Swain et al., 2016a; Zeng et al., 2015; Zhang et al., 2021). The mechanism of strong acid leaching involves the dissolution of metal ions within an acidic environment facilitated by H^+ ions. Additionally, hydrofluoric acid is working for the dissolution of germanium from silicate glass matrices (W. Chen et al., 2017).

Organic acids such as oxalic acid are also utilized for the recovery of indium and gallium via a complexolysis process. These organic acids can be involved in chelation reactions with metal ions, forming soluble complexes (Cui et al., 2019). For instance, indium ions (In^{3+}) can form complexes with carboxyl groups in oxalic acid, resulting in complexation. The higher solubility of these complexes allows for the transfer of indium ions from e-waste to the solution.

In these leaching processes, the significance of kinetic studies lies in the profound comprehension of reaction rates and mechanisms. This understanding helps in optimizing operational conditions, thus enhancing metal recovery rates and purity. By regulating reaction

conditions such as acid concentration, reaction temperature, solid-liquid ratio, particle size of samples, reaction and agitation time, and catalysts, more efficient transformations and dissolution of metal ions can be achieved. Moreover, kinetic studies contribute to a deeper understanding of the interaction between strong mineral and organic acids with metal ions, ultimately leading to improved recovery efficiency.

3.1.2 Kinetic studies of the recovery step

In solvent extraction methods, the transfer of substances between organic and aqueous phases relies on chelation reactions between extractants and metal ions. For instance, bis(2-ethylhexyl) phosphoric acid as an organic phase extractant can engage in chelation reactions with indium ions, forming complexes (Gupta et al., 2007; Virolainen et al., 2011; J. Yang et al., 2013). Kinetic studies examine the coordination of the extractant with metal ions and the rates of chelation reactions. Subsequently, stripping involving the use of strong acids such as HCl can redissolve metal ions previously complexed in the organic phase, facilitating the purification and refinement of indium.

Ionic liquid extraction methods employ ionic liquids as the organic phase to form chelation complexes with metal ions, achieving separation and extraction. For instance, phosphonium ionic liquid (i.e. Cyphos IL 104) can form complexes with indium ions (Dhiman & Gupta, 2020). Kinetic studies focus on the structure of ionic liquids and the rates of chelation reactions with metal ions. The stripping process similarly employs strong acids (i.e. HCl) to dissolve metal ions from previously formed complexes in the organic phase, enabling further purification.

Solid-phase extraction (ion exchange) employs ion exchange resins with specific functional groups to adsorb and separate metal ions. For instance, Amberlite™ resin can adsorb indium ions, and kinetic studies centred around adsorption rates and resin performance (Ferella et al., 2016). The stripping process similarly employs strong acids (i.e. H₂SO₄) to dissociate indium ions from the resin, laying the foundation for subsequent purification steps.

Precipitation methods rely on chemical reactions to generate hydroxide precipitates for metal ion recovery. Adjusting pH using NH₄OH and precipitate Na₂S, for instance, can lead to indium precipitation (Fang et al., 2019; Hu et al., 2014; Silveira et al., 2015). Kinetic studies focus on precipitation rates and the effects of conditions. In this process, metal ions combine with hydroxide ions and sulfide ions to form solid precipitates, which can be obtained through filtration or precipitation separation techniques.

555 Additionally, cementation is a chemical process involving the deposition of one metal onto the
556 surface of another metal to achieve separation and extraction. Through contact with zinc
557 powder, indium ions undergo reduction reactions, successfully recovering indium (Rocchetti
558 et al., 2016). Kinetic studies observe reduction rates and reaction mechanisms. This process
559 involves the reduction and deposition of metal ions on a metal surface, with kinetic studies
560 contributing to the optimization of operational conditions for enhanced recovery efficiency.

561 Electrowinning involves the reduction of metal ions to metal through electrochemical reactions,
562 generating metal precipitates in the electrolyte. Indium ion recovery, for example, can be
563 achieved through low-current electrolysis (D. Choi et al., 2014). Kinetic studies focus on
564 electrolysis rates and electrode reaction mechanisms. During electrolysis, metal ions are
565 reduced to metal on the electrode surface, forming solid deposits and thus enabling successful
566 recovery.

567 Supercritical fluid separation leverages the properties of supercritical fluids to separate and
568 extract target substances from solid samples or liquid mixtures (Argenta et al., 2017; Zhan et
569 al., 2020). The combination of supercritical CO₂ and co-solvents has been demonstrated to
570 enhance the efficiency of recovery reaction kinetics, aiding in the transformation of indium
571 from a solid state to a soluble ionic state (Argenta et al., 2017). Kinetic studies emphasize the
572 solubility of supercritical fluids and the rates of chelation reactions. Under supercritical
573 conditions, fluid density, and solubility change with variations in temperature and pressure,
574 and kinetic studies contribute to a better understanding of these influencing factors.

575 Through these specific recovery method examples, we gain deeper insights into the principles
576 and kinetic characteristics of each technique, thereby providing more precise guidance and
577 understanding for optimizing the recovery process. These kinetic studies not only uncover the
578 behavior of metal ions in different methods but also provide robust scientific foundations for
579 achieving efficient metal recovery. Simultaneously, these studies offer crucial clues for
580 controlling operational conditions, enhancing recovery rates, and ensuring purity.

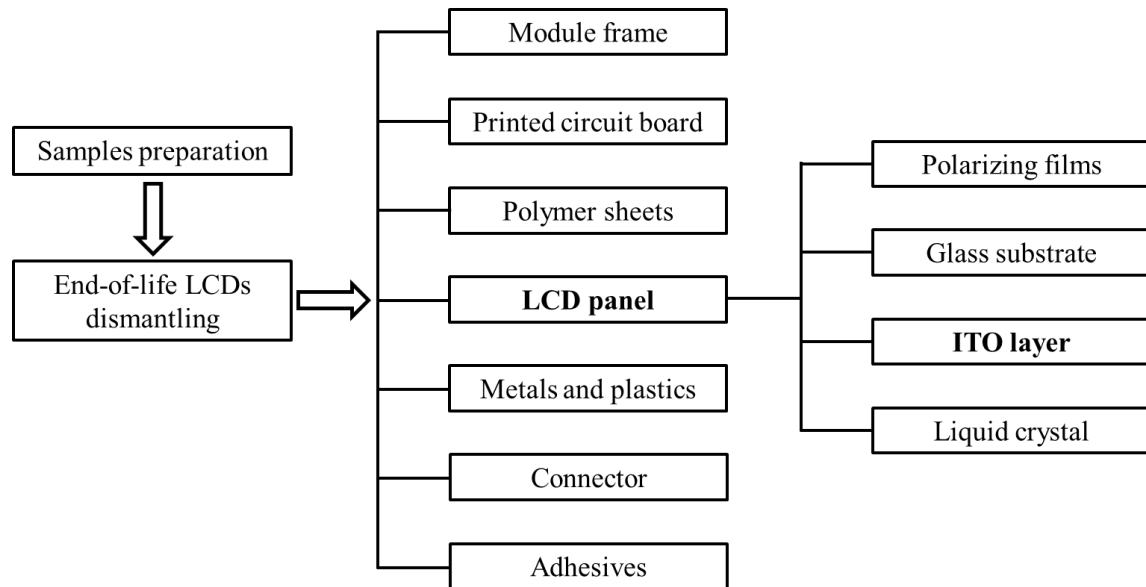
581 **3.2 Indium recovery from EoL LCDs via hydrometallurgical and biohydrometallurgical** 582 **routes**

583 **3.2.1 Pre-treatment of EoL LCDs**

584 **3.2.1.1 Manual dismantling of LCDs to access the ITO film**

585 Pre-treatment of end-of-life LCDs involves dismantling and separating valuable parts, such as
586 the LCD panel, from other parts, such as the module frame, printed circuit board, polymer

587 sheets, metal and plastics, connectors, and adhesives. The first step is to manually disassemble
 588 the LCDs to access the ITO film layer (Figure 6).



592 Figure 6 Manual dismantling of spent LCDs

594 3.2.1.2 Removing polarizing films and liquid crystals

595 After manual disassembly, polarizing films and liquid crystals should be removed from the
 596 LCD panel in the next pre-treatment step (Cui et al., 2020; Danilo Fontana et al., 2015).
 597 Polarizing films generally consist of a layer of iodine-doped polyvinyl-alcohol (PVA)
 598 sandwiched between two protective layers of cellulose triacetate (TAC) (Dodson et al., 2012).
 599 In addition, the removal of organic materials of PVA and TAC from LCD panels is required
 600 for more efficient grinding of LCD panels (Silveira et al., 2015). Therefore, thermal and
 601 chemical treatments were tested to remove polarizing films from previous studies, as shown in
 602 Table 3.

603 The optimal method for removing polarizing films is thermal treatment (Ferella et al., 2016;
 604 Fontana et al., 2015; Lee et al., 2013; Li et al., 2009; López-Yáñez et al., 2019; Savvilotidou
 605 et al., 2015). As detailed in Ferella's study, thermal treatment with liquid nitrogen does not
 606 damage the surface of LCD glass, and liquid crystals are cleaned using ultrasound (Ferella et
 607 al., 2016; Fontana et al., 2015). In addition, Li et al. (2009) reported that thermal shock at 230-

240 °C could be used to remove up to 90 wt% of the polarizing film. Ultrasonic treatment was then used to remove liquid crystals (10 min of 40 kHz (P = 40W)).

Based on the energy consumption and pollutant emission of thermal treatment, chemical treatment has also been proposed to remove polarizing films and liquid crystals (Cui et al., 2020; Fontana et al., 2015; Silveira et al., 2015; Wei et al., 2016). Without heating, a longer treatment time (i.e. 20 h) is required to remove polarizing films with acetone (Silveira et al., 2015). Acetone in a hot water bath of 80-100 °C can reduce the reaction time to 35 min (Cui et al., 2020).

Savvilitidou et al. (2015) used a combination of thermal and chemical treatments to remove the polarizing films by implementing a thermal shock at 200 °C. It was observed that the polarizing film started to soften and bulge after 7 min, after which the glue and liquid crystals remaining on the panel were removed by acetone liquid. Since acetone is considered toxic, the polarizing films can be removed manually, but this task is time-consuming (Li et al., 2020; Zhang et al., 2017). It may not be necessary to remove the polarizing films prior to hydrometallurgical leaching (Assefi et al., 2018; Gabriel et al., 2020; Upadhyay et al., 2021). However, it is better to remove polarizing films and liquid crystals for biohydrometallurgy due to their physiological toxicity for microorganisms (Cui et al., 2020). Therefore, thermal treatment combined with ultrasound and acetone should be considered as a pre-treatment to remove polarizing films and liquid crystals from waste LCDs.

Table 3 The common methods of removing polarizing films and liquid crystals from spent LCD panels

Method	For polarizing films	For liquid crystals	Time	Reference
Thermal treatment	Liquid nitrogen	Ultrasonic treatment 35 kHz	10-20 min	(Fontana et al., 2015)
	230-240 °C	Ultrasonic treatment 40 kHz		(Li et al., 2009)
Chemical treatment	Acetone	Acetone	20 h	(Silveira et al., 2015)
	Water bath of 80-100 °C for 5-20 min and then acetone bath for 30 min		Total 35-50 min	(Cui et al., 2020)
Thermal and chemical	Thermal shock 200 °C for 7 min and then soaking in acetone		> 7 min	(Savvilitidou et al., 2015)
Others	Manually peeled	Acetone with 4 h	> 4 h	(Zhang et al., 2017)
	Manually peeled	Without treatment		(Li et al., 2020)

3.2.1.3 Comminution of LCD panels to obtain powder samples

Comminution methods of spent LCD panels reported in the literature over the last decade are described in Table 4. In general, LCD panels are manually crushed to produce small pieces (3-5 cm) that are easily ground into powder by mills (Gabriel et al., 2018, 2020; Jowkar et al., 2018). The traditional method is ball milling, which has been studied by many researchers who have investigated different parameters such as temperature and grinding time (Dhiman & Gupta, 2020; Ferella et al., 2016; Gabriel et al., 2020; Jowkar et al., 2018; Silveira et al., 2015; Yen et al. 2016). Silveira et al. (2015) compared three mills and found that a porcelain ball mill was optimal for obtaining small particle sizes (average 150 μm) in 120 min with minimal material loss (0.18 wt%) compared to knife and hammer mills. Other mills, such as cutting mills, blade mills, planetary ball mills, ring mills, and rod mills can also be used. Ferella et al. (2016) found that the rod mill was a good option to achieve a 52 wt% finest fraction (average 212 μm) with the highest indium concentration in 30 min. Yen et al. (2016) found that planetary ball milling for 120 min at 300 rpm was required to achieve a particle size of about 96 μm , while Assefi et al. (2018) found that the ring mill could grind LCDs to powder with a particle size of 10 μm within 1 min after grinding with a guillotine blade.

For a more efficient method, high-energy ball milling in a planetary ball mill with a jar and 5 mm balls made of ZrO_2 is performed within a short time of 1 min, obtaining LCD powder with a minimum particle size of 7.5 μm (Lee et al., 2013; Qin et al., 2021; Zeng et al., 2015). The LCD panel can also be crushed by a multi-function disintegrator at 31,000 rpm and achieve a particle size of 250 μm , saving time up to 10 min (Xie et al., 2019). A high-speed crushing shear is used to crush LCD panels for a short time of 5 min and achieve a smaller particle size (< 75 μm) (Luo et al., 2019). These grinding methods significantly reduced the working time. After obtaining the finer particle powder, the ground samples were dried in a vacuum oven (the temperature range of 60-110 $^{\circ}\text{C}$) until a constant weight was reached (Ferella et al., 2016; Xie et al., 2019).

Method	Operative parameters	Time	Particle size (μm)	References
Ball milling		4 h	< 37	(Jowkar et al., 2018)
Ball milling	Porcelain ball mill with 60 rpm	2 h	150	(Silveira et al., 2015)
Ball milling	Alumina ball with polarizing films	4 h	< 5	(Gabriel et al., 2020)
Ball milling	Rod ball with wet condition (water)	0.5 h	< 212 of 52 wt%	(Ferella et al., 2016)
Ball milling	Planetary ball mill with 300 rpm	2 h	96	(Yen et al., 2016)
Ring mill		1 min	10	(Assefi et al., 2018)
High energy ball milling	Planetary mill with a jar and balls of 5 mm size made of ZrO_2	1 min	7.5	(Lee et al., 2013)
High energy ball milling	Planetary mill with a jar and balls of 5 mm size made of ZrO_2	0.5 h	< 75 of 97.6 wt%	(Qin et al., 2021)
Multi-function disintegrator	31,000 rpm	10 min	250	(Xie et al., 2019)
High-speed crushing shear		5 min	< 75	(Luo et al., 2019)

659

660 3.2.1.4 Characterization methods of LCD samples

661 The collected LCD treated samples can be characterized using various qualitative and
662 quantitative methods (Table 5). X-ray diffraction (XRD) helps to identify the crystalline
663 mineral phases (Li et al., 2020; Luo et al., 2019; Zhang and Xu, 2016). Scanning electron
664 microscope (SEM) analyzes the surface structure and morphology (Cadore et al., 2019; Cui et
665 al., 2019; Li et al., 2020; Luo et al., 2019). Energy dispersive X-ray fluorescence spectrometer
666 (EDX) and energy dispersive spectrometer (EDS) analyze elemental composition (Maarefvand
667 et al., 2020; Yang et al., 2013), as well as X-ray fluorescence (XRF) analyses, provide
668 elemental compositions information (Ferella et al., 2016; Gabriel et al., 2020; Silveira et al.,
669 2015; Zeng et al., 2015). Field emission scanning electron microscopy (FE-SEM) and laser
670 light diffraction analyze the particle size of samples (Dhiman & Gupta, 2020; Gabriel et al.,
671 2020). X-ray photoelectron spectroscopy (XPS) analyzes binding energy and intensity (D. Choi
672 et al., 2014; Cui et al., 2019; Krishna Rama et al., 2015). Laser-induced breakdown

spectroscopy (LIBS) spectra and the parallel factor analysis (PARAFAC) model characterize different elements (Castro et al., 2020). Instrumental Neutron Activation Analysis (INAA) detects the concentration of metals in solid samples (Andrade et al., 2019). Brunauer-Emmett-Teller (BET) theory gives the surface area of LCD powder according to gas sorption (Lee et al., 2013).

Various methods have been employed to determine the precise concentration of different elements in solid WEEE samples, including the common use of strong acids like aqua regia. However, the analysis of WEEE demands suitable reference materials, which has been addressed by Andrade et al. (2019) for printed circuit boards using dilute aqua regia (50% v/v) with 1/100 of S/L ratio in the microwave system at 240 °C. Nonetheless, the application of this method to LCDs is limited due to their different composition. Consequently, current characterization techniques lack accuracy for the wide range of elements present in LCD waste, necessitating the development of specialized techniques. Overcoming this limitation is crucial for advancing our understanding of elemental composition and enhancing e-waste recycling. In this context, further research and innovation are required to address these challenges.

Microwave plasma-atomic emission spectrometer (MP-AES), inductively coupled plasma-optical emission spectrometer (ICP-OES), and inductively coupled plasma mass spectrometry (ICP-MS) are then used to detect the concentration of metals in the leachate (Akcil et al., 2019; Assefi et al., 2018; Cui et al., 2019; Yen et al., 2016; Zeng et al., 2015; Zhang et al., 2015).

693 Table 5 Characterization for pre-treatment of spent LCDs

E-waste	Characterization methods	Major elements	Reference
LCD screens	Alkaline fusion and analyzed by ICP-OES, XRD, and SEM	Sr, Co, Zn, Fe, Cu, and Ni	(Jowkar et al., 2018)
LCD screens	HNO ₃ -HCl-HF-H ₂ O ₂ (3:1:1:1, v/v) mixture digestion and analyzed by ICP-OES		(Xie et al., 2019)
Discarded LCD screens	Aqua regia method digestion and analyzed by MP-AES, FE-SEM, EDX, and XRD	Sn, Zn, Fe, Al, Mn, Ca, and Sr	(Dhiman and Gupta, 2020)
LCDs	Mixed acids (HNO ₃ , HCl) digestion and analyzed by ICP-MS		(Savvilotidou et al., 2015)
LCD screens of discarded cell phones	Aqua regia digestion, XRF, SEM and EDS	Si, Sr, Ca, Al, Ba, Sb, and Sn	(Silveira et al., 2015)
LCD panel glass	Aqua regia digestion and analyzed by ICP-OES, SEM, and EDX	Al, Fe, Zn, Sn, Mg, Ni	(Yang et al., 2013)
LCD monitors	XRF and laser light diffraction	Si, Al, Ca, As, K, Sn	(Gabriel et al., 2020)
LCD glass	XRF, XRD, SEM, EDS, FTIR, and ICP-AES	Si, Al, Ba, Sr, Ca, Fe, Mg	(Zeng et al., 2015)
LCD panels	SEM, XRD, XPS, XRF, and ICP-OES	Si, Al, B, Ca, Sr, Fe, Mg, Ba, Sn, Cr, Na, K and Cu	(Cui et al., 2019)
LCDs	SEM and XRD	Al	(Luo et al., 2019)

694

695 3.2.2 Indium leaching from EoL LCDs via hydrometallurgical and 696 biohydrometallurgical routes

697 Table 6 summarizes the techniques for indium leaching from spent LCDs using
698 hydrometallurgy and biohydrometallurgy as reported in the literature. In general, single strong
699 mineral acids, such as HCl, H₂SO₄, and HNO₃, are commonly used to leach elements from solid
700 samples (Ferella et al., 2016; Fontana et al., 2015; Gabriel et al., 2020; Pereira et al., 2018; Qin
701 et al., 2021; Silveira et al., 2015). The mixture of strong mineral acids has also been tested with
702 different concentration ratios and temperatures (Assefi et al., 2018; Lee et al., 2013; Li et al.,
703 2009; Savvilotidou et al., 2015). Organic acids, produced by microorganisms, including
704 bacteria and fungi from organic waste streams, have been reported as promising for the
705 recovery of indium from spent LCDs compared to conventional inorganic acids (Argenta et al.,
706 2017; Cui et al., 2019; Li et al., 2020; López-Yáñez et al., 2019). Oxidizing and reducing
707 chemical agents (i.e. H₂O₂ and MnO₂ as oxidants, and N₂H₄ as reductant) have been considered

in the mineral acid leaching process to increase the leaching reaction rate and improve the leaching yield of target metals (Dhiman & Gupta, 2020; López-Yáñez et al., 2019; Swain et al., 2016a; Zeng et al., 2015). Nevertheless, the recovery of target metals from leachates generated by strong inorganic acids or organic acids is complicated because many major elements have been dissolved in the low pH leachates. Therefore, selective leaching, such as bioleaching, produces less complex solutions that facilitate selective recovery steps (purification and separation) (Jowkar et al., 2018; Xie et al., 2019; Yang et al., 2013)

Table 6 Methods for indium leaching and bioleaching from spent LCDs

E-waste	Total In content (mg/kg)	Leachant	Optimum conditions (S/L: g/mL)	Leaching yield (%)	Other metals	Reference
Mineral acid leaching process						
LCD monitors	300	6 M HCl 0.5 M H ₂ SO ₄ 4 M HNO ₃	60 °C, 4 h; Room temperature, 2 h; 4 M HNO ₃ , 60 °C, 4 h	99.3% 98.2% 87%	Si, Al, Ca, As, K, and Sn	(Gabriel et al., 2020)
LCD glass	260	6 M HCl	1/3 of S/L, 25 °C, without shredding, 6 h	90%	Sn, Al, and Cr	(Fontana et al., 2015)
LCDs (non-crushing)	120	0.8 M HCl	300 W ultrasonic waves at room temperature, 1 h	96.8%	Al, Fe, In, Ca, Mg, Sr, and Mo	(Zhang et al., 2017)
LCDs	330	3 M HCl	1/2 of S/L, 0.5 h	70%	Al, Ca, Fe, Zn and Cu	(Yen et al., 2016)
LCDs of mobile phone		1 M H ₂ SO ₄	1/20 of S/L, 90 °C, 500 rpm agitation, 1 h	96.7%	Sn	(Pereira et al., 2018)
LCD panels		1 M H ₂ SO ₄	1/10 of S/L, 80 °C, 3 h,	100%	Al, Si, Fe, Sn, Zn, and Cr	(Ferella et al., 2016)
LCD screens of cell phones	0.614% (XRF)	1 M H ₂ SO ₄	1/50 of S/L, 90 °C, 500 rpm agitation, 1 h	96.4%	Si, Sr, Ca, Al, Ba, Sb, and Sn	(Silveira et al., 2015)
LCD panels	100	2 M H ₂ SO ₄	1/5 of S/L, 80 °C, 10 min	50%-90%	Al, Ca, Fe, Mn, Mo, and Sn	(Rocchetti et al., 2015)

LCDs	530	3:2 of HCl: H ₂ O	1/5 of S/L, 80 °C, mild agitation, 1 h	60%	As and Sb	(Savvilitid ou et al., 2015)
LCD panels	261	45:5:50 of 38% HCl:69% HNO ₃ :H ₂ O	1/1 of S/L, 0.5 h	86%	Sn	(Lee et al., 2013)
LCD panels	156	0.4 M H ₂ SO ₄	1/2 of S/L, 70 °C, 0.5 h	99.5%		(Houssaine Moutiy et al., 2020)
LCD panels	30	Aqua regia of 3 M HCl and 0.5 M HNO ₃	1/1 of S/L, 70 °C, ultrasonic wave, 0.5 h	99.5%		(Assefi et al., 2018)
Discarde d LCD screens		3 M HCl with oxidant 30 % H ₂ O ₂	75 °C, 400 rpm agitation, 2 h	98.7%	Sn, Zn, Fe, Al, Mn, Ca, and Sr	(Dhiman and Gupta, 2020)
LCD glass		5 M HCl with oxidant 10 % H ₂ O ₂	1/2 of S/L, 75 °C, 400 rpm agitation, 2 h	44%	Sn	(Swain et al., 2016a)
LCD glass	In ₂ O ₃ 0.057% (XRF)	3 M HNO ₃ with oxidant 1 g MnO ₂	3/1000 of S/L, 50 °C with particle size < 75 µm, 3 h	92.6%	Si, Al, Ba, Ca, Fe, Mg, Cr, As and Ni	(Zeng et al., 2015)
Organic acid leaching process						
LCD panels	576	0.5 M Oxalic acid	1/20 of S/L, 70 °C, 45 min	100%	Si, Al, B, Ca, Sr, Fe, Mg, Ba, Sn, Cr, Na, K and Cu	(Cui et al., 2019)
LCD screens	535	0.2 M Oxalic acid	3/10 of S/L, 90 °C, stirring at 500 rpm, 10 min with particle size <74 µm	100%	Cr, Mg, Fe, Ba, Sr, and Ca	(Li et al., 2020)
LCD screens of cell phones	602	1 M Citric acid with 5% H ₂ O ₂ 1 M Malic acid with 5% H ₂ O ₂	1/20 of S/L, 90 °C, 2 h	74.5% (citric acid); 70.9% (malic acid)		(Argenta et al., 2017)
Waste LCD panels		1 M Citric acid with reductant 0.2 M N ₂ H ₄	1/50 of S/L, pH = 5, 16.6 h	98.9%		(López- Yáñez et al., 2019)

Bioleaching process						
LCD screens	405	Adapted <i>A. thiooxidans</i>	4/25 of S/L, pH 2.6, initial 8.6 g/l of sulfur, within 15 days	100%	Sr, Co, Zn, Fe, Cu, and Ni	(Jowkar et al., 2018)
LCD screens	300	<i>A. thiooxidans</i>	3/200 of S/L, pH 2, 10 g/L sulfur and a 10% bacterial suspension	100%	B, Al, Mg, Fe, Ba, Sn, Cr, As	(Xie et al., 2019)
Mobile phone touch screen	69	Adapted <i>A. ferrooxidans</i>	1/4 of S/L, pH 2, 2% (v/v) inoculums, 10 days	100%	Al, Sr, Mn	(Rezaei et al., 2018)
LCD panels	0.0906 % (XRF)	mixed culture of <i>A. ferrooxidans</i> and <i>A. thiooxidans</i>	1/100 of S/L, iron, and sulfur medium inoculated with mixed bacteria	94.7 % after 35 days	Sn, Cu, Pb, Al	(Willner et al., 2022)
Indirect bioleaching-based process						
LCD panels	580	<i>Aspergillus niger</i>	Fermentation broth with pH 4, 125 rpm, 50 g/L of sucrose for 15 days, 70 °C with 1.5 h of leaching	100%	Al, Ca, Sr, Fe, Mg, Ba, Sn, Cr	(Cui et al., 2021)

3.2.2.1 Indium leaching with strong mineral acids

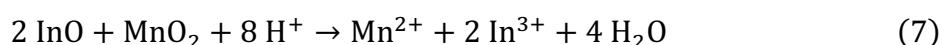
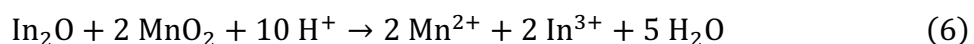
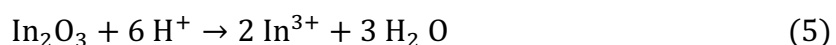
Strong mineral acids have been tested for the leaching of indium from waste LCDs using HCl, HNO₃, and H₂SO₄. According to Gabriel et al. (2020), HCl and H₂SO₄ were found to be more effective than HNO₃, with the best indium leaching yield obtained using 6 M HCl at 60 °C within 4 h, resulting in a 99.3% indium leaching yield. At the same time, the 0.5 M H₂SO₄ leaching process can also leach 98.2% of the total indium at room temperature in 2 h. However, the leaching efficiency of indium with HNO₃ was found to be lower, dissolving less than 50% of the indium in the leachate. Similar results have been reported by other researchers comparing the leaching of indium with strong mineral acids (HCl, HNO₃, and H₂SO₄) (Fontana et al., 2015; Yang et al., 2013). The reaction of indium oxide with HCl is the fastest, and the reaction with HNO₃ is the slowest (Gabriel et al., 2020; Yang et al., 2013). The amount of indium dissolved in 6 M HCl takes 2 h to reach an equilibrium value, while the reactions with HNO₃ and H₂SO₄ take twice as long to reach the same situation (Yang et al., 2013). HCl as a reagent for indium leaching from EoL products helps to limit the dissolution of non-target metals (i.e. Mo), thus contributing to the reduction of metal impurities in the leaching solution (Zhang et al., 2017).

On the other hand, leaching with H₂SO₄ shows the best potential for indium leaching from EoL products in terms of economic aspects, energy consumption, and corrosiveness (Ferella et al., 2016; Gabriel et al., 2020; Pereira et al., 2018; Silveira et al., 2015). Ruan et al. (2012) also reported that the use of H₂SO₄ to leach indium from LCDs could reduce the dissolution of toxic arsenic, which is also present in LCDs.

Indium leaching from EoL products has also been investigated using different acid mixtures, such as HCl mixed with HNO₃ and HCl mixed with H₂SO₄ (Lee et al., 2013; Savvilotidou et al., 2015). It was reported that HCl mixed with HNO₃ was an effective method at high temperatures, while HCl mixed with H₂SO₄ had lower indium leaching capacity due to the lower activity of H₂SO₄ (Assefi et al., 2018; Lee et al., 2013; Li et al., 2009; Savvilotidou et al., 2015). In addition, Li et al. (2009) reported that a strong oxidative acid, such as HNO₃, mixed with another strong acid, such as HCl, can accelerate the dissolution of indium. However, a mixture of strong oxidative acids and strong acids could contribute to the formation of Sn black precipitate (SnO), which was found to affect the extraction of indium.

Increasing the reaction temperature by reacting with ultrasonic waves was found to improve the leaching efficiency of indium (Ferella et al., 2016; Silveira et al., 2015; Zhang et al., 2017). It was reported that single and mixed acid leaching combined with ultrasonic waves improved the indium leaching yield (more than 95%) due to the combination of energy input and percussion. In addition, the ultrasonic waves allow the solution to undergo convective motions that bring fresh H⁺ to the surface of the solid and remove metal ions. Another advantage of this approach is that non-target metals from spent LCDs were rarely affected by ultrasonic agitation (except for In and Al).

Oxidants, such as H₂O₂ and MnO₂, were also tested with the aim of increasing the indium leaching efficiency (Dhiman and Gupta, 2020; Swain et al., 2016a; Zeng et al., 2015). When the leaching process was tested using 3 M HCl and 1 M 30% H₂O₂ as oxidant, under magnetic stirring at 400 rpm for 2 h, 98.7% of the total indium was leached (Dhiman and Gupta, 2020). To improve the indium leaching efficiency and avoid undesirable side-stream reactions such as the formation of toxic Cl₂, the addition of MnO₂ as an oxidant to the leaching solution limits the galvanic interaction of indium oxides (In₂O and InO) (Zeng et al., 2015). The related reactions of In₂O₃, In₂O and InO are as follows:



Considering the low concentration of indium in the leachate with a single leaching step, the concentrated technique of the multistep leaching approach (the same leachate for leaching fresh waste samples in the multi-steps) was used in LCDs to achieve quantitative leaching. Rocchetti et al. (2015) tested six steps of the above approach to leach indium from spent LCDs. In the fifth step, the concentration of indium in the leachate reached almost 3 times (117 mg/L) that of the first step using 2 M sulfuric acid at 80 °C for 10 min (each step). Although this method can concentrate indium in the leachates to save reagents and reduce CO₂ emission, it does not achieve a good leaching yield, which reaches about 50% after the sixth step. Therefore, other techniques were tested for indium leaching with a low concentration, such as the use of organic acids.

3.2.2.2 Indium leaching with organic acids

Organic acids have been used for indium leaching from EoL products because they are milder, more selective, less toxic, more biodegradable under aerobic and anaerobic conditions, and easier to control during metal extraction than mineral (Argenta et al., 2017; Cui et al., 2019; Fontana et al., 2020; Li et al., 2020). Oxalic acid has shown good leaching efficiency and has been used for indium leaching from LCDs because this organic acid can maintain the proton concentration level to ensure efficient indium dissolution while limiting the dissolution of other non-target metals (Cui et al., 2019). Cui et al. (2019) reported that indium leaching yield could reach 100% with 0.5 M oxalic acid at an S/L ratio of 1/20 g/mL at 70 °C in 45 min. Li et al. (2020) proposed a method using a temperature-controlled acidic stirred reactor with oxalic acid, which could improve the leaching efficiency and reduce the consumption of oxalic acid compared to the study by Cui et al. (2019). Citric and malic acids were also used to leach indium from discarded LCD screens, and nearly 76.5% of indium was extracted after 3 h with a S/L ratio of 1/20 g/mL at 70 °C (Argenta et al., 2017). In addition, the addition of the oxidant H₂O₂ and reductant N₂H₄ to the media can further improve the leaching yield, as shown in previous research on strong mineral acids (Argenta et al., 2017; López-Yáñez et al., 2019).

3.2.2.3 Indium bioleaching

Bioleaching is considered a promising approach for leaching indium from WEEE due to the abundance and versatility of microorganisms. This technique has the advantage of being low-cost and environmentally friendly (Jowkar et al., 2017; Ogi et al., 2012; Pennesi et al., 2019; Xie et al., 2019). However, few biological studies are related to indium leaching from e-waste. Microorganisms such as *Acidithiobacillus ferrooxidans* (*A. ferrooxidans*), *Acidithiobacillus thiooxidans* (*A. thiooxidans*), and *Aspergillus niger* fermentation broth have been reported to

reach 100% indium leaching yield. Jowkar et al. (2018), who published the first report on indium bioleaching using the acidolysis mechanism, involved adapted *A. thiooxidans* from LCDs, resulting in a 100% indium leaching yield. The main reaction involves the acidolysis by the biogenic sulfuric acid produced by bioleaching bacteria (Sethurajan et al., 2018). In addition, Xie et al. (2019) also reported that the use of *A. thiooxidans* could accelerate the leaching rate of indium with a S/L ratio of 3/200 g/mL at pH 2 in the presence of 10 g/L sulfur and a 10% bacterial suspension. In the work of Rezaei et al. (2018), indium could also be leached from the touch screen of the mobile phone using adapted *A. ferrooxidans* with a 100% leaching yield within 10 days. The involved bioleaching mechanism can be classified as redoxolysis, wherein *A. ferrooxidans* catalyzes the oxidation of ferrous (Fe^{2+}) to ferric ions (Fe^{3+}). Subsequently, the ferric ions further oxidize target insoluble metals, converting them into soluble metals (Sethurajan et al., 2018). Furthermore, Willner et al. (2022) demonstrated that mixed bacteria of *A. ferrooxidans* and *A. thiooxidans* inoculated with iron and sulfur medium could achieve a high leaching yield of both indium (94.7%) and tin (98.2%). *Aspergillus niger* fermentation broth has also been explored for indium recovery from waste LCDs through an indirect bioleaching-based process, and indium bioleaching exhibited a significant achievement with a 100% yield of indium attained within a short time (1.5 h at 70 °C) (Cui et al., 2021). The primary reaction mechanism involves the production of organic acids using bacteria *Aspergillus niger*, which subsequently release H^+ from acidic functional groups of organic acids and proteins of fermentation broth, facilitating bioleaching of indium. While there are relatively few studies related to bioleaching and indirect bioleaching-based approaches for indium from e-waste, the potential for exploring new bacteria and improving the efficiency of these processes makes them an area of ongoing interest for researchers in the field.

3.2.3 Indium recovery from EoL LCDs by hydrometallurgical and biohydrometallurgical routes

Table 7 summarizes the major techniques tested for indium recovery from spent LCD leachates generated by hydrometallurgical and biohydrometallurgical approaches. These techniques, including solvent extraction, ionic liquid extraction, solid-phase or ion-exchange extraction, precipitation, cementation, electrowinning, supercritical fluid separation, and biorecovery, have been tested and achieved good recovery yields when implemented under optimal conditions.

E-waste	Method of extractant	Initial In content (mg/L)	Optimum conditions (O/A: organic and aqueous phase ratio; S/L: g/mL)	Recovery yield	Other metals	Reference
Solvent extraction						
LCD panel glass	DEHPA for extraction and HCl for stripping	200 in H ₂ SO ₄ leachate	0.1 M DEHPA diluted in kerosene, 1 M HCl, 1/1 of O/A, 1500 rpm agitation, 10 min	99% (90% of purity)	Al, Fe, Zn, and Sn	(Yang et al., 2013)
LCD screen wastes	DEHPA for extraction and HCl for stripping	740 in H ₂ SO ₄ leachate	1.5 M HCl		Sn	(Virolainen et al., 2011)
TFT-LCD scrap	D ₂ EHPA for extraction and HCl for stripping	30.2 in H ₂ SO ₄ leachate	30% D ₂ EHPA, 1/5 of O/A, 5 min for extraction, 4 M HCl, 5/1 of O/A for stripping	97%	Al, Sr, Fe, As, Zn, Ti, Cu, Sn, and Cr	(Ruan et al., 2012)
LCDs of mobile phone	D ₂ EHPA for extraction and HCl for stripping	32.6 in H ₂ SO ₄ leachate	30% D ₂ EHPA diluted in kerosene, 1/40 of O/A, pH 0.5, 20 min for extraction, 4 M HCl for stripping, 10/1 of O/A, 10 min for stripping	96.7% extraction and 61.10% stripping	Sn	(Pereira et al., 2018)
LCDs	A hollow fiber-supported liquid membrane with strip dispersion using D ₂ EHPA as an extractant	141 in HCl leachate	0.25 M D ₂ EHPA, pH 2, 20 min for extraction, 2 M HCl for stripping	94% extracted	Al, Ca, Fe, Zn and Cu	(Yen et al., 2016)
LCD glass	polyethylene glycol (PEG) 1,10 phenanthroline as a ligand, ammonium sulphate	85 in HCl leachate	25% w/w of [PEG 3,350] and 12% w/w of [(NH ₄) ₂ SO ₄], 2 h	80-95% in the bottom phase and 5-20% in the top phase	Sn, Al, and Cr	(Fontana et al., 2015)
Ionic liquids extraction						
Discarded LCD screens	Phosphonium ionic liquid (<i>Cyphos IL 104</i>) for extraction, HNO ₃ for stripping	160 in HCl leachate	0.1 M Phosphonium ionic liquid (<i>Cyphos IL 104</i>) diluted in toluene, 2/3 of O/A for extraction, 4 M HNO ₃ , 3/2 of O/A for stripping	98.9% extraction with a purity of 100%	Sn, Zn, Fe, Al, Mn, Ca, and Sr	(Dhiman and Gupta, 2020)
LCDs	Betainium bis (<i>trifluoromethylsulfonyl</i>) imide ([Hbet][Tf2N])	30 in acid	10 mL 50% (v/v) ionic liquid/ascorbic acid, 1/50 of S/L, 90 °C, 24 h	98.63% In was extracted	Al	(Luo et al., 2019)
Solid-phase extraction (ion exchange)						
LCD screens of mobile phone	Nylon 6/DEHPA nanofibers for extraction, HCl for stripping	32.6 in H ₂ SO ₄ leachate	Nylon 6/30% DEHPA nanofibers, pH 0.5, 7.5 min, 1/300 of S/L for extraction, 1.5 M HCl 1/20 of S/L, 5 min for stripping	74% extraction and 92% stripping	Sn	(Cadore et al., 2019)
LCD panels	5% wt/vol Amberlite™ resin, 2 M H ₂ SO ₄	26.8 in H ₂ SO ₄ leachate	5% wt/vol Amberlite™ resin, pH 3, 1/10 of S/L, 24 h for extraction, 2 M H ₂ SO ₄ , 2/5 of S/L, 1 h for stripping	100%	Al, Si, Fe, Sn, Zn, and Cr	(Ferella et al., 2016)

LCD panels	Macroporous resin (Lewatit TP 208) for extraction, HCl for stripping	30 in mineral acids	0.5 g Lewatit TP 208, pH 2, 25 °C, 30 min for extraction, 2M HCl, 500 rpm agitation, 5 min for stripping	99.5%		(Assefi et al., 2018)
Precipitation						
LCD screens of discarded cell phones	NH ₄ OH	0.2992 kg	NH ₄ OH (28.0-30.0 vol % of NH ₃), pH 7.4	99.8 wt% In was extracted	Si, Sr, Ca, Al, Ba, Sb, and Sn	(Silveira et al., 2015)
Cementation						
LCDs	Zn powder		100 g/L of Zn powder, pH 2-3	99.8%	Al, Ca, and Fe	(Rocchetti et al., 2016)
Electrowinning						
TFT-LCD panels	Low current electrolysis with the Potentiostat/Galvanostat		Current density at 0.2 A cm ⁻² in 15 wt% NaNO ₃ electrolytes for 30 min.	75% for ITO	Sn	(D. Choi et al., 2014)
Supercritical fluid separation						
LCD screens of cell phone	scCO ₂ extraction with 1 M citric acid and 5% H ₂ O ₂	602 mg/kg	1/20 of S/L, 15 MPa, 100 °C, 30 min	94.6%	Sn	(Argenta et al., 2017)
Biorecovery						
Aqueous solutions (InCl ₃)	Gram-negative bacterium <i>Shewanella algae</i>	115	Room temperature, pH 2.4–3.9, 10 min	100% In was extracted		(Ogi et al., 2012)
metal-system with indium and iron	Nature and waste biomass of brown alga <i>Ascophyllum nodosum</i>		pH 3	63 mg/g in nature biomass, 48 mg/g in waste biomass	Fe	(Pennesi et al., 2019)
Discard LCD screens	The hyper-accumulator plant <i>Eleocharis acicularis</i>	300 and 600 in HNO ₃ leachate	24 ± 1 °C, pH 5, 15 days	60 mg and 122 mg uptake		(Upadhyay et al., 2021)

3.2.3.1 Solvent extraction and ionic liquids extraction

Solvent extraction, also known as liquid-liquid extraction, is a widely used separation technique for recovering indium from EoL product leachates. It is based on different solubilities in two different immiscible liquids, usually an aqueous solution (polar) and an organic solvent (non-polar) (Fontana et al., 2020). The advantages of this method are that the extraction process is simpler, and the solvents can be reused (Pradhan et al., 2018). Numerous studies have tested

a wide variety of extractants to recover indium from LCD leachate. Typically, different organophosphate extractants such as bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272), trialkylphosphine oxide mixture (Cyanex 923), tributyl phosphate (TBP), and bis(2-ethylhexyl) phosphoric acid (DEHPA) also known as di-2-ethylhexyl phosphoric acid (D₂EHPA) are added to the extraction system (Pereira et al., 2018; Ruan et al., 2012; Virolainen et al., 2011; Yang et al., 2013; Yen et al., 2016).

DEHPA has so far been confirmed as a widely used and best extractant for the selective separation of indium and tin from LCD leachate due to the advantages of high loading capacity and good selectivity over other metals (i.e. Fe, As, Cu, Cd, and Zn) (Fontana et al., 2020; Virolainen et al., 2011; Yang et al., 2013). In the work of Yang et al. (2013), different organic systems such as Cyanex 272, Cyanex 923, TBP, and DEHPA were reported for indium extraction from acidic leachate generated from discarded LCD panels. The results showed that DEHPA is a good option and more than 99% indium with 90% purity was extracted from low concentration sulfuric acid by 0.1 M DEHPA diluted in kerosene after stripping with 1 M HCl. Virolainen et al. (2011) also studied three types of solvent systems, including TBP, DEHPA, and a mixture of the two, which suggested that DEHPA could extract both indium and tin from H₂SO₄ and separated indium after stripping with 1.5 M HCl, while the stripping efficiency for indium was 94%.

In addition, up to 97% of the total indium concentration was recovered from scrap thin-film transistor (TFT) LCDs by H₂SO₄ leaching and solvent extraction with 30% D₂EHPA within 5 min after stripping with 4 M HCl (Ruan et al., 2012). Pereira et al. (2018) applied solvent extraction with D₂EHPA to concentrate indium from EoL mobile phone LCDs, and after adjusting the best conditions, the indium concentration was 236 times higher than the initial concentration, reaching 7,712 mg/L of indium after stripping.

However, the disadvantages of using D₂EHPA extraction technique make it poor to separate iron from indium, because the concentration of iron in the solution is similar to that of indium and co-extracted with indium to the organic solution (Yang et al., 2013; Yen et al., 2016). Nevertheless, a novel solvent extraction using crown ethers of 12C5 as the extractant has been proposed and has shown good selectivity for In (III) over Sn (II). Therefore, it is expected to demonstrate selective recovery of indium from waste LCD leachate in the future (Xu et al., 2021).

Compared with the classical solvent extraction, a supported liquid membrane with strip dispersion (SLM-SD) has been developed for the extraction of indium from spent LCDs due to the advantages of a good mixing system, which avoids emulsification and enables more

efficient indium extraction. More than 94% of indium can be extracted with 0.25 M D₂EHPA after stripping with 2 M HCl for 20 min using the SLM-SD technique (Yen et al., 2016). In addition, polyethylene glycol (PEG)-based aqueous biphasic systems are also used to recover indium from e-waste LCDs due to their characteristics of low toxicity, low corrosiveness, and low flammability. In a study by Fontana et al. (2015), using a PEG-(NH₄)₂SO₄-water system with 1,10-phenanthroline as a ligand, they found that indium can enter the lower (salt-rich) phase at 80-95% and the upper (PEG-rich) phase at 5-20%. They also found that indium separation is the independent composition in this system, and the indium concentration increased by nearly 30% when the PEG concentration increased.

To overcome the lack of flammability and toxicity of traditional separation organic solvents in the hydrometallurgical methods. Ionic liquids (ILs) are considered green extraction solvents, and they are a promising and developing technique for indium extraction and recovery from EoL products (Alguacil & López, 2020; Dhiman & Gupta, 2020). Recently, [tetradecyl-(trihexyl) phosphonium bis-(2,4,4-trimethylpentyl) phosphinate] (Cyphos IL104), one of the phosphonium ionic liquids, diluted in toluene, was used as an extractant to recover indium from discarded LCD leachate (98.9% recovery yield) (Dhiman and Gupta, 2020). In addition, Luo et al. (2019) reported that the use of ILs can be a more convenient way to recover indium directly from discarded LCDs. They used the functionalized ionic liquid betainium bis(trifluoromethylsulfonyl)imide ([Hbet][Tf₂N]), and achieved 98.6% indium recovery from solid LCD samples after cooling and stratification under the optimal conditions within 24 hours.

3.2.3.2 Solid-phase extraction

Recently, solid-phase extraction has been recognized as a promising technique for indium recovery from EoL products. It has the potential to replace conventional solvent extraction due to the advantages of low solvent consumption, low cost, shorter time, and easier process operation (Assefi et al., 2018; Cadore et al., 2019; Ferella et al., 2016; Płotka-Wasyłka et al., 2016). However, there are very few reports using solid-phase extraction to recover indium from LCDs.

Cadore et al. (2019) reported the use of Nylon 6 polymer nanofibers modified with DEHPA extractant to selectively recover indium from spent LCD mobile phone screens. Cation-exchange resin in solid-phase extraction has also been used to extract indium from LCDs. According to Ferella et al. (2016), Amberlite™ IRC748 resin, a chelating resin with a high affinity for metal cations (i.e. indium), was used in indium recovery. The indium extraction yield was 100% with 5% wt/vol Amberlite™ resin in the optimum condition at pH 3 with a

S/L ratio of 1/10 g/mL within 24 h. The use of macroporous resins for the selective recovery of indium from scrap LCD panels was reported because macroporous styrene-divinylbenzene resins show a more practical approach to metal absorption with the advantages of high performance and simple operation. Three macroporous polystyrene-divinylbenzene resins, including Lewatit TP 208, Lewatit TP 260, and Amberlite IRA 743, were successfully used to adsorb indium. The Lewatit TP 208 showed a higher recovery yield of 99.5% for the adsorption of indium from scrap LCD panels due to the most symmetric and lower steric effect in the interaction with indium, compared to other resins of Lewatit TP 260 and Amberlite IRA 743 (Assefi et al., 2018).

3.2.3.3 Precipitation

Precipitation is an alternative method for the extraction of indium from EoL products leachates. The use of ammonium hydroxide (NH_4OH) solution to precipitate indium as indium hydroxide from spent LCDs leachate obtained by H_2SO_4 , the results of the experiment showed that 99.8 wt% of indium present in the solution with the good condition at pH 7.4 and standing for 24 h (Silveira et al., 2015).

However, the precipitation method has its limitations. Other elements (i.e. aluminum) that have similar properties to indium, may also precipitate along with the desired indium. As a result, the indium is not selectively leached, resulting in a lower indium purity. Therefore, it is critical to explore alternative methods that can selectively extract indium while avoiding the precipitation of other elements. Further research is needed to optimize the precipitation method and to develop alternative methods to extract indium selectively from e-waste.

3.2.3.4 Cementation

Cementation is a well-established and suitable method for recovering indium from EoL products, especially in the presence of zinc as a cementing agent. Rocchetti et al. (2016) reported the recovery of indium sponge by cementation with zinc powder, since zinc has a lower reduction potential than indium and this process allows the reduction of trivalent indium to metallic indium. It was found that a pH range of 2 to 3 provided the most efficient operating conditions, resulting in the recovery of 99.8% of indium. In addition, the indium cementation process has the added benefit of reducing the need for reagents during the recovery process, although the final indium product may contain impurities such as aluminum, calcium, and iron. However, additional research is needed to achieve a significant level of indium purity when using zinc as a cementing agent for the purpose of extracting indium from LCD leachates.

Further studies are needed to optimize process conditions and to explore alternative methods to achieve higher indium purity levels when using zinc as a cementing agent in the recovery of indium from LCD leachates.

3.2.3.5 Electrochemical separation/Electrowinning

The use of electrochemical separation in recovering and recycling indium from EoL products is rarely reported, especially from discarded LCD screens. This is explained by the fact that the indium recovery process is strongly influenced by different factors, such as electrolyte composition as well as the presence of complexing agents in the leachates (J. H. Choi et al., 2014; Grimes et al., 2017). However, D. Choi et al. (2014) reported the recovery of ITO from obsolete TFT LCD panels using an electrochemical technique, which could obtain 75% of ITO (In_2O_3 and SnO_2) from the recovery process. But the recovered indium could not be reused directly due to the unsuitable ratio of indium and tin. According to Grimes et al. (2017), the extraction and the separation of indium from very dilute solutions that contain indium, tin, and lead, which simulated the leaching solution composition of LCDs, was successful by using a novel cylindrical mesh electrode electrolysis system under the optimum conditions. In the three-stage process, indium was recovered 98% of total indium in the presence of the indium hydroxide phase at the anode of the cylindrical mesh electrode cell by using a complexing agent of 0.1 M thiocyanate (SCN^-) within 24 h. Furthermore, the electrolytic refining technique integrated solvent extraction using 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ether (PC88A) as an extractant could be used to purify indium concentration to a maximum of 99.99% from etching e-waste (Kang et al., 2011).

3.2.3.6 Supercritical fluid extraction

Supercritical Fluid Extraction (SFE) is a promising new technique for recovering indium from LCDs, and it is considered to be more attractive than conventional recovery methods. SFE has several advantages, including high diffusivity, low viscosity, high solubility, and no surface tension, which are essential for efficient recovery. In addition, the use of CO_2 as a solvent in SFE is more environmentally friendly due to its non-toxic, non-flammable, economical, and recyclable properties (Argenta et al., 2017; Pradhan et al., 2018).

Supercritical CO_2 with co-solvents has been shown to increase the efficiency of the recovery reaction kinetics by facilitating the conversion of indium from a solid form to a soluble ionic form. Argenta et al. (2017) reported a recovery yield of 94.6% of indium from waste LCD mobile phone screens using supercritical CO_2 and co-solvents (1 M citric acid and 5% H_2O_2)

within 30 min. This process was found to be six times faster than the conventional method of using citric and malic acids.

In addition to its speed and efficiency, the SFE technique was shown to selectively leach indium without leaching tin, demonstrating its ability to extract indium while avoiding the loss of other valuable metals. As a result, SFE shows great potential for recovering high-purity indium from EoL products such as LCDs. However, further research is needed to optimize the SFE process and to determine its feasibility and scalability for industrial applications.

3.2.3.7 Indium biorecovery

Microbial biosorption is a promising technology for metal recovery due to the ability of some microorganisms to selectively bind and concentrate specific metals from dilute solutions. However, few studies have focused on the biosorption of indium from very low concentrations.

In the first report by Ogi et al. (2012), a novel recovery system was constructed using the Gram-negative bacterium *Shewanella algae* to recover indium from aqueous InCl_3 solutions. They found that indium can be recovered rapidly, with complete recovery within 10 min, and that indium can be concentrated more than 4,300 times even from very low concentrations ($< 1 \text{ mg/L}$). Furthermore, Pennesi et al. (2019) found that indium could be adsorbed by natural and waste biomass of the brown alga *Ascophyllum nodosum*, with the maximum sorption capacity estimated at 63 mg/g and 40 mg/g, respectively. However, competition with iron may affect indium adsorption in real waste LCD leachates. Alternatively, phytoextraction with the hyperaccumulator plant *Eleocharis acicularis* was applied for indium extraction from waste LCD leachates (usually acidic and saline) by its biomass based on high acidity and salinity tolerance. The results showed that the biomass accumulation of indium was achieved at 122 mg/g in dry weight, and the final product of indium-exposed plant biomass can be a candidate for graphite biocomposites (Upadhyay et al., 2021).

Therefore, microbial biosorption and phytoextraction are potential alternative technologies for the recovery of indium from waste LCD leachates, although further research is needed to optimize the processes and improve their efficiency.

3.3 Gallium recovery from EoL LEDs via hydrometallurgical and biohydrometallurgical routes

Gallium recovery from EoL products is still a challenge, according to the latest European Commission report (European Commission, 2020). Currently, industrial waste streams such as Metal-Organic Chemical Vapor Deposition (MOCVD: a system for depositing high-purity

crystalline compound for LEDs) dust and GaN/GaAs waste are commonly used as secondary sources to supply gallium to industry (Chen et al., 2018a; Hu et al., 2014; Swain et al., 2015a and 2015b). However, there is limited experimental data on gallium leaching and recovery from spent LEDs. Therefore, a knowledge gap persists regarding gallium recovery from spent LEDs. Lu et al. (2017) reported that the structures of LEDs are more complex than other gallium secondary sources, such as GaAs scrap, because the chips with GaN-combined quartz substrates are denser and more difficult to separate and recover. Nevertheless, the increasing amount of EoL LEDs is still a good source of gallium due to its higher concentration compared to primary ores. Several preliminary research studies have been conducted on gallium recovery from spent LED chips containing GaN, GaAs, and InGaN (Maarefvand et al., 2020; Pourhossein & Mousavi, 2019; Van den Bossche et al., 2019; Zhan et al., 2020; Zhang et al., 2021; Zhou et al., 2019). Various pre-treatment methods and hydrometallurgical and biohydrometallurgical technologies have been tested at a laboratory scale for gallium recovery from spent LEDs.

The pre-treatment of spent LEDs plays a critical role in the dissociation of their complex structures. Therefore, this review focused on different approaches dedicated to the pre-treatment of different types of spent LEDs. Although some studies have focused on pyrometallurgy, more environmentally friendly routes such as hydrometallurgy and biohydrometallurgy are discussed.

3.3.1 Pre-treatment of EoL LEDs

Pre-treatment of EoL LEDs is an important step in the recovery of valuable materials and components. This process includes both mechanical and chemical methods to improve recovery efficiency. The first step is to physically free and separate the gallium-containing LED chips from the less valuable parts of the EoL LEDs. Once the chips are obtained, they are typically cut into small pieces and ground with a mill or mortar to produce a powder. The size of the particles can be adjusted by sieving the powder with different sieve apertures, with the recommended size usually being less than 1,000 μm due to the presence of chips in the range of 106-1,000 μm . After obtaining the powder, a thermal pre-treatment may be required to enrich the concentration of elements and modify the structure of the undissolved gallium, especially if the LED structure contains GaN (Maarefvand et al., 2020; Nagy et al., 2017; Swain et al., 2015a). This pre-treatment is critical to increase the solubility of gallium in leach solutions, which can ultimately lead to better recovery rates.

To facilitate the recovery of LED chips from bulk material, polymers and adhesives (epoxy resin and other additives) are removed in advance (Maarefvand et al., 2020; Zhan et al., 2020). Polymers are typically removed by incineration due to their flammability and low melting point. This process leaves a crispy residue that is easily removed. On the other hand, adhesives, epoxies, and other additives can be removed using solvents such as acetone and anhydrous ethanol. The use of these solvents helps to completely separate the chips from the waste LED components. After the unwanted components have been removed, electrostatic separation is used to separate the non-conductive fraction of the chips from the LED powder. This step ensures that only the valuable components are recovered for further processing (Nagy et al., 2017).

For spent GaN LEDs, thermal treatment and pyrolysis play a critical role in the pre-treatment process. These processes oxidize gallium nitride to gallium oxide in the air or convert gallium nitride to gallium with nitrogen gas to improve solubility in leaching solutions (Maarefvand et al., 2020; Zhou et al., 2019). Figure 7 shows the pre-treatment process for the LEDs.

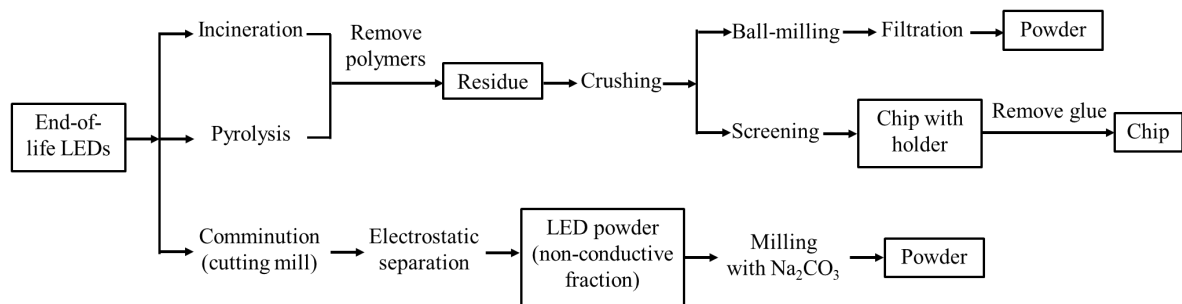
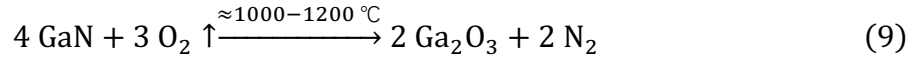
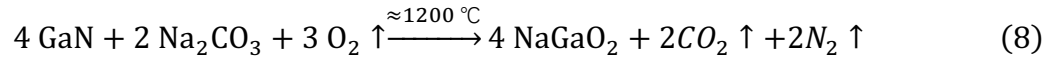


Figure 7 Flow chart of LEDs pre-treatment

Gallium nitride (GaN) is a highly durable crystal that has a high binding energy, making it difficult to dissolve in lixivants. However, there are several methods that have been proposed to improve the efficiency of gallium leaching from GaN. One such method is the chemical-thermal treatment with mechanochemical activation, which involves the use of the alkaline salt Na_2CO_3 . This treatment can convert GaN into soluble NaGaO_2 in the presence of Na_2CO_3 with annealing, as reported by Swain et al. (2016b). Nagy et al. (2017) have also proposed a chemical-thermal treatment with Na_2CO_3 that can improve the gallium leaching efficiency. Another method involves thermal oxidation without oxidants, where insoluble GaN can be converted to Ga_2O_3 in the air at a high temperature of 1000-1200 °C, as reported by Maarefvand et al. (2020). The chemical reactions involved in the formation of NaGaO_2 and Ga_2O_3 are given

by Equations (8) and (9), respectively. Other alkaline salts, such as LiBO₂ and NaOH, have also been used for alkali roasting in the recovery of gallium from spent LEDs (Chen et al., 2018a).



Thermal treatment can also be used for direct gallium recovery. Zhan et al. (2018) performed vacuum metallurgical separation on GaAs-based LEDs to recover different metals based on their boiling and evaporation points at different pressure conditions. The system successfully separated gallium and arsenic, achieving a gallium recovery yield of 98.92% at high pressure of 20 Pa and 1273 °C in 60 min. However, the limited temperature gradient of the experimental equipment caused the overlapping of gallium and arsenic, making it difficult to obtain high purity of gallium and arsenic separately, requiring additional steps for purification.

To determine the elemental composition of spent LEDs, acid digestion is commonly used. Chen et al. (2018a) reported that aqua regia with hydrofluoric acid (ratio 5/1) is efficient in completely dissolving solid samples. However, if the samples contain silver, nitric acid is recommended to avoid AgCl precipitation. The acidic leachate can then be analyzed using an inductively coupled plasma-optical emission spectrometer (ICP-OES) or atomic absorption spectroscopy (AAS) (Annoni et al., 2020; Chen et al., 2018a; Hu et al., 2014; Nagy et al., 2017; Pourhossein et al., 2021; Zhou et al., 2019).

In addition to determining the total metal concentration of spent LEDs, various analytical techniques such as scanning electron microscopy (SEM), X-ray diffraction (XRD), energy dispersive spectroscopy (EDS), and X-ray fluorescence analysis (XRF) can be used for their characterization (Chen et al., 2018a; Hu et al., 2014; Maarefvand et al., 2020; Nagy et al., 2017; Swain et al., 2015a; Yang et al., 2023). These techniques can provide information on the crystal structure, elemental composition, and morphology of spent LEDs.

3.3.2 Gallium leaching from EoL LEDs via hydrometallurgical and biohydrometallurgical routes

Gallium recovery from LED industry waste and spent LEDs can be achieved by hydrometallurgical and biohydrometallurgical routes.

Table 8 provides an overview of the different approaches that have been investigated in the literature. The GaN and GaAs wastes from the MOCVD process and the LED industry have

been studied due to their similarity to the common chips from spent LEDs. Leaching of GaAs waste is comparatively easier than that of GaN waste. However, the toxicity of arsenic during the leaching process should be considered to prevent environmental contamination (Hu et al., 2014; Mir et al., 2022).

On the other hand, the insolubility of GaN, even in strong acids, makes it relatively difficult to process. Therefore, numerous studies have been conducted to improve the gallium leaching yield from GaN and GaAs by strong inorganic acids under different pressure and temperature conditions, with or without catalysts.

In addition, indirect bioleaching-based processes have also been tested to achieve optimal gallium recovery. These processes use microorganisms to catalyze the leaching process, which can increase the leaching yield while minimizing the environmental impact. However, further research is needed to optimize bioleaching conditions for efficient gallium recovery. Overall, hydrometallurgical and biohydrometallurgical routes offer promising avenues for the recovery of gallium from LED industry waste and spent LEDs.

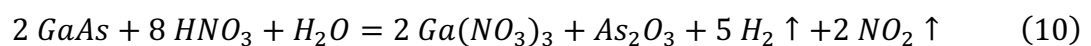
Table 8 Methods for gallium leaching from LED industry wastes and spent LEDs

E-waste	In and Ga (mg/kg)	Leachant	Optimum conditions (S/L: g/mL)	Leaching yield	Other metals	Reference
Strong inorganic acid leaching process						
GaAs, scrap from LEDs	50.8% Ga	1.5 M HNO ₃	1/40 of S/L, 200 rpm agitation, 40 °C, 1.5 h	99.6% Ga	As	(Hu et al., 2014)
Waste GaN from MOCVD dust	62.1% Ga, 1.86% In	4 M HCl with 5 wt% NaNO ₃	1/20 of S/L, 400 rpm agitation, 100 °C, 1 h, NaNO ₃ as catalyst	89.1% Ga	Al, Fe	(Swain et al., 2015b)
waste GaN from LED industry dust	97.76% Ga, and 2.24% In	4 M HCl and 1/1 of Na ₂ CO ₃	1/50 of S/L, 400 rpm agitation, 100 °C leaching after annealing with Na ₂ CO ₃	99.9% In		(Swain et al., 2015a)
SMD LEDs (GaN)	712.9 Ga	4 M HCl and 1/1 of Na ₂ CO ₃	1/50 of S/L, 80 °C, 2 h leaching after annealing with Na ₂ CO ₃	73.7% Ga	Cu	(Nagy et al., 2017)
Waste LEDs (GaN) from used light		4 M HCl	93°C, 2 h for leaching after oxidation without an agent	99.5% Ga		(Maarefvan d et al., 2020)
GaN waste from LED industry	3.38% Ga	0.25 M HCl with pressure	1/30 of S/L, 200 °C (15 atm pressure), 3 h	91.4% Ga	As, Fe, Al, Si, and Cr	Chen et al., 2018a)
Waste LEDs	37 of Ga	Subcritical water, 3% H ₂ O ₂ ,	300 °C, 300 rpm agitation, 400 min	98.5% Ga	As, Ag	(Zhang et al., 2021)

Waste GaN from MOCVD dust	74% Ga, 6% In	2 M NaOH for Ga, 2 M H ₂ SO ₄ for In	1/10 of S/L, 500 rpm agitation, 80 °C, 3 h for Ga after annealing with Na ₂ CO ₃ , leaching residues in 1/20 of S/L, 600 rpm agitation, 80 °C, 4 h for In	90.0% Ga 94.3% In	Al, Mg, Si	(Fang et al., 2019)
MOCVD dust	71% Ga, 6.6% In	2 M NaOH for Ga	1/20 of S/L, 200 rpm agitation, 90 °C, 3 h for Ga, after calcinating at 1200 °C for 3 h	92.7% Ga with 99.3% purity	Al, Mg, Si	(Yang et al., 2023)
Organic acid leaching process						
Surface mounted device LEDs	116.43	0.7 M Oxalic acid	90 °C, 1/100 of S/L, 48-75 µm of particle size, 1 h	90.4% Ga	Fe and Cu	(Zhou et al., 2019)
Indirect bioleaching-based process						
GaN chemical		<i>Arthrobacter creatinolyticus</i>	pH 9, 15 days	18% Ga		(Maneesuwannarat, Teamkao et al., 2016)
Discarded pin-type LEDs	401 Ga and 124 In	Adapted <i>A. ferrooxidans</i> with biogenic ferric ion 4-5 g/L biogenic ferric ion from adapted <i>A. ferrooxidans</i> culture	1/50 of S/L, 29 °C, pH 2, 140 rpm agitation, 30 days for direct bioleaching 1/50 of S/L, 29 °C, pH 2, 140 rpm agitation, 15 days for step-wise indirect bioleaching	60% Ga 84% Ga	Sn, Cu, Ni, Ag, Al, Pb, Cr, As, Zn, Au, and Ba	(Pourhosseini and Mousavi, 2018) (Pourhosseini & Mousavi, 2019)

3.3.2.1 Gallium leaching with strong mineral acids and alkaline

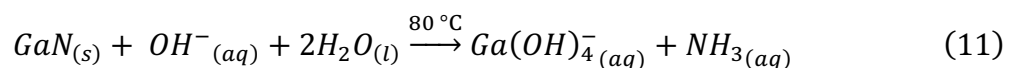
Various strong inorganic acids such as HCl, HNO₃, and H₂SO₄ have been tested for leaching gallium from e-waste. HNO₃ was found to be the most effective leachant for gallium recovery from GaAs scrap when added at relatively high concentrations compared to HCl and H₂SO₄ (Annoni et al., 2020). Hu et al. (2014) have confirmed that HNO₃ is the best technique for dissolving gallium and arsenic with high yields of 99.6% and 100%, respectively, under optimal conditions (1.5 M HNO₃ in 1.5 h at 40 °C). The reaction of GaAs with HNO₃ is an exothermic process and a self-catalytic reaction because the generated NO₂ gas enhances the reaction, according to the following chemical reaction:



In contrast, when dealing with the type of GaN waste generated by the LED industry. Chen, et al. (2018a) found that the optimal acidic gallium leaching occurred with HCl when the optimal conditions were adjusted. However, the gallium leaching yield was very low (8.9%) even when the temperature was increased up to 90 °C to accelerate the reaction rate. Pre-treatment with alkaline salt (i.e. NaOH) significantly improved the gallium leaching yield to 73.3% with HCl. Also, the gallium leaching yield with HCl under optimal conditions was improved to more than 90% after annealing with Na₂CO₃ (Swain et al., 2015b). Nagy et al. (2017) reported that 99.5% of gallium was leached from samples of new SMD LEDs. 91.4% of gallium could be achieved in the leaching process by using 4 M HCl at 93 °C for 2 h after thermal pre-treatment, even without oxidants (Maarefvand et al., 2020).

Without high temperature pre-treatment, Chen et al. (2018a) reported a high gallium leaching yield of 98.5% using pressurized acid leaching with HCl at 200 °C and 15 atm vapor pressure, even with a low concentration of HCl (0.25 M). Zhang et al. (2021) found that high temperature and pressure in the presence of oxidants such as H₂O₂ for subcritical water treatment can lead to a high gallium leaching efficiency of more than 80%. However, high temperature and pressure require extra stringent measures to safely operate the experimental setup. Different catalysts (i.e. NaNO₃, HNO₃, H₂O₂, and Na₂CO₃) have been used in HCl leaching to improve gallium leaching efficiency. Swain et al. (2015b) found that NaNO₃ increased gallium leaching efficiency from 64.6% to 89.1%, and the following order of efficiency was Na₂CO₃ < H₂O₂ < HNO₃ < NaNO₃.

Alkaline leaching with NaOH has also been investigated for gallium leaching from GaN-type wastes, due to the amphoteric property of gallium and the stability of Ga(OH)₄ chemical species in an alkaline solution. Fang et al. (2019) reported that gallium could be leached out with an efficient yield of 90% using 2 M NaOH at 80 °C, as the thermodynamic dissolution of GaN in the NaOH solution shows that the Gibbs free energy ($\Delta G_{80\text{ °C}} = -102.4\text{ kJ/mol}$) is negative, and the reaction (Eq. 11) is spontaneous at a temperature of 80 °C. Additionally, Yang et al. (2023) reported a gallium leaching yield of 92.7% with a purity of 99.3% using 2 M NaOH at 90 °C after calcination by converting nitrogen from GaN into diatomic nitrogen gas instead of ammonia or ammonium.

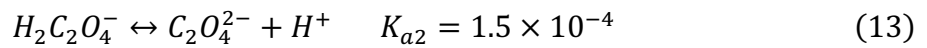
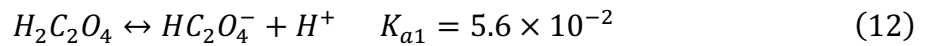


3.3.2.2 Gallium leaching with organic acids

Organic acids are being investigated as a potential alternative to mineral acids for gallium leaching from spent LEDs, due to their easier implementation and lower environmental impact.

Zhou et al. (2019) conducted experiments to investigate the potential of three different organic acids (oxalic acid, citric acid, and DL-malic acid) for gallium leaching from spent SMD LEDs. The results showed that oxalic acid had the highest efficiency, with 83% of the gallium being leached. This percentage was higher than citric acid (71%) and DL-malic acid (72%). After optimizing the leaching conditions, a gallium leaching yield of more than 90% could be achieved within 60 min.

One reason for the high efficiency of gallium leaching with oxalic acid may be the formation of iron oxalate precipitates (FeC_2O_4) resulting from the reaction of iron ions with oxalic acid. This promotes the release of H^+ from oxalic acid, which is not observed with other organic acids tested. Another reason is that oxalic acid can maintain a stable H^+ concentration during the leaching process, which is critical for gallium dissolution. Similar reactions have been reported for other metals, such as Ca^{2+} and Sr^{2+} (Cui et al., 2019). Therefore, oxalic acid leaching shows potential as a promising recovery technique for gallium from EoL LEDs. The possible related reactions of Fe and Ga leaching are:

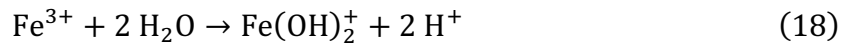
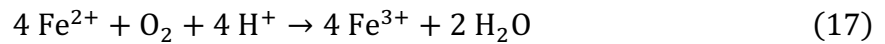


3.3.2.3 Gallium bioleaching

Bioleaching is an environmentally friendly and energy-saving method that has been successfully applied to the recovery of gallium from waste LCDs. Although the number of studies on the bioleaching of gallium from waste LEDs is limited, progress has been made in recent years.

The heterotrophic bacterium *Arthrobacter creatinolyticus* (*A. creatinolyticus*) has been studied for gallium leaching from chemicals ($< 38 \mu\text{m}$ particle size). Although a low leaching yield (18%) was achieved after 15 days of incubation, the results provide important insights into the fundamental mechanisms of gallium bioleaching. In particular, the interaction of Ga with amino acids, peptides, and proteins seems to be related to the binding mechanism with a carboxyl group and an amine group by binding gallium ions from GaN and forming metal complexes that promote the leaching of gallium from spent GaN (Maneesuwannarat, Vangnai, et al., 2016).

Iron-oxidizing bacteria, such as *A. ferrooxidans*, have been used to leach gallium from discarded pin-type LEDs (Pourhossein and Mousavi, 2018). The adaptation of these bacteria to tolerate toxic metals and flame retardants from spent LED media significantly increased the leaching efficiency of gallium. The results show that *A. ferrooxidans* was able to tolerate the maximum concentration of spent LED powder (20 g/L) and was able to reach approximately 60% of gallium (Pourhossein and Mousavi, 2018). Iron, which is the largest metallic component in the total metal weight of LEDs, played an important role in maintaining the pH value stabilized at 2-2.5 in the direct bioleaching process by oxidation of ferrous ions and hydrolysis of ferric ions in the aqueous solution. Throughout the reaction process, the pH could be kept stable by the hydrolysis of ferric ions (Fe^{3+}), which releases H^+ into the solution, even though the above bacteria initially oxidize ferrous ions (Fe^{2+}) to ferric ions (Fe^{3+}) using protons. Related reactions of Fe are:



Bioleaching can be a promising approach to improve gallium leaching from EoL products. One such method is the stepwise indirect bioleaching approach, which uses biogenic iron from adapted bacteria to enhance the recovery of gallium from spent LEDs. This method addresses the negative effects of bacterial adhesion in direct bioleaching of spent LEDs. The results showed that an 84% leaching yield of gallium was achieved at a pulp density of 20 g/L and pH 2 within 15 days, which is an improvement over the 60% yield achieved by direct bioleaching (Pourhossein & Mousavi, 2019). This stepwise indirect bioleaching method is a low-cost, environmentally friendly, and easier controlled method that can recover gallium from low concentration sources. These results suggest that this approach could be a promising technique for the recovery of gallium from waste LEDs.

3.3.3 Gallium recovery from EoL LEDs via hydrometallurgical and biohydrometallurgical routes

Table 9 summarizes the methods implemented for the recovery of gallium from spent LEDs leachates as reported in peer-reviewed literature.

1216 Table 9 Methods for gallium recovery from spent LEDs leachates

E-waste	In and Ga (mg/kg)	Extractant	Optimum conditions	Recovery yield	Other metals	Reference
Solvent extraction						
LEDs	8 of Ga in HCl leachate	Cyanex 272 for extraction and HCl for stripping	0.5 M Cyanex 272, 0.01 and 0.1 M HCl multi-stripping Ga	91% Ga extraction with 99% purity	Fe, Ni, Al, Cu, Ni, Mn	(Gupta et al., 2007)
Ionic liquids extraction						
GaAs and InAs from waste LEDs and semiconductors		[P ₄₄₄₁₀][Br ₃] as an ionic liquid, NaBr solution, pure water, and NaOH for stripping	Gallium was stripped by pure water before NaBr (remove As), and Indium was stripped by NaOH	96.5% Ga and 99% In precipitation	As	(Van den Bossche et al., 2019)
Membrane separation						
SMD red-emitting chip LEDs	1307 of Ga	Nanofiltration 90 membrane	10 atm pressure, 20-25 °C, 2.4 L/min of feed flow, pH 2-9	85% Ga	As, Zn, Fe, Cu, Si, Au	(Annoni et al., 2020)
Precipitation						
GaAs scraps of LEDs		0.1 M Na ₂ S	5 mL/min of flow rate, 0.7 of the molar ratios of S to (Ga+As) pH 3.5-7 for Ga	98.5% As precipitation, 98.5% Ga in solution	As	(Hu et al., 2014)
Waste LEDs		pH adjustment for Ga, NH ₄ OH for In	precipitation, pH 1-3 for In precipitation after residue dissolved in H ₂ SO ₄	99.8% Ga and 99.1% In		(Fang et al., 2019)
Supercritical liquid extraction						
Surface mounted device LEDs	41 of Ga and 21 of In	Anhydrous ethanol and ultrapure water	300 °C, 60% water in the water-ethanol mixture, 240 min	93.10% Ga and 85.72% In	As and Ag	(Zhan et al., 2020)
Indirect bioleaching-based process						
Wafer fabrication industry wastewater	4-35	DFOB and DFOE for complexation, EDTA for decomplexation	pH 2-9, molar ratio of Ga and DFOB/E of 1/1 for complexation, pH 3.5 with 6 times EDTA for	100% Ga complexation and > 95% Ga decomplexati	As, Al, Mg, Ca, Zn, P	(Jain et al., 2019)

1217

1218 **3.3.3.1 Solvent extraction**

1219 The recovery of gallium from spent LEDs leachates by solvent extraction has not been widely
1220 reported. Among the solvents tested, dialkylphosphine oxide (Cyanex 272) was found to be a
1221 superior extractant due to its low aqueous solubility, good recyclability, and resistance to
1222 hydrolysis compared to tributylphosphate (TBP) and di(2-ethylhexylphosphoric acid) (DEHPA)
1223 (Gupta et al., 2007). It is reported that gallium can be effectively recovered from spent LED
1224 leachates using Cyanex 272 solvent and ternary separations with various concentrations of HCl.
1225 It was found that 90-95% of the total gallium was extracted with 99% purity after adjusting the
1226 conditions. The good hydrolytic stability and regeneration of the Cyanex 272 extractant also
1227 make it a suitable candidate for large-scale recycling industries.

1228 However, the multi-step removal of non-target metals such as Ni, Mn, Cu, Al, and Fe increases
1229 the cost of gallium recovery. Therefore, there is a need to develop a simpler single-step method
1230 for selective recovery of gallium to reduce the overall process cost. Despite these limitations,
1231 the use of solvent extraction for gallium recovery from spent LED leachates has great potential
1232 and warrants further investigation.

1233 **3.3.3.2 Ionic liquids extraction**

1234 The use of ionic liquids (ILs) as an extraction method for target metal recovery has gained
1235 increasing attention due to their non-volatile and non-electrostatic charging properties. In
1236 recent years, a hydrophobic trihalide ionic liquid, tributyldecylphosphonium tribromide
1237 [P44410][Br₃], has been used as an oxidant for the extraction of gallium and indium from spent
1238 LEDs, including those containing GaAs and InAs. This approach has several advantages,
1239 including the avoidance of the highly toxic arsenic formation of AsH₃ during acid leaching and
1240 the ability to recycle ILs for multiple extraction cycles. Van den Bossche et al. (2019) reported
1241 the recovery of gallium and indium from semiconductors and LEDs containing GaAs and InAs
1242 using this method, achieving 96% recovery of gallium after stripping with ultrapure water and
1243 99% recovery of In(OH)₃ precipitated after stripping with NaOH solution. Finally, by adding
1244 Br₂ to the solution, ILs could be reused and recycled for another extraction cycle, contributing
1245 to a green and circular economy. The direct approach to recovering gallium and indium without
1246 the leaching step is a promising technique. However, this approach has not been implemented
1247 for spent GaN LED material.

3.3.3.3 Membrane separation

Membrane separation has been shown to be a promising approach for the purification of metals, including gallium (Annoni et al., 2020). Nanofiltration and ultrafiltration membranes have been tested for gallium recovery. The results show that even though gallium ions (radius size: 0.0621 nm) easily pass through an ultrafiltration membrane (size > 100 nm), gallium precipitates are retained by the ultrafiltration membrane as pH increases (i.e. pH < 2.51, 22% of gallium precipitation). However, a nanofiltration membrane was a good way to reject gallium. The positive metal ions, such as gallium ions, are repelled due to the expected positive membrane charge in the nanofiltration membrane process when pH is low. The recovery yield of gallium from a synthetic solution can reach up to 98.4% when the pH is around 2. In actual acidic spent LED leachate, the recovery yield of gallium can achieve 85% using a nanofiltration membrane under optimal conditions of 10 atm pressure at room temperature and a feed flow rate of 2.4 L/min. Additionally, the nanofiltration membrane does not degrade at pH 0.18, making it suitable for most acidic treated leachates. However, the cost of the recovery system is increased due to the need for acid control at low conditions, and the recovery yield and purity need to be improved. Despite these limitations, the use of nanofiltration membranes for gallium recovery offers a promising solution for the purification of this valuable metal.

3.3.3.4 Precipitation

Precipitation is a widely used method for recovering gallium from waste materials. This process involves adjusting the pH using an acid or a base. However, in the case of gallium and arsenic recovery from GaAs leachates, NaOH is not preferred due to the co-precipitation of these two metals. Hu et al. (2014) reported that the maximum precipitation percentage of gallium with $\text{Ga}(\text{OH})_3$ occurs in the pH range of 4-6, while arsenic precipitation reaches a maximum percentage at pH 6.

Sodium sulfide (Na_2S) is an effective precipitant for gallium recovery from GaAs leachates. This approach achieves a highly selective separation of gallium and arsenic through Na_2S titration. The hydrolysis of S^{2-} and release of OH^- in solution can raise the pH to 1 in acidic leachates, resulting in 79% arsenic precipitation compared to 6% gallium precipitation. In this approach, Na_2S first reacts with As to form a precipitate of As_2O_3 rather than As_2S_3 , allowing the separation of gallium and arsenic (Hu et al., 2014).

However, Chen et al. (2012) reported that the use of Na_2S solution not only recovered As but also co-precipitated Ga. The low separation efficiency of GaAs (49.1% Ga and 29.6% As precipitates) was attributed to the high addition flow rate of Na_2S solution, which could react

with Ga and As simultaneously due to the excess of dissolved sulfide species. To improve the separation efficiency, Hu et al. (2014) optimized the Na₂S flow rate to 5 mL/min and found that 0.1 M Na₂S could precipitate 98.5% As and 1.5% Ga, resulting in the successful recovery of gallium from spent LEDs leachate.

In addition, the precipitation of gallium and indium could also be achieved with high recovery yields (more than 99%) through pH adjustment using H₂SO₄ and NH₄OH solution, respectively. Fang et al. (2019) reported that adjusting the pH of the solution with H₂SO₄ solution to the range of 3.5-7 results in the maximum amount of Ga(OH)₃ precipitate. Similarly, adjusting the pH with NH₄OH solution in the range 1-3 resulted in the precipitation of In(OH)₃.

Overall, chemical precipitation by adjusting pH with acid or base is a promising approach to recovering critical elements from waste materials. It is a simple and safe process, and the residue and leachate can be recycled for subsequent steps, resulting in a high recovery rate of critical elements.

3.3.3.5 Supercritical fluid separation

Supercritical fluid separation is an advanced technique that can effectively separate various metals from e-waste. One method that has been investigated is the use of a subcritical water-ethanol mixture, which has shown promising results in the recovery of gallium, indium, arsenic, and silver from e-waste LEDs. In a study conducted by Zhan et al. (2020), the optimum recovery conditions were found to be at a temperature of 300 °C and water content of 60% in the water-ethanol mixture, which allowed for the recovery of 93.1% gallium, 85.7% indium, 93.8% arsenic, and 99.9% silver in only 4 h.

This method has several advantages, including high efficiency, environmental friendliness, and the potential for large-scale application. The subcritical water-ethanol mixture is a non-toxic solvent that can be easily recycled and does not produce any harmful waste products. It also provides a sustainable solution for recovering valuable metals from e-waste, which can help reduce the environmental impact of this growing problem.

3.3.3.6 Indirect biorecovery-based approach

The use of an indirect biorecovery-based approach offers a promising and environmentally friendly approach for gallium recovery from low concentration wastewater. The first research to demonstrate the new technology for gallium recovery has been studied. Siderophores, such as desferrioxamine B (DFOB) and desferrioxamine E (DFOE) have been investigated for the selective and sensitive recovery of gallium from wafer fabrication wastewater (Hofmann et al.,

2020; Jain et al., 2019). These natural chelator-siderophores, produced by the bacterium *Streptomyces*, were found to bind gallium with 100% yield and form more stable complexes than other metals, such as zinc. More importantly, this approach could selectively recover gallium without complexing non-target elements, such as arsenic, copper, magnesium, zinc, and calcium (Jain et al., 2019).

The GaLIophore technology, which uses DFOB/DFOE to recover gallium from low concentration wastewater, has shown impressive results. In experiments, more than 90% of gallium decomplexation was achieved and DFOB/E regeneration was achieved with 100% efficiency by using ethylenediamine tetraacetic acid (EDTA) six times. This approach has been successfully applied to the recovery of gallium from wastewater by reversed-phase chromatography, and the recycling of DFOB/E has been demonstrated (Jain et al., 2019). The "GaLIophore technology" has been patented by a German company under the patent number DE102019108803B4 and its potential for widespread application in the field of gallium recovery is an exciting development for the future.

3.4 Indium and gallium recovery from EoL PVs via hydrometallurgical and biohydrometallurgical routes

The production of renewable energy through PVs, or solar panel systems, is a promising approach to mitigate the environmental impacts associated with non-renewable energy sources. However, the sustainability of PV technology is challenged by the scarcity and high demand for TCEs, such as indium and gallium, that are used in PV components. Therefore, it is imperative to establish efficient and cost-effective methods to recover indium and gallium from spent PVs, in order to reduce the dependence on primary resources and minimize the environmental impact (Schmidt et al., 2019).

Unfortunately, the complex structure of PVs, which typically includes layers of different materials and coatings, and the low concentration of TCEs in spent PVs, pose significant challenges for the effective and selective recovery of these elements. As a result, conventional methods of metal extraction from primary resources are often unsuitable or inefficient for PV recycling, and alternative approaches must be explored. Two potential routes for the recovery of indium and gallium from spent PVs are hydrometallurgy and biohydrometallurgy. However, the complexity of the PVs structure and other factors have limited the application of critical metals recovery.

3.4.1 Pre-treatment of EoL PVs

Pre-treatment is a critical step in the recovery of valuable metals from spent PV modules and can be divided into two main stages. The first stage involves selective dismantling to remove hazardous or non-valuable components. This is followed by the second stage, which aims to upgrade or concentrate the target metals through mechanical and physical treatment (Maneesuwannarat, Teamkao, et al., 2016). The treatment process for EoL PVs typically involves dismantling the panels, cutting into smaller pieces, grinding into finer powders, screening through various hole sizes, and finally drying in an oven. While there is limited literature on the treatment of EoL PVs, Savvilotidou and Gidakos (2020) have reported on three methods for pre-concentrating EoL CIS panels after manual dismantling and cutting. These methods include thermal treatment and gravimetric process, mechanical shredding, screening, chemical treatment, and thermal treatment. Among the above methods tested, the first pre-concentration method proved successful in recovering 96.3% of indium from CIS panels. Pre-treatment, therefore, plays a crucial role in the efficient recovery of valuable metals from spent PV modules and can significantly improve the subsequent recovery process.

3.4.2 Indium and gallium leaching from EoL PVs via hydrometallurgical and biohydrometallurgical routes

Table 10 summarizes the literature leaching methods for indium and gallium from spent PVs (GaAs PV, CIGS, and CIS PV).

1364 Table 10 Methods for indium and gallium leaching from spent PVs

E-waste	In and Ga (mg/kg)	Leachant	Optimum conditions (S/L: g/mL)	Leaching yield	Other metals	Reference
Inorganic and organic acid leaching process						
Spent CIS_CuInSe photovoltaic panels	0.02% In	1 M 30% H ₂ SO ₄	1/ 20 of S/L, 90 °C, 1h	87.3% In	Ag, Si	(Savvilitidou and Gidarakos, 2020)
Spent CIGS_CuIn _{0.5} Ga _{0.5} Se ₂	19% In 9% Ga	4 M H ₂ SO ₄	1/10 of S/L, 90 °C, 4 h after annealing with particle size <63 µm	98% In and Ga	Cu, Se	(Lv et al., 2019)
EoL CIGS panel_CuInGaSe ₂	600 In 90 Ga	1M citric acid and 0.4 M H ₂ O ₂	1/10 of S/L, 80 °C, 1 h	> 90% of In and Ga	Cu, Se	(Amato and Beolchini, 2019)
Alkali leaching process						
CIGS chamber waste		7 M NaOH	1/10 of S/L, 60 °C, 3 h	3.37% In 97.26% Ga	Cu	(Ma et al., 2020)
Indirect bioleaching-based process						
GaAs from solar cell waste		<i>Cellulosimicrobium funkei</i> (<i>C. funkei</i>)	Growth supernatant at death phase of <i>C. funkei</i> , 150 rpm agitation, pH 7, 30 °C, 15 days	70% Ga	As	(Maneesuwanarat, Vangnai et al., 2016)

1365

1366 **3.4.2.1 Indium and gallium leaching with acids and alkali**

1367 For CIS PVs, Savvilitidou and Gidarakos (2020) reported that efficient leaching of indium
1368 (87.3% of leaching efficiency) from CIS PVs using sulfuric acid under optimal conditions of a
1369 S/L ratio of 1/20 g/mL at 90 °C for 1 h after thermal pre-treatment and gravimetric separation.
1370 The same leaching technique was also used for indium recovery from LCDs (Savvilitidou et
1371 al., 2015).

1372 For CIGS PVs, the complexity of their structure, as well as the presence of numerous metals,
1373 makes the leaching of indium and gallium more challenging. To address this challenge,
1374 recovery methods combining pyrometallurgical and hydrometallurgical approaches have been
1375 employed (Lv et al., 2019; Ma et al., 2020). In the hydrometallurgical leaching process, H₂SO₄
1376 was used to leach indium and gallium after annealing, and approximately 98% of indium and

gallium could be leached from spent CIGS panels under optimal conditions of 4 M H₂SO₄ (Lv et al., 2019).

Other studies have tested different strong mineral acids (i.e. HCl, H₂SO₄, HNO₃) and organic acids (i.e. citric acid) as leachants in the presence of mobilizing agents, such as H₂O₂ and glucose (Amato and Beolchini, 2019). The results suggest that leaching indium and gallium from EoL CIGS PVs using citric acid and H₂O₂ as a catalyst could lead to high leaching yields of more than 90% at a temperature of 80 °C within 1 h. The use of glucose as a mobilizing agent in combination with citric acid further improved the leaching yield to over 70% in 3 h, while only citric acid leaching achieved a leaching yield of 40% (Amato and Beolchini, 2019). Furthermore, Ma et al. (2020) reported the use of NaOH to separate indium and gallium from indium gallium oxides based on their different dissolution characteristics. The results showed that using a concentration of 7 M NaOH obtained dissolution yields of indium and gallium of 3.37% and 97.26%, respectively. This indicates that a high concentration of NaOH has a strong selectivity for separating indium and gallium, providing a promising method for their future recovery.

3.4.2.2 Indium and gallium bioleaching

Bioleaching has emerged as a promising and environmentally friendly method for recovering indium and gallium from EoL PVs. While research in this field is limited, Maneesuwannarat, Vangnai, et al. (2016) have made significant strides by investigating the use of microorganisms to leach gallium from GaAs scraps found in solar cells. Their study showed the potential of *Cellulosimicrobium funkei* (*C. funkei*) growth medium supernatant for gallium leaching. The presence of various amino acids produced and released by *C. funkei* in the growth medium supernatant was found to contribute to the leaching process based on the ability of *C. funkei* to solubilize gallium from GaAs by producing both organic acids and metabolites that can oxidize or reduce gallium ions. Encouragingly, the research successfully demonstrated the leaching of indium from thin-film GaAs solar cell waste using *C. funkei*, offering a promising and eco-friendly approach. Despite the lengthy incubation period of 15 days, the gallium leaching efficiency remained noteworthy, reaching approximately 70%. Nevertheless, further research is needed to fully uncover the potential of bioleaching in the recovery of indium and gallium from EoL PV panels.

3.4.3 Indium and gallium recovery from EoL PVs via hydrometallurgical and biohydrometallurgical routes

The recovery of valuable metals such as indium and gallium from EoL PVs (CIS and CIGS) is essential to meet the growing demand for these metals in various applications. Several methods have been proposed in the literature to achieve this goal, including hydrometallurgical and biohydrometallurgical routes. This section summarizes some of the main methods reported in the peer-reviewed literature.

For CIS photovoltaic panel leachates, Savvilitidou and Gidarakos (2020) achieved indium recovery by adjusting the pH to 7.0-7.2 using NH_4OH solution for 24 h. They recovered 74.8% of pure indium hydroxide. Similarly, Van den Bossche et al. (2019) reported that more than 99% of the indium could be precipitated by the addition of NaOH after the removal of gallium.

In the case of CIGS material leachate, indium, and gallium were separated from copper by precipitation using NH_4OH solution due to the different precipitation pH values of the metals. Lv et al. (2019) achieved a precipitation efficiency of 99.6% for indium and 99.5% for gallium under optimal conditions of pH 3.5 within 400 rpm stirring at a temperature of 50 °C. The precipitates were then roasted at 800 °C to obtain indium and gallium oxide. The solubility constants of the different products (Cu, Ga, and In) are:

$$\text{Cu}(\text{OH})_2 \quad K_{sp} = 2.2 \times 10^{-20} \quad (20)$$

$$\text{Ga}(\text{OH})_3 \quad K_{sp} = 7.0 \times 10^{-36} \quad (21)$$

$$\text{In}(\text{OH})_3 \quad K_{sp} = 6.3 \times 10^{-34} \quad (22)$$

However, it is difficult to achieve selective precipitation of indium and gallium due to the low solubility constants mentioned above. Therefore, solvent extraction was tested for the separation of indium and gallium after the removal of other metals, such as selenium and copper. Using di-(2-ethylhexyl) phosphoric acid (P204) as an extractant and kerosene as a diluent, Lv et al. (2019) were able to separate indium and gallium with high recovery efficiencies of 97.7% and 97.4%, respectively.

To obtain pure gallium from spent PVs, electrolysis is always used after extraction by hydrometallurgical techniques. Chen et al. (2011) tested nickel-copper and platinum-stainless steel electrolysis to increase the gallium recovery efficiency from GaAs waste of silicon wafer fabs. The results show that the use of platinum-stainless steel could achieve more than 90% of gallium with a purity of 94%, while electrolysis with nickel-copper achieved a recovery yield of 56% of gallium with a purity of 92%. Therefore, platinum-stainless steel electrolysis would be a promising extraction method for gallium recovery that can contribute to significant economic gains in manufacturing.

3.5 Germanium recovery from EoL OFs via hydrometallurgical routes

In the global germanium market, nearly 30% of the total amount of germanium is supplied by obsolete products, particularly from the recycling of electronic devices. Recently, due to the rapid development of optical technologies has increased the demand for fiber optic cables containing germanium (Chen et al., 2017; Ruiz et al., 2018). Meanwhile, germanium is expected to increase in EoL products that can be recycled in the next two decades, as the lifetime of related electrical and electronic equipment is about 20 years. Therefore, the recycling of germanium from EoL OFs is seen as an encouraging way to obtain more germanium and reduce the tension caused by the scarcity of germanium sources. Considering the limited previous research on biohydrometallurgy, this section focuses only on exploring hydrometallurgical routes for germanium recovery from EoL optical fibers.

3.5.1 Pre-treatment of end-of-life OFs

There is a lack of comprehensive reports in the literature on the pre-treatment of spent optical fibers (OFs). However, a noteworthy study by Chen et al. (2017) provides a detailed method for a two-step pre-treatment approach. First, the samples were cut into 1-meter-long pieces using an electric saw. Next, a stripping machine was used to separate the pieces into different sections, including fibers, steel wires, plastic sheaths, and reinforcements. This process allowed the removal of the plastic sheaths, resulting in fiber bundle tubes consisting of glass fibers coated with acrylic resin. In the second pre-treatment step, fibers from the bundle tubes were ground to fine powder. This facilitated compositional analysis and served to streamline the subsequent leaching and extraction processes. In a more recent study, Chen et al. (2020) investigated the use of organic solvents such as acetone and ethanol to soften the plastics adhering to the fiber bundle tubes. The aim of this method was to obtain relatively pure glass fibers, as a plastic coating of more than 50% was found to be detrimental to germanium recovery efficiency. Overall, the research efforts of Chen et al. (2017, 2018b, 2020) shed light on the pre-treatment of spent OFs by providing a comprehensive methodology involving the removal of plastic sheaths and the extraction of glass fibers. The subsequent investigation of organic solvents for plastic softening further contributes to optimizing the recovery efficiency of valuable components from spent OFs.

3.5.2 Germanium leaching from OFs via hydrometallurgical routes

3.5.2.1 Germanium leaching with mineral acids

After the pre-treatment of the sample, there are two different ways to leach germanium from spent OFs (Table 11) (Chen et al., 2017, 2018b, 2020). One is directly leaching by mineral acids, such as HCl, H₂SO₄, HNO₃, and HF. Considering the fact that decreased germanium leaching efficiency and the formation of germanium oxide precipitation in a strong acid solution, 0.1 M H₂SO₄ solution was studied as a leachant (Chen et al., 2017, 2018b, 2020). Since germanium is evenly distributed in materials and doped in silicon, it is necessary to remove or dissolve silicon before recovering germanium (Chen et al., 2018b). In the leaching process, hydrofluoric acid was added to dissolve silicon to extract germanium, as silicon only reacts with hydrofluoric acid. The optimal conditions for germanium and silicon leaching efficiency were achieved by adjusting the S/L ratio to 1/100 g/mL, at a temperature of 25 °C for 3 h and using mixed acids of 0.1M H₂SO₄ and 5% v/v HF, resulting in yields of 98.3% and 99.5% for germanium and silicon, respectively (Chen et al., 2017).

There is an alternative leaching method that involves alkali roasting followed by dilute sulfuric acid leaching. The alkali roasting process converts silica into a soluble form of silicate using chemicals such as NaOH and KOH at a temperature of 500 °C within 2 h. The results show that leaching efficiency was greater than 99.5% when the pH value was lower than 5. This is because several tests show that germanium and silicon would precipitate as the pH approaches neutral (Chen et al., 2018b).

However, the use of hydrofluoric acid in direct leaching and roasting prior to acid leaching has potential drawbacks, such as environmental pollution and increased energy requirements.

Table 11 Methods for germanium leaching and recovery from spent OFs and associated leachates

E-waste	Method	Leachant/Extractant	Optimum conditions (S/L: g/mL; O/A: organic/aqueous phase)	Ge leaching yield	Other metals	Reference
Waste fiber optic cables	Acid leaching	0.1 M H ₂ SO ₄ 5% v/v HF	1/100 of S/L, 25 °C, 3 h	98.3% (100 mg/L) Ge and 99.5% Si leaching	Si, Fe, Mg, and Ca	(Chen et al., 2017)
		0.1 M Trioctylamine (TOA) diluted into kerosene and mixed with 0.2 M tri-n-butyl phosphate (TBP), NaOH	Tartaric acid-germanium mole ratio of 1/4, 1/5 of O/A, pH 2, 5 min of extraction; 1.5 M NaOH, 1/1 of O/A, 5 min of stripping	91.3% extraction, 99.2% stripping		
	Roasting and acid leaching	NaOH, for roasting H ₂ SO ₄ for leaching	NaOH/SiO ₂ mole ratio of 6, 500 °C, 2 h for roasting; 1/40 of S/L, pH < 5 for leaching	> 99.5% Ge leaching		
Waste optical fibers	Solid-phase extraction	IRA900 resin and citric acid for extraction, 1 M HCl for stripping	Citric acid/Ge molar ratio of 4, pH 3 for extracting; 25 °C for stripping	92% extraction 99% stripping	Si, Fe, Mg, and Ca	(Chen et al., 2018b)

3.5.3 Germanium recovery from OFs via hydrometallurgical routes

3.5.3.1 Solvent extraction

Trioctylamine (TOA) has been found to be an effective and cost-effective extractant for germanium recovery (Table 11) (Chen et al., 2017). Prior to extracting germanium from leachate, the addition of tartaric acid, which reacts with germanium to form anion complexes, could improve the efficiency of germanium extraction by increasing the ionic radius of the complexes. Although silicon could react with tartaric acid, its extraction rate was slow and negligible under the given reaction conditions of acid concentration and time. TOA as an extractant was mixed with kerosene while adding tri-n-butyl phosphate (TBP), which could avoid forming the third phase when separating germanium from silicon. The results showed that under optimal conditions (pH 2, organic/aqueous phase ratio of 1/5, TOA and TBP concentration of 0.1 M and 0.2 M, tartaric acid/germanium molar ratio of 5 in 5 min), the germanium recovery efficiency could reach 91.3%, while the silicon extraction efficiency is

1509 less than 10%. After stripping with NaOH or chloride distillation, more than 99% of the
1510 germanium was recovered with GeO_2 or GeCl_4 (Chen et al., 2017).

1511 **3.5.3.2 Solid-phase extraction**

1512 Germanium could be efficiently adsorbed by anionic resins, such as amberlite IRA900 Cl^- and
1513 amberlite IRA958 Cl^- (Table 11) (Chen et al., 2018b). Therefore, anionic resins could be used
1514 to extract germanium with an agent of citric acid, which could react with germanium and form
1515 anion complexes. Chen et al. (2018b) reported the recovery of germanium from spent OFs
1516 using the anion resin IRA900 (Alfa-Aesar) in combination with citric acid agents. Germanium
1517 could be adsorbed in IRA900, while other metals, such as silicon and sodium, were hardly
1518 absorbed at the pH of 3. The sorption efficiency for germanium was found to be 92%, which
1519 was higher than that of other metals. By using HCl, 99% of the germanium could be removed
1520 from the resin. Finally, the concentration and calcination of the stripped germanium led to the
1521 production of GeO_2 with a purity of 99% at 500 °C.

1522 **4 Further research perspectives**

- 1523 1) Expanded research on EoL products as a secondary resource: There is limited research
1524 regarding the recovery of indium, gallium, and germanium from EoL products like PVs
1525 and OFs. While considerable research has been conducted on metal recovery from primary
1526 resources and related industrial wastes, more attention should be directed towards
1527 developing efficient and sustainable recovery methods for these TCEs from secondary
1528 waste streams like e-waste, not only limited to LCDs, LEDs, PVs, and OFs.
- 1529 2) Exploring specific pre-treatment methods: We emphasize the need for exploring specific
1530 pre-treatment methods for different electronic waste. The existing literature often lacks
1531 comprehensive pre-treatment approaches, mainly focusing on specific research targets. For
1532 example, pre-treatment methods for waste LCDs are well-established, but spent LEDs
1533 require more research due to their complex structures of different LED types and limited
1534 concentration methods for the target elements. Additionally, there is a research gap in pre-
1535 treatment methods for waste PVs and OFs. We encourage further research to develop
1536 efficient and customized pre-treatment methods for these specific targets.
- 1537 3) Improvement of biohydrometallurgical processes: Biohydrometallurgy shows great
1538 promise as an environmentally friendly approach for recovering indium, gallium, and
1539 germanium. However, the implementation of biohydrometallurgical processes for these
1540 TCEs from secondary products is still limited and poorly described in previous research.

Further investigation and optimization of these eco-friendly methods are essential to facilitate the "closing the loop" in the recycling of EoL products and ensure a circular economy for TCEs.

- 4) Technology integration: In order to achieve sustainable metal recovery from e-waste, it is crucial to integrate and combine various recovery technologies effectively with the development of a suitable flowsheet for circular hydrometallurgy (Binnemans & Jones, 2022). In addition, developing integrated processes that combine hydrometallurgical and biohydrometallurgical methods can enhance metal recovery efficiency, minimize environmental impact, and maximize mass, energy, space, and time efficiency, like indirect bioleaching and biorecovery of gallium by using siderophores.

5 Conclusions

This review highlights the critical importance of indium, gallium, and germanium in high-tech applications. Sustainable recovery methods from EoL products like LCDs, LEDs, and OFs are being investigated, providing viable solutions to address supply shortages in the EU manufacturing industry and highlighting the potential of EoL products as secondary sources. Waste LCDs contain significant indium, waste LEDs offer promising gallium sources, waste PVs contain indium and gallium, and spent OFs can be a secondary source of germanium. These EoL products offer viable pathways to mitigate TCEs supply shortages.

The recovery of indium, gallium, and germanium from EoL products primarily involves hydrometallurgical and biohydrometallurgical methods, which outcompete pyrometallurgical approaches in terms of performance. The hydrometallurgical approach includes leaching with mineral and organic acids, followed by selective recovery through various extraction methods, with pH, leaching agent, reaction time, temperature, and agitation rate being critical operating factors. Biohydrometallurgy, which employs microorganisms for selective metal recovery, holds promise as an eco-friendly EoL product recycling technique, but further research is necessary before full-scale implementation.

Regarding the recovery of indium from EoL LCDs, pre-treatment involves manual dismantling and comminution to access the ITO film and concentrate indium. Various leaching methods, including strong mineral acids, organic acids (oxalic acid), and bioleaching (*A. ferrooxidans* and *A. thiooxidans*), are explored, achieving a high leaching yield (more than 95% in optimal conditions). Solvent extraction with DEHPA and D₂EHPA, precipitation with ammonium hydroxide, and cementation with zinc powder are effective extraction methods, but challenges remain in separating other elements from indium, like Al, Fe, Zn, and Sn. Solid-phase

extraction, electrochemical separation, and supercritical fluid extraction show promise for high purification. Further research is needed to optimize these techniques for sustainable indium recycling.

Recovering gallium from EoL LEDs presents challenges but is crucial due to its value as a metal source. Pre-treatment is vital for dissociating complex LED structures, with careful handling of toxic arsenic in GaAs LEDs and Na_2CO_3 annealing for GaN LEDs. Various leaching methods using strong mineral acids, alkaline leaching, and organic acids are being explored. HNO_3 and HCl were found to be effective for gallium recovery from GaAs and annealed GaN waste, respectively, achieving 99% leaching yield. Bioleaching with *A. ferrooxidans* shows promise. Solvent extraction and ionic liquid extraction offer high gallium purity but face non-target metal removal challenges. Nanofiltration, precipitation, and supercritical fluid separation provide sustainable options. Further optimization is needed for efficient and eco-friendly gallium recovery. The GaLIophore technology exhibits the potential for high gallium recovery from low concentration wastewater. Each method has distinct advantages and challenges, showing promise for sustainable gallium retrieval from discarded LEDs.

Effective pre-treatment is essential for concentrating target metals from EoL PVs. For indium and gallium leaching, H_2SO_4 and citric acid with H_2O_2 demonstrated high leaching yields (around 90%) for CIGS PVs. NaOH alkali leaching showed a 97% yield for gallium. Indirect bioleaching with *C. funkei* showed potential, achieving approximately 70% gallium extraction yield. NH_4OH precipitation and solvent extraction with P204 achieved high efficiency in indium and gallium separated recovery (> 97%) from CIGS PVs. Platinum-stainless steel electrolysis exhibited promise for pure gallium extraction. Thus, developing efficient and eco-friendly methods is crucial to meet the demand for these valuable metals from EoL PVs.

For the recovery of germanium from EoL OFs, pre-treatment involves removing plastic sheaths and extracting glass fibers to optimize the recovery process. Germanium leaching from waste OFs can be achieved using mineral acids or alkali roasting followed by acid leaching, with a high leaching yield of 98%. Hydrofluoric acid or alkali roasting effectively dissolves silicon, enabling efficient germanium extraction. In the extraction process, solvent extraction using TOA and tartaric acid shows promising results with a 91% germanium recovery rate and minimal silicon extraction (< 10%). Additionally, solid-phase extraction with anionic resins provides an effective method for selective germanium recovery from waste OFs. These hydrometallurgical routes offer environmentally friendly ways to obtain germanium from EoL OFs, contributing to sustainable resource utilization. Although biohydrometallurgical

approaches have not been developed for EoL OFs at present, the development of this field is worth attention.

Overall, the investigation of sustainable recovery technologies for indium, gallium, and germanium from EoL products is crucial for ensuring a stable and long-term supply of these TCEs for high-tech applications. Further advancements in the optimization and implementation of these recovery processes will contribute to efficient and environmentally friendly recycling of e-waste.

6 CRediT authorship contribution statement

Kun Zheng: Conceptualization, Data gathering, Writing – original draft, Writing – review & editing. **Marc F. Benedetti:** Conceptualization, Supervision, Writing – review & editing, Funding acquisition. **Eric D. van Hullebusch:** Conceptualization, Supervision, Writing – review & editing, Funding acquisition.

7 Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary Materials for

Recovery technologies for indium, gallium, and germanium from end-of-life products (electronic waste) – A review

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Text S1 Methodology for literature selection

In this section, we explain the methodology and criteria that were utilized for the selection of relevant literature, with emphasis on traceability and transparency. Our goal is to ensure that the selected articles were highly relevant and recently published (within the last 8 years) regarding the research topic, thereby supporting the foundation of this review.

Data collection was carried out in scientific databases such as ScienceDirect, SpringerLink, and Google Scholar. The search terms include indium (or gallium or germanium) leaching (or bioleaching or extraction or recovery), critical metal recovery, secondary source, electronic waste (or waste electrical and electronic equipment (WEEE) or end-of-life (EoL) products) pre-treatment or hydrometallurgy (or biohydrometallurgy), waste (or spent or end-of-life or discarded) light crystal displays (LCDs) (or LCD monitors/panels/screens/glass), waste (or spent or end-of-life or discarded) light emitting diodes (LEDs) (or GaN/GaAs or MOCVD dust or LED industry), waste (or spent or end-of-life or discarded) photovoltaics (PVs) (or CIS/CIGS panels or solar cell), and waste (or spent or end-of-life or discarded) optical fibers (or fiber optics).

The literature selection process focused exclusively on original research articles while excluding review articles, books, reports, and non-scholarly sources that lacked peer-reviewed research findings. Additionally, we only considered research samples sourced from electronic waste to coordinate with our research theme, categorizing them into distinct sections based on different types of electronic waste. Our methodology also entailed considering pre-treatment methods for concentrating indium, gallium, and germanium from a batch of electronic waste, followed by the evaluation of hydrometallurgical and biohydrometallurgical routes for leaching and extraction, excluding pyrometallurgical processes.

To efficiently manage the selected literature, we employed the Mendeley reference management tool. Finally, we accurately extracted key information related to the research topic, encompassing methods, findings, and limitations, from the chosen literature. This extracted data was thoughtfully integrated into the review article to provide readers with a comprehensive understanding of the research topic.

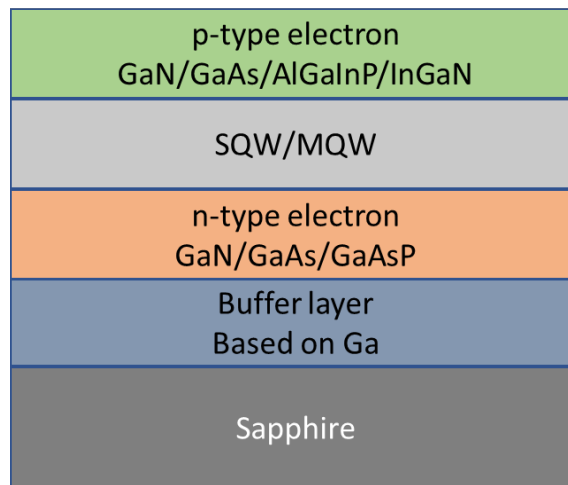


Figure S1 Common LED chip structure. Modified from Tan et al. (2009)

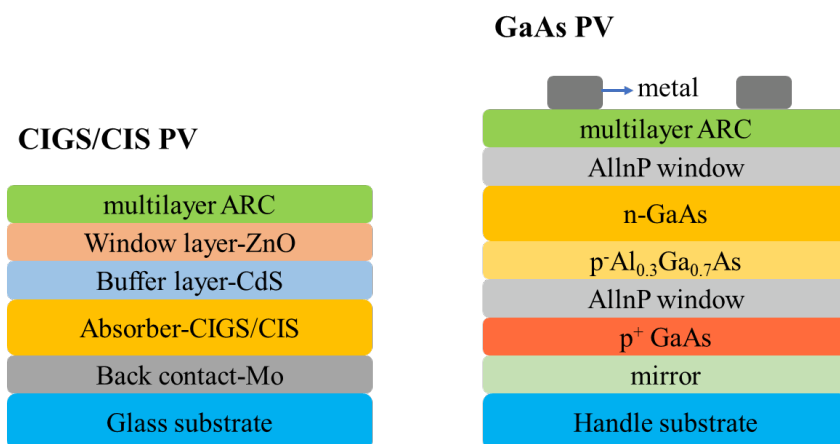


Figure S2 Schematic structure of CIGS PV and GaAs PV. Modified from Polman et al. (2016)

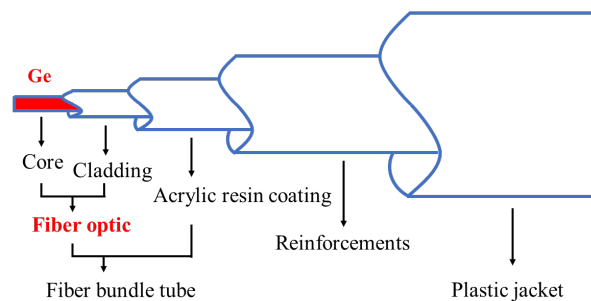


Figure S3 Typical structure of OFs. Modified from Zhang et al. (2019)

Table S1 Summary of indium, gallium, and germanium stability constants with different ligands in the optimal conditions from the literature.

Ligand	Species	log K	Ionic strength and temperature	Reference
Hydroxide	InOH ²⁺	-4.31	0.1 M KNO ₃ , 25 °C	(Wood & Samson, 2006)
	GaOH ²⁺	-2.6	0 M, 25 °C	(Wood & Samson, 2006)
	H ₄ GeO ₄ ⁰	-9.27	0.1 M KNO ₃ , 20 °C	(Wood & Samson, 2006)
	Ge(OH) ₄	55.6	0.1 M KNO ₃ , 25 °C, pH 1-2	(Filella & May, 2023)
Fluoride	InF ²⁺	12.5	1 M NaClO ₄ , 25 °C	(Wood & Samson, 2006)
	GaF ²⁺	5.58	25 °C	(Wood & Samson, 2006)
	GeF ₄	5.17	20 °C	(Filella & May, 2023)
Sulphate	InSO ₄ ⁺	3.04	0 M, 25 °C	(Wood & Samson, 2006)
	GaSO ₄ ⁺	2.77	0 M, 25 °C	(Wood & Samson, 2006)
Phosphate	In(HPO ₄) ⁺	7.4	0.2 M	(Wood & Samson, 2006)
	Ga(HPO ₄) ⁺	7.26	1 M NaClO ₄ , 25 °C	(Wood & Samson, 2006)
Chloride	InCl ²⁺	4.3	2 M NaClO ₄ , 25 °C	(Wood & Samson, 2006)
	GaCl ²⁺	0.01	0.69M HClO ₄ , 20 °C	(Wood & Samson, 2006)
Bisulfide	In(HS) ²⁺	10.5	1 M NaClO ₄ , 25 °C	(Wood & Samson, 2006)
Nitrate	InNO ₃ ²⁺	0.41	> 1 M NO ₃ ⁻	(Ashworth & Frisch, 2017)

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