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Review

Separation Strategies for Indium Recovery: Exploring Solvent Extraction, Ion-Exchange, and Membrane Methods

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Abstract

Indium is a strategically important metal, essential for the production of transparent conductive oxides, flat panel displays, thin-film photovoltaics, and advanced optoelectronic devices. Due to its limited natural abundance and its occurrence in trace amounts alongside other metals in both primary and secondary sources, the recovery of indium through efficient separation techniques has gained increasing attention. This review discusses three major separation strategies for indium recovery: solvent extraction, ion-exchange, and membrane processes, applied to both synthetic solutions and real leachates. D2EHPA has demonstrated its applicability as an effective agent for indium separation, not only in solvent extraction but also as an impregnating agent in polymer resins and membranes. While solvent extraction achieves high recovery rates, ion-exchange resins and membrane-based methods offer significant advantages in terms of reusability, reduced chemical consumption, and minimal environmental impact. The selective separation of indium from impurities such as Fe^{3+} and Sn^{2+} remains a key consideration, which can be addressed by optimizing feed solution conditions or adjusting the selective stripping stages. A comparative overview of these methods is provided, focusing on separation efficiency, operational conditions, and potential integration into close-loop systems. The article highlights recent innovations and outlines the challenges involved in achieving sustainable indium recovery, in line with circular economy principles.

Keywords: indium; leaching; solvent extraction; ion exchange; polymer resin; nanofiltration; membranes; liquid membranes; ionic liquids; recycling; WEEE

1. Introduction

Indium is one of the components essential for materials used in advanced technologies (Table 1). Most of global indium consumption (60% [1], 80% [2]) is used for indium tin oxide (90% In_2O_3–10% SnO_2; ITO) thin films, which combine optical transparency with high electrical conductivity [3]. Owing to these properties, ITO is widely applied in flat-panel display technologies, including liquid crystal displays (LCDs), organic light-emitting diodes (OLEDs), plasma displays, and touch screens, as well as in solar cells and anti-reflective and antistatic coatings [3,4]. According to estimates [5], consumer electronics represent about 51% of total ITO consumption, primarily driven by smartphones, televisions, and tablets, whereas the contribution of automotive displays and instrument clusters is anticipated to grow. In 2025, the global ITO market was valued at about 1.8 billion USD and is expected to increase to near 2.3 billion USD over the subsequent five years.

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Table 1. Indium content in highly technological devices (based on [4,6,7]).

Electronic Device	Indium Content, mg/unit (ppm)	Photovoltaic Cell	Indium Content, mg/unit
Mobile Phone	10 (330 ± 198)	CdTe	15
Smartphone	(25 ± 20)	GaInP	120
Computer	40	GeIn	120
Screen	82	CuInGaSe	120
PC Monitor	(172 ± 24)	Silicon SHJ	47–120 (4.2–10.7 mg/W)
Tablet	(176 ± 93)		
Notebook	(134 ± 95)		
LCD TV	(166 ± 66)		
LED TV	3		
LED Light	30		

Recently, interest in thin-film copper-indium-selenide CIS and copper-indium-gallium-selenide CIGS has also increased due to their high energy conversion efficiency, low fabrication cost and simple covering of both rigid and flexible substrates [8]. Despite their relatively marginal share in photovoltaic panels, the global market for CIGS thin-film solar cells is growing, projected to reach 2.9 billion USD (near 2% market share) in 2026 and 5.4 billion USD by 2033 [9]. Future growth in indium demand is expected to be driven by the increasing use of indium phosphide InP, which plays a crucial role in advanced fiber-optic telecommunication networks associated with next-generation (5G/6G) technologies, as well as in specialized semiconductor materials required for high-performance computing and artificial intelligence applications [10,11].

Although the semiconductor sector is the fastest-growing area of indium applications [12], soldering and brazing continue to account for the large market share [13]. This dominance arises from indium's essential role in electronic manufacturing, where it enables the formation of durable and highly conductive joints used from printed circuit boards and automotive components to aerospace systems and cryogenic equipment.

Demand for indium is reflected in its global production trends. While overall output remains relatively modest, at about 1000 tonnes per year [14], refinery production has exhibited a steady increasing tendency over the past few years (Figure 1a). This growth has been accompanied by a marked increase in indium prices, from about 315 USD/kg in 2020–2021 to about 867 USD/kg in January 2026, driven by constrained supply due to China's export-license cadence, stable consumption in ITO applications, emerging semiconductor uses, and supportive EU and USA policies encouraging stockpiling and supply diversification [15]. China is the leading producer of indium, supplying about 70% of refined metal output worldwide [2] (Figure 2b). At the same time, it holds the largest refined indium reserves, estimated at about 1100 t (2024), corresponding to 61% of the total [16].

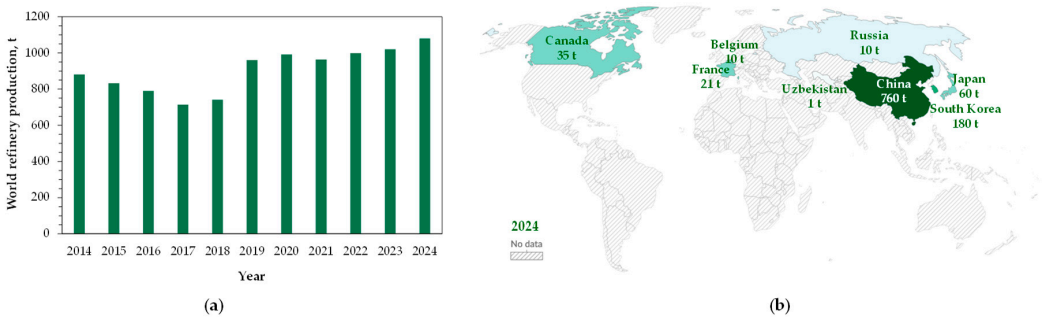


Figure 1. Global refinery production of indium: (**a**) in 2014–2024 (Adapted from Ref. [9]); (**b**) by country in 2024 (Adapted from Ref. [14]; map reprinted from Ref. [16] under License CC BY).

The combination of demand for high-purity indium driven by emerging applications [2,6,12], the high concentration of global production in one region [2,17], and the resulting risk to supply chain continuity has led countries such as the USA [18], Canada, United Kingdom or Australia [19] to classify this metal as critical. Similarly, the European Union designated indium as a critical material starting in 2010 as 81% of its import originated from China [20]. However, the most recent 2023 list [1] has removed it from this category, now classifying indium as a non-critical metal (Figure 2a). This shift reflects the fact that current sourcing of indium within the EU (mainly from France 38%, Belgium 25%, China 14%) now exceeds its consumption, while its economic importance has diminished due to the more precise allocation of applications within the region (Figure 2b).

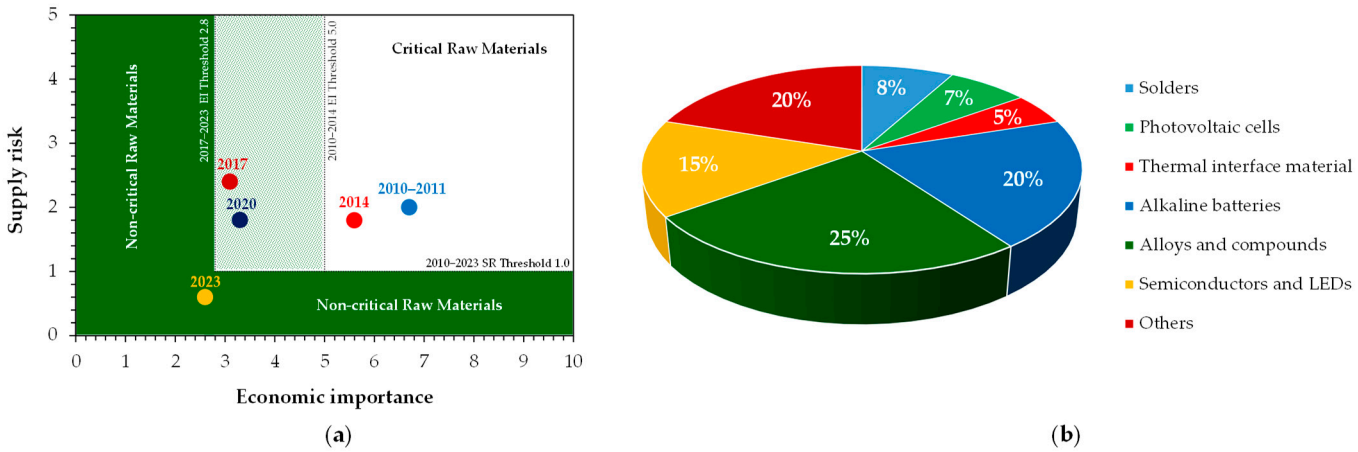


Figure 2. Indium as a raw material for the EU: (**a**) position in the criticality matrix from 2010 to 2023 (based on [1,20]; (**b**) indium applications in 2023 (based on [1]).

Indium is regarded as a relatively scarce metal (0.052 ppm in the Earth's crust [21]) and does not form independent mineral deposits. It is obtained as a by-product, with sphalerite (zinc sulfide) ore representing its principal source (95%), along with some lead, copper and tin minerals [22]. Indium occurs at very low concentrations in natural resources (0.05–1870 ppm, with a mean value of 56 ppm in indium-bearing ore deposits [22]), but also in potentially spent materials (Table 1). Consequently, hydrometallurgical processing yields leachates with indium ions concentrations from a few to several hundred mg/L, whereas major metals typically occur at levels of a few to several tens of g/L (Table 2). As a result, indium separation is technically demanding and requires highly selective and efficient recovery strategies combined with simultaneous preconcentration.

Motivated by these considerations, this review examines three major separation strategies for indium recovery: solvent extraction, ion exchange, and membrane-based processes. The applicability of these techniques is closely linked to metal speciations of aqueous systems; therefore, the selection of ion-capturing extractants and their effectiveness are discussed in relation to leaching liquor composition, the preliminary removal of base metal cations, and the feasibility of subsequent recovery of a high-purity indium product. Particular emphasis is placed on their application in recycling streams for metal recovery from waste materials, as secondary sources currently slightly dominate the global supply of indium (52% in 2023 [2]).

Table 2. Concentration of indium and main accompanying metals in leachates of primary and secondary materials.

Raw Material	Leaching Medium	Indium, mg/L	Base Metals, g/L	Ref.
Sphalerite; 230 ppm In	H_2SO_4	42	Zn 120; Fe 9; Cu 0.6	[23]
Sphalerite; 315 ppm In	Bioleaching: H_2SO_4 + Fe^{3+}	33	Zn 21; Fe 18; As 4; Mn 0.5; Cu 0.4; Cd 0.3	[24]
Pb-Zn-S flotation tailings; 14 ppm In		1.2	Zn 0.7; Fe 10; As 0.5; Mn 0.2; Al 0.1; Cu 0.05	
Flotation silver concentrate *; 649 ppm In	H_2SO_4	99	Zn 95; Fe 16; Cu 1	[25]
In-Ge residue *	H_2SO_4	91	Ge 625; Fe 10; Zn 4; Si 0.3	[26]
ZnO flue dust *	H_2SO_4	2920	Zn 16; As 10; Al 2; Fe 2; Sn 0.5; Mg 0.4	[27]
Zinc smelting slag *	H_2SO_4	26	Zn 10; Fe 3	[28]
LCD panel; 205 ppm	H_2SO_4	201	Sn 0.006	[29]
LCD panel	H_2SO_4	33	Sn 0.004	[30]
LCD panel; 200 ppm	HCl	4357	Al 2; Fe 0.3; Sn 0.2; Cr 0.1	[31]
LCD panel	HCl	160	Fe 2.9; Al 1.2; Sn 0.5; Mn 0.2; Zn 0.1	[32]
LED screen; 107 ppm In	Bioleaching: H_2SO_4 + Fe^{3+}	6.3	Al 3.1; Fe 1.3; Sr 0.2	[33]
CIGS solar cell; 99 ppm In	HNO_3	~1800	Zn 3.8; Cu 1.3; Ga 0.5	[34]
CIGS solar cell; 100 ppm In	HNO_3	41 ± 1	Zn 0.1; Mo, 0.2	[35]

* From zinc hydrometallurgy.

2. Solvent Extraction

Solvent extraction (SX) is a separation technique involving the transfer of ions from an aqueous phase to an immiscible organic phase across a liquid–liquid interface. Upon contact of the two phases, an equilibrium is established, resulting in an unequal distribution of ions between them. The organic phase loaded with the target ions can be further purified through scrubbing to remove co-extracted impurities, followed by back-extraction (stripping) into an aqueous phase using relatively small amounts of a stripping agent, thereby yielding a purified and concentrated product solution. Owing to its high selectivity, which can be tuned by appropriate control of the aqueous phase pH in a given aqueous–organic system, and the fast and reversible nature of mass transfer, solvent extraction can be implemented as an integral part of a nearly closed-loop hydrometallurgical processing route (Figure 3).

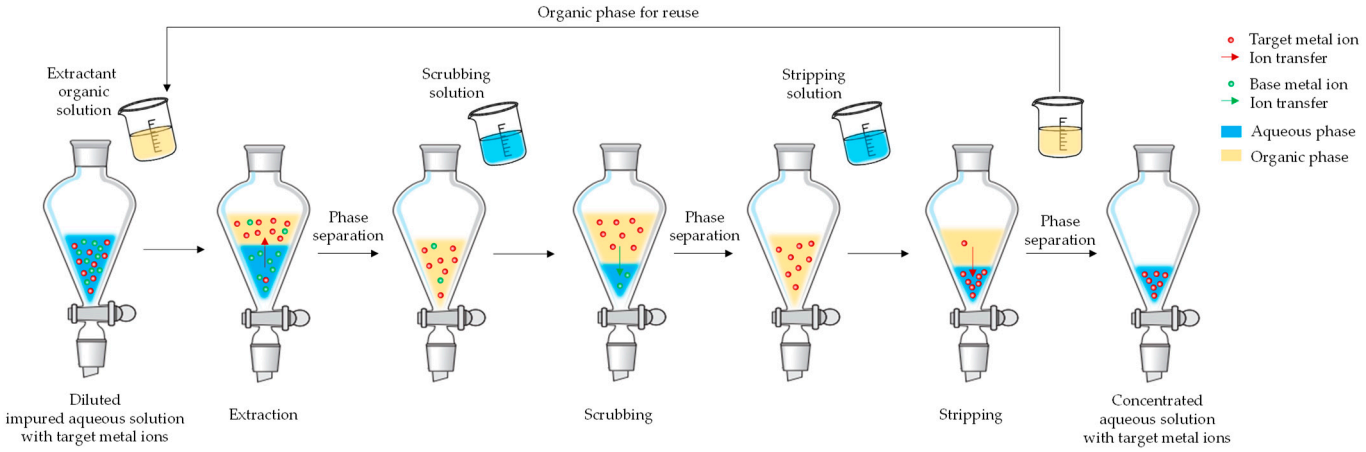


Figure 3. General scheme of solvent extraction.

2.1. Conventional Extractants

Solvent extraction of indium typically employs a variety of commercial organic extractants, which can be classified into several groups according to the mechanism governing metal ion transfer:

- Cationic (acidic) extractants operate via an ion-exchange mechanism, in which metal cations are transferred from the aqueous phase in exchange for H^+ ions released from the extractant molecules. Representative examples include D2EHPA (P204) [26,27,30,33,35–43], Ionquest 801 (also known as P-507 or PC 88A) [38,44], Cyanex 272 [38] and Versatic 10 [40].
- Solvating (neutral) extractants act through solvation of the metal cation, forming electrically neutral complexes that are more soluble in the organic phase than in the aqueous phase. This group includes Cyanex 621 (TOPO) [29], Cyanex 923 (a mixture of four trialkylphosphine oxides) [45,46], N503 [47], and MIBK [48].
- Chelating extractants involve a mechanism similar to that of cationic extractants, characterized by the formation of stable chelate complexes with metal ions in the organic phase. These extractants are mainly hydroximes belonging to the LIX series, such as LIX 63 [40].

In addition to these conventional extractants, recent studies have investigated newly synthesized compounds specifically designed for indium separation from multicomponent solutions, including amino phosphonates [49], acid amide derivatives [34,50] or crown ethers [51]. Figure 4 presents the chemical structures of selected extractants, while Table 3 summarizes their operating conditions and separation efficiencies for indium recovery from both synthetic and real leaching solutions.

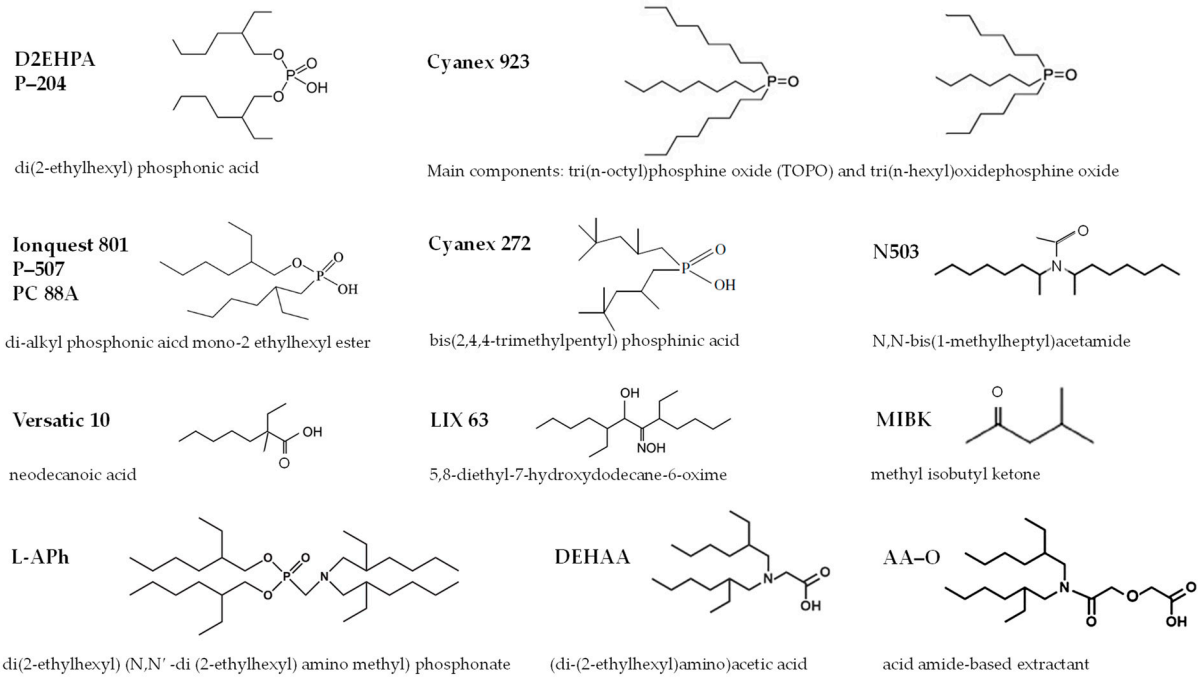


Figure 4. Structures of some extractants used in indium solvent extraction.

D2EHPA is the most extensively investigated extractant for indium recovery [26,27,30,33,35–43], although its mechanism and efficiency strongly depends on the type of solution. Thus, in nitrate and sulfate media, the extraction proceeds according to the reaction described in [37]:

$$[mIn^{3+}]_{aq} + [(2m + 1)(HR)_2]_{org} \leftrightarrow [In_mR_{2(2m + 1)}H_{m + 2}]_{org} + [3mH^+]_{aq} \quad (1)$$

Table 3. Solvent extraction of indium.

Aqueous Phase [1]	Other Ions (In:M) [2]	Extraction Stage	In Extraction Selectivity [3]	In Extraction Efficiency	Stripping Stage	In Stripping Selectivity	In Stripping Efficiency	Ref.
S: HNO_3	Ga^{3+} (1:1), Mo (1:2)	D2EHPA in kerosene	yes, for Ga at pH 1.5	97%	1 M HCl	no data	no data	[35]
S: H_2SO_4	Ga^{3+} (2:1)	D2EHPA in kerosene	S_{Ga} = 900–1300	99.9%	HCl, pH 0.2	no data	95%	[36]
					H_2SO_4, pH 0.2	no data	80%	
L: H_2SO_4 (ITO)	Sn^{2+} (1:25)	D2EHPA in kerosene	no	100%	1.5 M HCl	yes	94%	[37]
S: HCl	Fe^{3+} (1:3)	D2EHPA in kerosene	S_{Fe} = 6–61	95%	2 M HCl	no	45%	[38]
		Ionquest 801 in kerosene	S_{Fe} = 22–26	95%		no	70%	
S: H_2SO_4	Ga^{3+} (1:1)	LIX 63 + Versatic 10 in kerosene	no	~100%	0.05 M H_2SO_4	no	98%	[40]
L: H_2SO_4 (Zn residue)	Zn^{2+}(1:38), Ge^{4+}(22:1), Fe^{2+}(1:3)	D2EHPA in sulfonated kerosene	S_{Zn} = 1093 S_{Ge} = 1994	99%	6 M HCl	no data	98%	[43]
L: H_2SO_4 (Zn residue)	Fe^{2+}(1:130), Zn^{2+}(1:49), Ge^{4+}(1:7),	D2EHPA + YW100 in sulfonated kerosene	no (Ge^{4+})	~100%	4 M HCl	yes	~100%	[26]
L: H_2SO_4 (ZnO)	Zn, Fe, Al	P–507 in sulfonated kerosene + microwaves	yes	97.6%	1.5 M HCl	no data	99%	[44]
S: H_2SO_4	Fe^{3+} (1:10)	Cyanex 923 in toluene	no data	no data	1 M H_2SO_4	no data	95%	[45]
S: HCl				no data			97%	
S: HNO_3				no data			97%	
L: HCl (LCD)	Al, Fe, Cu, Y, Zn, Sn	Cyanex 923 in kerosene	no	97	6 M HNO_3	no	99%	[46]
S: HCl	–	N503 in sulfonated kerosene	no data	99%	H_2O	no data	98%	[47]
S: HCl	Ga^{3+} (1:1)	Ketone MIBK	no	99.8%	H_2O	yes	95%	[48]
S: HCl	Ga^{3+} (1:1)	L-APh in n-heptane	no	~95%	H_2O	no	75%	[49]
		Cextrant 230 in n-heptane	no	~95%	no data	no data	no data	
		BEADP in n-heptane	no	~30%	no data	no data	no data	
L: HNO_3 (CIGS)	Zn^{2+}(1:1), Ga^{3+}(2:1), Cu^{2+}(1:1)	AA–O amic acid-based extractant	no	99%	5 M HCl	yes	99%	[34]
S: NH_4NO_3	–	DEHAA	possible from Ga	90%	1 M HNO_3	no	96%	[50]
S: HCl-KCl	Fe^{3+}, Al^{3+}, Zn^{2+}, Sn^{2+}, Ca^{2+}	Crown ether B18C6	yes	~30%	1 M HCl	no data	98%	[51]

[1] S—synthetic solution; L—actual leachate (leached material). [2] In:M—indium to metal ion concentration ratio in aqueous phase. [3] S_M—separation factor D_{In}/D_M; D is distribution coefficient.

In chloride solutions, the cation-exchange:

$$[mInCl^{2+}]_{aq} + [(m + 1)(HR)_2]_{org} \leftrightarrow [In_mCl_mR_{2(m+1)}H_2]_{org} + [3mH^+]_{aq} \quad (2)$$

is accompanied by a solvation mechanism at high HCl concentrations (above 1 M):

$$[InCl_3]_{aq} + [(HR)_2]_{org} \leftrightarrow [InCl_3 \cdot 2HR]_{org} \quad (3)$$

where $(HR)_2$ is dimeric form of D2EHPA.

Lupi and Pilone [38] reported complete extraction of indium from acidic sulfate and nitrate solutions at pH values above 1, whereas extraction yields of up to 60% were observed in acidic chloride solutions. Other extractants also showed solution-dependent behavior. Thus, at constant pH, indium extraction decreased in the order

HNO_3 > H_2SO_4 > HCl for Cyanex 272 and D2EHPA, and HNO_3 > HCl > H_2SO_4 for Ionquest 801. In contrast, LIX 63 exhibited the highest indium extraction (about 30%) in sulfate media, while virtually no extraction was observed in nitrate-based solutions. Nevertheless, D2EHPA and Ionquest 801 exhibit the most favorable performance in sulfate and nitrate solutions, with Ionquest 801 remaining highly effective even in acidic chloride media. A major drawback of both extractant is the co-extraction of Fe^{3+} ions. For example, when using 15% D2EHPA, nearly complete extraction of In^{3+} (100%) and substantial Fe^{3+} extraction (97%) was observed. This lack of selectivity necessitates additional treatment steps, such as reductive stripping with zinc powder [38] or the reduction in Fe^{3+} to Fe^{2+} using metallic iron [26] before the solvent extraction stage. Interestingly, D2EHPA can exhibit selective indium extraction over gallium ions in nitrate [35] or sulfate [36] media when solvent extraction is carried out under highly acidic conditions, at a pH of about 1.5. Alternatively, selective separation of indium from tin [37] or germanium [26] ions from the loaded organic phase (nonselective extraction stage) can be achieved by using more concentrated HCl solutions (1.5–4 M), with indium being stripped in the first step.

Grigorieva et al. [42] analyzed the role of proton-donor additives to D2EHPA in improving indium stripping from the loaded organic phase. They reported that despite the high indium distribution ratio with D2EHPA (100–1000), modification of the organic phase led to an antagonistic extraction effect. This effect depended significantly on the type and structure of the compounds, as intermolecular associations (H-complexes) were formed between the additives and D2EHPA. Indium extraction decreased in the following order for the additive used: 4-bromophenol > 4-t-butylphenol > octanol, 2-ethylhexanol > 4-nitrophenol > 2-nitrophenol > 2,6-di-t-butylphenol > octanoic acid > Versatic 10. However, these additives facilitated efficient indium stripping from the loaded organic phase.

Improvements in indium separation from accompanying ions using D2EHPA can be achieved by modifying the solvent extraction setup relative to conventional batch systems (e.g., shaking in a separatory funnel, Figure 3). Le et al. [41] demonstrated that in a T-type microreactor (Figure 5a), the aqueous and organic phases flow in a slug-flow regime, forming discrete slugs that travel along the microchannel, resulting in an alternating sequence of aqueous and organic segments. This maximizes the interfacial area, thus enhances extraction efficiency and improves selectivity toward indium when high extractant concentrations (30–35%) are applied. For instance, at a D2EHPA concentration of 35%, the extraction efficiency of In^{3+} reached about 80% in both conventional and microfluidic systems; however, the co-extraction of impurities (Fe^{3+}, Zn^{2+}, Al^{3+}, and Mg^{2+}) decreased from 1–10% in conventional extraction to 1–4% under microfluidic conditions. As a result, the microfluidic method improved the separation factors (Figure 5b), although this effect was strongly pH-dependent and varied markedly within a narrow pH window (0.2–0.8). Compared with conventional extraction, microfluidic extraction reduced the required contact time by half, achieving an indium extraction efficiency of 99% at a contact time of 60 s (30% D2EHPA).

In turn, Chang et al. [27] investigated the separation of In^{3+} and Fe^{3+} ions in sulfate leachate using the same extractant (25% D2EHPA), but with an impinging stream-rotating packed bed contactor. In this setup, both the aqueous and organic phase streams contacted countercurrently, while the mixed phase moved outward and exited the device via centrifugal force. This arrangement resulted in 99% indium extraction with less than 5% iron co-extraction, yielding a separation factor of 3090. However, this effective separation could only be achieved if the iron content remained below 7 g/L, with indium concentrations at 3 g/L. Undoubtedly, this technique outperforms other types of extractors, as it achieved better extraction results for the same feed solutions compared to conventional systems (separatory funnel: 98% In^{3+}, 16% Fe^{3+}, $S_{In/Fe}$ 287; annular centrifugal contactor: 99%

In^{3+}, 7% Fe^{3+}, $S_{In/Fe}$ 1625), while maintaining the same high indium stripping efficiency (99.8 ± 0.1%, 3 M HCl).

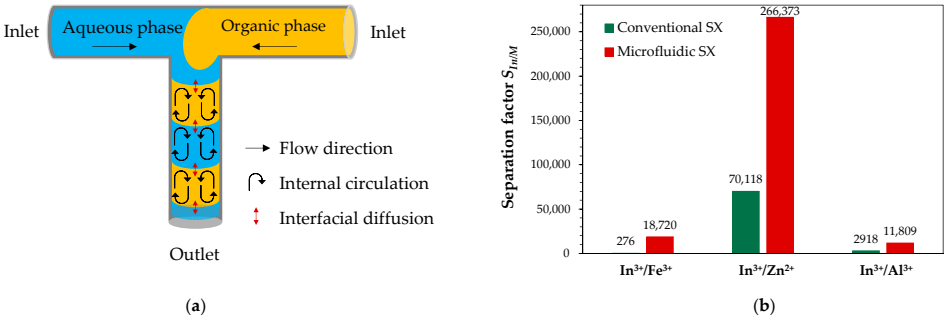


Figure 5. Scheme of T-shape microfluidic reactor (**a**,**b**) comparison of separation factors for conventional and microfluidic solvent extraction with D2EHPA at optimal conditions, adapted from Ref. [41].

Li et al. [44] proposed microwave-assisted heating for both indium extraction from solution using the P507 extractant and subsequent stripping with acid. This approach significantly reduced the time required to reach equilibrium. Under optimized conditions (25% P507, O/A = 1:2, 40 °C, 2 min, 70 W), nearly 98% of indium was extracted, while only 2.5% of iron and less than 1% of aluminum and zinc were co-extracted, resulting in high separation factors ($S_{In/Fe}$ ~8000, $S_{In/Zn}$ ~1330, $S_{In/Al}$ ~4440). Subsequently, more than 99% of indium was stripped under the best process parameters (1.5 M HCl, O/A = 2:1, 40 °C, 3 min, 90 W).

In parallel with innovative developments in extraction equipment and process configurations, significant efforts have been devoted to the chemical synthesis of new extractants. Sasaki et al. [50] synthesized DEHAA (Figure 4) via the reaction of di-2-ethylhexylamine with bromoacetic acid. The resulting extractant exhibited a high indium extraction efficiency in acidic nitrate solutions (pH_{50} 2.5). The presence of amino functionalities played a key role in the selective extraction of indium over gallium and zinc, while maintaining high stripping efficiencies that depended on the stripping medium: 1 M HNO_3 enabled the recovery of 96% of indium and 98% of zinc, whereas 1 M HCl resulted in 95% indium and 86% gallium stripping. More recently, Xu et al. [34] synthesized a new extractant (denoted AA-O, Figure 4) using the same secondary amine and diethanolic anhydride. This amide–acid-based ligand was evaluated for the separation of indium and gallium from CIGS leachates. Two separation protocols were proposed: (i) selective extraction at different pH values (indium at pH 2.9 and gallium at pH 3.4), followed by stripping with 0.5 M HCl; or (ii) co-extraction of indium and gallium at pH 3.4, followed by selective stripping of indium with 5 M HCl and gallium with water. With increasing cycle number, extraction efficiencies showed a slight decline from nearly quantitative values; however, the effect was more pronounced for gallium (about 50% extraction after 9–10 cycles) than for indium, which maintained extraction efficiencies of about 95% after the same number of cycles. In turn, Xu et al. [46] synthesized aminophosphonate extractants for the separation of gallium and indium from chloride media. One of these (denoted as L-APh, Figure 4), demonstrated promising performance with a separation factor $S_{Ga/In}$ of 995. Although the extractant has a higher capacity for gallium than for indium, about 25 g/L In^{3+} can be loaded by 30% extractant (at 33 g/L Ga^{3+}) with stripping performed using water, H_2SO_4, or HNO_3.

Chen et al. [51] leveraged indium's ability to form anionic chloride complexes at high chloride concentrations (0.5 M KCl) to weaken the hydration of In^{3+} ions in solution, which was identified as the primary factor limiting extraction efficiency. The formation of complexes between $InCl_4^-$ and various crown ethers was shown to enhance indium

extraction. Moreover, one of the extractants, benzo-18-crown-6 ether (B18C6), although exhibiting a relatively low extraction efficiency (30%), demonstrated excellent selectivity for In^{3+} over competing metal ions (Fe^{3+}, Al^{3+}, Zn^{2+}, Sn^{2+}, and Ca^{2+}) with their extraction yields remaining below 5%. Additionally, B18C6 showed quantitative stripping (98%) using 1 M HCl.

2.2. Ionic Liquid Extractants

Although traditional extractants used in solvent extraction demonstrate good performance for indium separation from aqueous streams, in recent years, novel "green extractants" have been tested. These include ionic liquids, which can capture targeted ions from aqueous solutions more selectively and efficiently due to the possibility of task-specific design of the extractant molecule by selection of its structural components, i.e., sterically demanding large organic cation and small organic or inorganic anion [52]. Complicated synthesis methods make ionic liquids relatively expensive. However, unlike classical organic phases, ionic liquids exhibit negligible volatility, are non-flammable, do not release vapors, and possess high thermal and chemical stability, thereby increasing the safety of the process implementation. In the context of indium recovery, a series of ionic liquid extractants [28,32,53–58] were explored, and their performance is summarized in Table 4.

Nayak and Devi [53] investigated the extraction of indium from an acid chloride solution using Cyphos IL 101 ($R_3R'PCl$), which can operate under a solvation mechanism, leading to the formation of an indium–ionic liquid complex in the organic phase:

$$[In^{3+} + 3Cl^-]_{aq} + [R_3R'PCl]_{org} \leftrightarrow [R_3R'PInCl_4]_{org} \quad (4)$$

The extraction process was strongly dependent on acid concentration, with nearly complete indium extraction (97%) achieved only at high acid concentrations (2–5 M) at equilibration time within 5–10 min. Among the stripping agents tested, 1 M solutions were more effective than 0.1 M solutions. The efficiency of back-extraction with more concentrated agents increased in the following order: HNO_3 (34%) < HCl (70%) < NH_{3aq} (71%) < H_2SO_4 (100%). Further studies with binary metal solutions showed that indium could be selectively extracted only in the presence of Ni^{2+} ions. Partial selectivity was observed for mixtures with Cu^{2+} (up to 25%) and Al^{3+} (up to 14%), while no selectivity was noted in the presence of Ga^{3+} (99.7%) and Sn^{2+} (99%). In all cases, In^{3+} extraction remained at high levels of 97–100%. The application of Cyphos IL 101 to real LCD panel leachates showed that although the extraction stage was not selective, indium distributed between the raffinate (with Cu^{2+}) and organic phase (with Sn^{2+}). However, selective stripping with 0.1 M H_2SO_4 resulted in obtaining an indium sulfate solution as the final product.

Gómez et al. [54] conducted liquid–liquid extraction using Cyphos IL 101 with various acid-based solutions, demonstrating that indium extractability increases with acid concentration (up to 5 M) and for 5 M acids, the following efficiencies were noted: HNO_3 (~10%) < H_2SO_4 (~20%) < HCl (~90%). For the HCl-based solution, various diluents (pentane, hexane, heptane, cyclohexane, toluene) were also tested, with toluene being selected as the optimal choice. The authors proposed an anion-exchange extraction mechanism for indium extraction under these conditions.

$$[In^{3+} + 3Cl^- + H^+]_{aq} + [R_3R'PCl]_{org} \leftrightarrow [HCl]_{aq} + [R_3R'P{\cdot}InCl_3]_{org} \quad (5)$$

Table 4. Solvent extraction of indium with ionic liquids.

Aqueous Phase [1]	Other Ions	Extraction Stage [2]	In Extraction Selectivity	In Extraction Efficiency	Stripping Stage	In Stripping Selectivity	In Stripping Efficiency	Ref.
L: HCl (LCD)	Sn^{2+}, Cu^{2+}	Cyphos IL 101 in kerosene	no	~100%	0.1 M H_2SO_4	yes	99.7%	[53]
L: HCl (LCD)	Al^{3+}, Zn^{2+}, Cu^{2+}	Cyphos IL 101 in toluene	no	~100%	0.1 M H_2SO_4	yes	97%	[54]
S: HCl	–	Cyphos IL 104 in toluene	no data	98%	0.1 M HCl	no data	100%	[55]
L: HCl (LCD)	Al^{3}+, Ca^{2+}, Fe^{3+}, Sn^{2+}, Sr^{2+}, Zn^{2+}, Mn^{2+}	Cyphos IL 104 in toluene	no	95%	0.001M HNO_3	yes	99%	[32]
L: [Hbet][Tf_2N]–H_2O (LCD)	Fe^{2+}	[Hbet][Tf_2N]	no	98%	0.5 M $H_2C_2O_4$	no	95%	[56]
S: H_2SO_4	Cr^{3+}, Fe^{3+}, Sn^{2+}, Cr^{6+}, Zn^{2+}, Mn^{2+}	[PJMTH][HSO_4] in Solvesso 100	no	94–98%	0.1 M H_2SO_4	no data	no data	[57]
S: HCl	Cu^{2+}, Fe^{3+}, Sn^{4+}, Co^{2+}, Zn^{2+}, Ni^{2+}	[A324H][Cl] in Solvesso 100	no	80–100%	0.1 M HCl	no data	100%	[58]
	–	Aliquat 336 in Solvesso 100	no data	60–100%	no data	no data	no data	
S: H_2SO_4	Fe^{2+}	[BMIm][PF_6] + TBP + D2EHPA	yes	98%	1.5 M HCl	no data	100%	[28]

[1] S—synthetic solution; L—actual leachate (leached material). [2] Abbreviations and names of ionic liquids; Cyphos IL 101—trihexyl (tetradecyl) phosphonium chloride; Cyphos IL 104—trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate; [Hbet][Tf_2N]—Betainum bis(trifluoromethylsulfonyl)imide; [PJMTH][HSO_4]—amine Primene JMT bisulfate; [A324H][Cl]—Tri-isooctyl amine chloride; Aliquat 336—N-methyl-N,N-dioctyloctan-1-aminium chloride; [BMIm][PF_6]—1-butyl-3-methyl-imidazolium hexafluorophosphate as the optimal choice.

The applicability of Cyphos IL 101 was also verified for real LCD leachates, and as before [53], no indium selectivity was achieved during liquid–liquid extraction. In^{3+} ions, along with Zn^{2+}, Pb^{2+}, Cu^{2+}, Cd^{2+}, and Al^{3+}, accumulated in the organic phase at levels above 98%, while Ga^{3+} and Cr^{3+} were partially distributed between the aqueous and organic phases. Meanwhile, Ti^{4+}, Sr^{2+}, Ni^{2+}, Mn^{2+}, Mg^{2+}, Fe^{2+}, and Ba^{2+} remained in the aqueous raffinate. Notably, ascorbic acid was used to reduce all Fe^{3+} to Fe^{2+}, preventing iron extraction into the organic phase. Complete stripping of indium was achieved with diluted H_2SO_4, which enabled the production of final products (metal or oxide) with a minimum purity of 99%.

Deferm et al. [59] analyzed indium chlorocomplexes present in aqueous and organic phases during extraction into undiluted ionic liquids with chloride anions: Cyphos IL 101 and Aliquat 336. They found that in HCl solutions (up to 12 M), indium exists as mixed complexes $[In(H_2O)_{6-n}Cl_n]^{3-n}$ ($0 \leq n \leq 6$), while in the ionic liquid, it exists as the $InCl_4^-$ complex. Thus, for both ionic liquids, the following extraction mechanism was confirmed:

$$[In(H_2O)_6{}^{3+}]_{aq} \leftrightarrow [In(H_2O)_{6-n}Cl_n{}^{3-n}]_{aq} \qquad 1 \leq n \leq 6 \tag{6}$$

$$[InCl_3(H_2O)_3]_{aq} \leftrightarrow [InCl_3(H_2O)_3]_{IL} \tag{7}$$

$$[InCl_3(H_2O)_3]_{IL} + [[IL^+][Cl^-]]_{IL} \leftrightarrow [[IL^+][InCl_4{}^-]]_{IL} + [3H_2O]_{aq} \tag{8}$$

where IL is undiluted ionic liquid.

Nayak and Devi [55] analyzed the liquid–liquid extraction of indium with Cyphos IL 104 from an acid chloride solution. Although this ionic liquid is a phosphinate salt ($R_3R'PA$), similar to Cyphos IL 101 (a chloride-type salt), it effectively captured metal ions (97%) only from more concentrated acids (2–5 M) through anion exchange. In this case, however, the efficiency of back-extraction with 1 M stripping agents increased in the following order: H_2SO_4 (24%) < NH_{3aq} (29%) < HNO_3 (81%) < HCl (100%). In turn, Dhiman and Gupta [32] investigated different acids as the aqueous phase and found that the extraction of In^{3+}

decreases sharply when the concentration exceeds 7 M for HCl (from 99%) and 1 M for HNO_3 (from 70%), but remains almost stable (30–45%) for H_2SO_4 at various concentrations (up to 10 M). For extraction from an acid chloride solution, a different mechanism was proposed, involving the formation of an adduct with two extractant molecules:

$$[In^{3+} + 3Cl^-]_{aq} + [2R_3R'PA]_{org} \leftrightarrow [2R_3R'PA \cdot InCl_3]_{org} \quad (9)$$

The applicability of Cyphos IL 104 was also tested for LCD leachates, where In^{3+} ions were extracted along with Zn^{2+} and Sn^{2+}. However, selectivity was achieved during the stripping stage by using 1 M HNO_3 for indium, 4 M HNO_3 for zinc, and concentrated HCl for tin.

Alugasil et al. [57,58] synthesized two ionic liquids using alkyl primary (Primene JMT) or tertiary (Hostarex A324) amines as precursors for [PJMTH][HSO_4] and [A324H][Cl], respectively. Both ionic liquids were investigated for indium extraction and process selectivity. [PJMTH][HSO_4] was highly efficient for indium extraction (89–98%) but lacked selectivity for Fe^{3+}, Cr^{3+}, Cr^{6+}, and Sn^{2+}, while high selectivity was obtained for Zn^{2+} and Mn^{2+} from acid sulfate solutions [57]. In this case, a general solvating mechanism for extraction was proposed, involving the formation of an adduct $([PJMTH\text{-}SO_4]_p)_q(In_2(SO_4)_3)$ in the organic phase, with stoichiometry dependent on H_2SO_4 concentration. In turn, anion exchange was proposed for indium extraction with [A324H][Cl] [58], leading to the formation of the [A324H][$InCl_4$] complex in the organic phase. This extractant was not selective and was more efficient at higher HCl concentrations in the aqueous solution reaching even complete indium extraction. However, its performance was inferior to Cyphos IL 101 and comparable to Aliquat 336. HCl was suitable as a stripping agent for both ionic liquids.

Luo et al. [56] synthesized the [Hbet][Tf_2N] ionic liquid and used it in a two-phase mixture with acidic water for the extraction of metals from waste LCDs:

$$6[Hbet][Tf_2N] + In_2O_3 \rightarrow 2[In(Hbet)_3][Tf_2N]_3 + 3H_2O \quad (10)$$

Although this process was not indium-selective, the ionic liquid was regenerated by stripping metals with oxalic acid. While all indium was recovered as an oxalate salt, the purity of the final product was not reported.

Gao et al. [28] tested different combinations of extracting systems to separate In^{3+}, Zn^{2+}, and Fe^{3+} ions from sulfuric acid solutinon. They used a mixture of the ionic liquid [BMIm][PF_6], TBP, and D2EHPA (P204) for the selective extraction of indium (97%), leaving iron and zinc ions in the raffinate. In this mixture, TBP acted as a diluent for the ionic liquid, as the latter does not dissolve in D2EHPA, although TBP itself does not function as an extractant. D2EHPA, however, is not selective (97% In, 19% Fe, 4% Zn). TBP and [BMIm][PF_6] together inhibited the –OH activity of D2EHPA, which suppressed the extraction of iron ions. Thus, the main indium extraction in the organic mixture involved the formation of an adduct within cation exchange:

$$[InSO_4^+]_{aq} + [2(HA)_2]_{org} \rightarrow [H^+]_{aq} + [InSO_4A \cdot (HA)_3]_{org} \quad (11)$$

where HA represents D2EHPA molecule.

3. Ion Exchange

Ion exchange (IX) is used for the separation, purification, and concentration of metal ions from aqueous solutions passed through a solid polymeric resin bed placed in a column (Figure 6). During the contact between the feed solution and the resin, the solution ions are captured by the solid exchanger, replacing them with an equivalent number of similarly

charged mobile ions from the resin. The resin bed, now loaded (saturated) with the target ions, is washed with water to remove any slimes, followed by an elution step in which the captured ions are displaced from their sites and flushed out of the column into the aqueous phase using relatively small amounts of an eluting agent. This step simultaneously restores the resin sites to their original states, thereby yielding a purified and concentrated product solution for further target metal recovery.

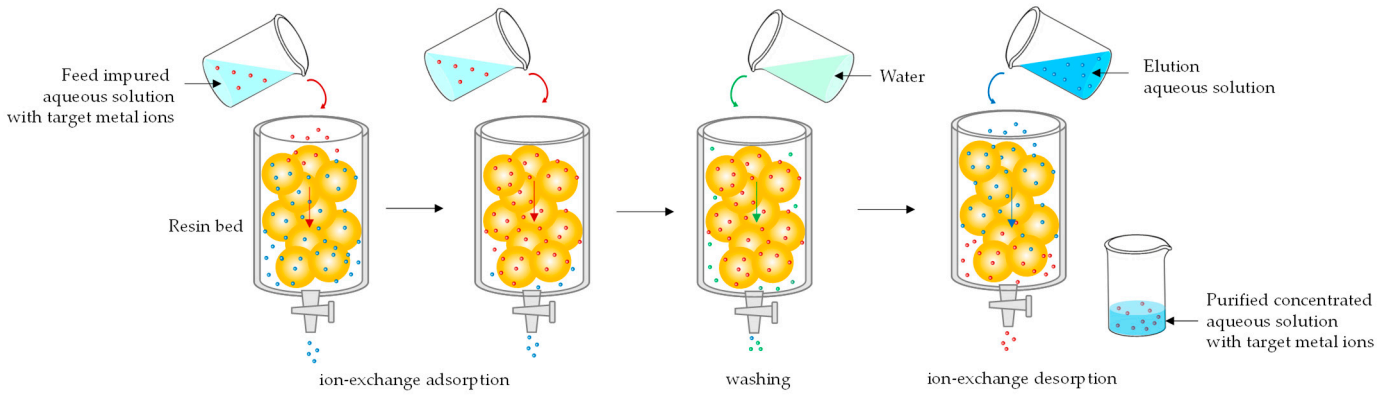


Figure 6. General scheme of ion-exchange separation with solid resin.

3.1. Polymeric Resins

Polymeric resins are composed of crosslinked polymere chains with anchored functional groups for ion exchange (either cationic or anionic) or chelating properties. Their sorption properties (Table 5) are governed not only by the solution pH but also by the form of indium present in the feed solution, such as simple metal cations and cationic or anionic complexes. Fortes et al. [60] compared the sorption capacity of In^{3+} and Fe^{2+} ions from acidic sulfate solutions (pH 0.5–2) on chelating resins (Ionac SR-5 with imidoacetic acid groups, Ionac SR-12 with diphosphonic acid groups, and S950 with phosphonic acid groups) and strong acid cation-exchange resin (Amberlite IR-120P). The sorption of indium ions from the binary solution on chelating resins was around 20% (2h contact time), while iron ions were also captured by the resin but at levels below 10%. The selectivity of the chelating resin SR-5 was higher than that of SR-12, while S950 and Amberlite were not selective.

Illés and Kékesi [31] used an unspecified anion-exchange resin for the recovery of indium from real leachate of LCDs. They utilized the fact that metal ions in acidic solutions with high chloride concentrations (HCl + NaCl, 5–6 M Cl^-) form anionic complexes. After loading the anion-exchange resin, the chromatographic column was washed with a 2 M Cl^- solution to eliminate some impurities. Further reduction in the chloride concentration to 0.25 M enabled selective stripping of indium, while the remaining metal ions (Zn, Sn, Bi) were removed with 1 M NaOH. The pure indium chloride solution was then used for electrowinning to produce metallic indium with a purity of 99.9997%.

Marinho et al. [61] developed a method for the selective recovery of metals from spent $PtSnIn/Al_2O_3$ catalyst. The material was leached with aqua regia, and the metals were subsequently sorbed using anion exchange resins (Amberlite IRA-400, Amberlite IRA-420, Dowex 1, and Amberjet 4200). Although sorption of metal chlorocomplexes was not selective, the metals could be eluted sequentially by using $Na_2S_2O_3$ for Pt, ascorbic acid for Sn, and EDTA for In, with the metal concentrations in the eluate increased in the order In > Pt > Sn.

Zhao et al. [62] enhanced the separation of indium from cadmium, copper, and zinc by forming only indium anionic chlorocomplexes in a water-acetone medium at low chloride concentrations. They tested two resins: cationic (Diaion CR11) and anionic

(Dowex 1 × 8), and different compositions of feed solutions. These solutions were HCl-based aqueous systems enriched with LiCl, with or without acetone. It was found that the recovery and purity of indium increased under the following conditions: aqueous solution without LiCl addition and cationic resin (63% recovery, 73% purity) < aqueous solution with LiCl addition and anionic resin (59% recovery, 87% purity) < aqueous-acetone solution with LiCl addition and anionic resin (84% recovery, 99% purity).

In turn, Kwak et al. [63] synthesized a new resin, poly(vinylphosphonic acid-co-acrylic acid), for indium separation at a pH of 8 (solution type not specified). Under optimal conditions, the maximum sorption capacity was 0.78 mmol/g. The preparation of the resin and its characterization were detailed, but the ion-exchangeable sorption mechanism was not provided.

3.2. Impregnated Polymeric Resins

Improvement in indium sorption on ion-exchange solid resins can be achieved by impregnation with solvents to enhance sorption and desorption kinetics. Fortin-Lecomte [64] tested a series of resins with different types and functional groups: cationic (Lewatit SP112, Amberlite IR 120), chelating (Lewatit TP207, TP260, Amberlite IRC 748, Puromet MTS9300), and anionic (Reilex HPQ), as well as impregnated resins (Lewatit VP OC 1026, TP 272). None of these resins were selective, but some exhibited a high sorption capacity for indium (over 80%), in the order: TP260 > VP OC 1026 > TP 207 > SP112. The selected resin for further studies was Lewatit VP OC 1026 impregnated with a minimum of 30% D2EHPA. This system was verified for its potential in separating indium from real LCD leachate. The metal ion uptake within the resin was near 76% indium, but also 51% tin and 45% molybdenum. Subsequent elution with 1 M HCl removed 74% indium, which was the dominant metal sorbed by the resin. The resulting solution contained over 200 mg/L of indium ions and less than 2 mg/L of other impurities (Fe, Al, Ca).

Li et al. [65] used the resin Cl-P204, impregnated with D2EHPA, for the separation of indium, gallium, and zinc from real leachate of gallium-indium waste material. The resin was highly effective for indium uptake (nearly 100%), but it was not selective, as 50% of tin was also captured. Stripping with HCl solutions in a series of columns allowed for the separation of indium and gallium, achieving 99% recovery of both metals.

An unconventional method was proposed by Roosendal et al. [66], who developed a process for the separation of indium from an iron-rich matrix solution. They used a supported ionic liquid phase, synthesized by impregnating Amberlite XAD-16N resin with the iodide form of the quaternary ammonium salt Aliquat 336 [A336][I]. This system utilized the formation of mixed complexes indium with iodide, which were selectively extracted into the ionic liquid. Due to the low stability of iron iodide in aqueous medium, this manner proved effective for indium separation. Tests conducted with both synthetic and real goethite leachates confirmed selective indium separation with a selectivity factor of $S_{In/Fe}$ of 5400. Among the stripping agents tested (HCl, H_2SO_4, H_3PO_4, citric acid at different concentrations), complete stripping of indium was achieved with recommended H_2SO_4 solution.

Table 5. Sorption of indium on ion-exchange resins.

Aqueous Phase [1]	Other Ions	Sorption Stage [2]	In Sorption Selectivity	In Sorption Efficiency [3]	Elution Stage	In Elution Selectivity	In Elution Efficiency	Ref.
S: H_2SO_4	Fe^{2+}, Fe^{3+}	Ionac SR-5 (Ch)	partial	20–40%	–	–	–	[60]
		Ionac SR-12 (Ch)	partial	10–20%	–	–	–	
		S950 (Ch)	no	10%	–	–	–	
		Amberlite IR-120P (C)	no	10%	–			
L: HCl (LCD)	Al^{3+}, Fe^{3+}, Sn^{2+}, Cr^{3+}, Zn^{2+}, Ni^{2+}, Cu^{2+}, Pb^{2+}	no data (A)	no	80%	HCl + NaCl (0.25 M Cl^-)	yes	no data	[31]
L: HCl (catalyst)	Pt^{4+}, Sn^{2+}, Al^{3+}	Amberlite IRA-400AR (A)	no	EF 13	no data	yes	no data	[61]
		Amberlite IRA-420 (A)	no	EF 19	0.1 M EDTA	yes	99%	
		Dowex 1 (A)	no	EF 20	no data	yes	no data	
		Amberjet 4200 Cl (A)	no	EF 18	0.1 M EDTA	yes	99%	
S: HCl (isotope target)	Cd^{2+}, Cu^{2+}, Zn^{2+}	Diaion CR11 (C)	no	63%	no data	no data	no data	[62]
		Dowex 1 × 8 (A)	no	59%	no data	no data	no data	
		Dowex 1 × 8 (A)/ water acetone	yes	84%	HCl	no data	no data	
L: H_2SO_4 (LCD)	Al^{3+}, Fe^{3+}, Sn^{2+}, Cr^{3+}, Zn^{2+}, Ni^{2+}, Mo^{3+}, Cu^{2+}	Levatit VP OC 1062	no	76%	1 M HCl	yes	74%	[64]
L: HNO_3 (Ga–In waste)	Ge^{3+}, Sn^{2+}, Zn^{2+}	CL-P204	no	~100%	3 M HCl	no	100%	[65]
S: HCl	Fe^{3+}	Amberlite XAD-16N—[A336][I]	yes	95%	0.1 M H_2SO_4	yes	100%	[66]

[1] S—synthetic solution; L—actual leachate (leached material). [2] Abbreviations for ion-exchange resins in parenthesis: C—cationic, A—anionic, Ch—chelating. [3] EF—enrichment factor.

4. Membrane Methods

Membranes are thin barriers (solid or liquid) that allow for the preferential transport of ions (or compounds) from one aqueous solution to another without the need for chemicals to separate target ions from impurities. The transport of species through membranes is driven by differences in pressure, concentration, or electrical potential on both sides of the membrane, depending on the membrane's pore size, fixed charges, or chemical affinity. Due to the variety of membrane types and configurations, several strategies have been proposed for indium separation from ionic mixture solutions, mainly utilizing nanoporous, ion-selective or liquid membranes (Figure 7).

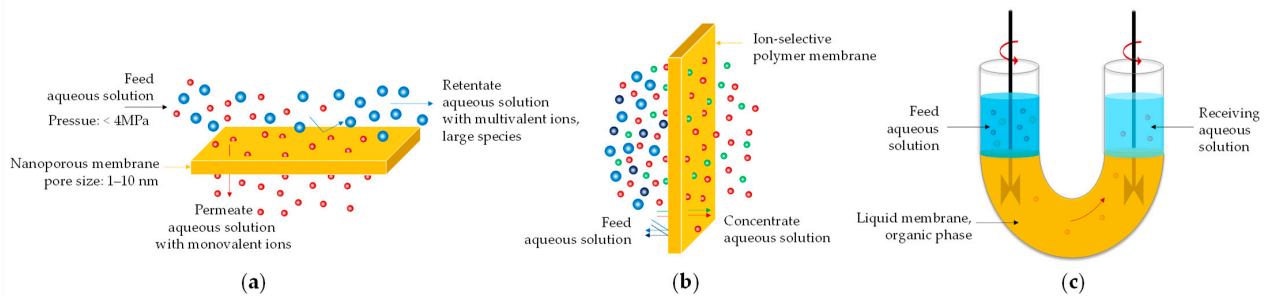


Figure 7. General scheme of ion separation through: (**a**) nanofiltration; (**b**) ion-exchange membrane; (**c**) bulk liquid membrane.

4.1. Nanofiltration

Nanofiltration is a common technique for the separation of mono- and multivalent ions in water effluents [67]. It is recognized as an energy-efficient process that can selectively separate ions based on size sieving and Donnan exclusion effects (Figure 7a). Wu et al. [68,69]

investigated the separation of In^{3+} ions from univalent sodium cations in chloride solutions using different membranes: NTR7450 (sulfonated polysulfone, negative surface charge), ES10 (aromatic polyamides, negative surface charge), and ES10C (aromatic polyamides, positive surface charge). They demonstrated that indium complexation significantly affects nanofiltration performance, as indium can form different ionic species with increased solution pH, including aqua complexes, anionic hydroxocomplexes, and polymeric hydrolysis products. This self-polymerization behavior is particularly important, as changes in indium nanofiltration can occur even in the absence of other inorganic or organic substances. In a consequence, as the feed solution is aged (up to 10 h), the rejection rate of indium gradually increased from 64% to 88%, due to the conversion of dissociated/hydrated indium into hydroxide, which can be effectively removed by the membrane. With increasing indium concentration in the feed solution, the rejection rates decreased in all tested membranes, which could be attributed to concentration polarization and ion-shielding effects. The best operating conditions for indium nanofiltration occurred at neutral pH, achieving 100% indium separation, while under acidic conditions, the performance of membranes with a negative surface charge decreased due to the change in indium speciation to the positively charged In^{3+} species.

Werner et al. [70] investigated the nanofiltration of indium and germanium sulfate solutions at different pH levels (2–12) using flat sheet membranes NP010 (polyethersulfone, negative membrane charge, pore radius 1.22 nm) and NF99HF (polyamide thin-film composite on polyester support, positive membrane charge, pore diameter 0.43 nm). They found that both cations could be separated by pH variation, which was related to changes in the speciation of the metals (formation of neutral or charged hydroxocomplexes at different pH ranges) and the membrane charge. It was shown that germanium did not exhibit pH-dependent separation behavior with the NP010 membrane, where permeate flux was dominated by indium at pH values above 4. In contrast, the NF99HF membrane enabled selective separation between pH 2 and 8, with germanium being enriched in the permeate.

Lahti et al. [71] developed a process for indium recovery from waste LCD panels by incorporating nanofiltration as an intermediate step between leaching and subsequent solvent extraction (Figure 8). They tested three membranes (Desal KH, AMS 3014, and AMS 3012) for indium preconcentration in aqueous solution before the subsequent indium purification. Indium retention increased for the tested membranes in the following order: AMS 3012 (84%) < Desal KH (89%) < AMS 3014 (94%). Two-step nanofiltration with the AMS 3014 retentate achieved a fivefold increase in indium concentration compared to the leaching liquor (677 mg/L), losing only 29 mg/L of indium in the permeates. However, the solution also contained highly concentrated impurity metal cations such as Al^{3+}, Cu^{2+}, and Fe^{3+} (6 g/L in retentate in comparison to 0.7 g/L in leachate). An additional positive aspect of nanofiltration was the reduction in organic impurities by 62%, while also reducing chemical and water consumption.

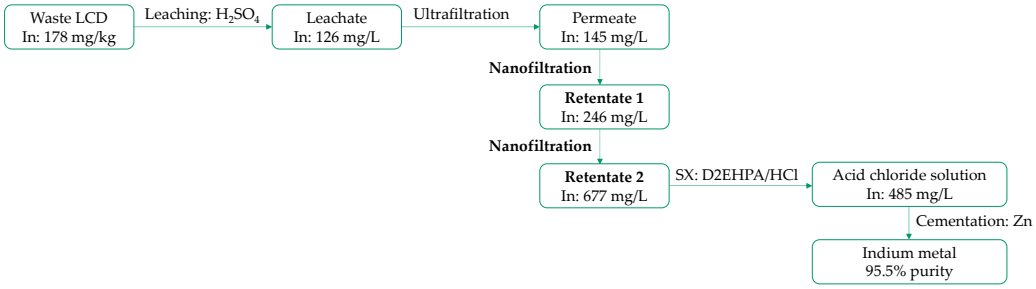


Figure 8. Scheme of indium preconcentration using nanofiltration in hydrometallurgical treatment of waste LCD (ultrafiltration step for removal polymeric material). Adapted from Ref. [71].

4.2. Ion-Exchange Membranes

Ion-exchange membranes consist of crosslinked polymeric chains with incorporated ionizable functional groups, enabling the selective binding and transport of oppositely charged ions (counterions) while repelling similarly charged ions (co-ions) through Donnan exclusion (Figure 7b). The movement of ions across the membrane is driven by concentration gradients (dialysis) or potential differences (electrodialysis). With their exceptional selectivity (86–99%), these membranes find applications in diverse fields, ranging from the treatment of aqueous solutions to energy-related processes [72].

Wang et al. [73] synthesized an amino-phosphorylated nanofiber membrane for the selective absorptive separation of indium ions from acidic chloride solutions. The sorption capacity (max. 55 mg/g) increased with the solution pH, with the highest performance observed at pH 3. These changes were correlated with the competitive behavior of H^+ ions in more acidic conditions on one hand, and the transformation of In^{3+} ions into $In(OH)_2^-$ or $In(OH)_3$ species at less acidic conditions on the other. The membrane demonstrated very high selectivity for indium separation from lead, zinc, copper, and iron ions, both in binary solutions and five-component mixtures, with separation factors ranging from 200 to 460.

De-la-Cruz-Moreno et al. [74] compared two methods for indium extraction from leaching solutions of jarosite residues from zinc refineries: solvent extraction with D2EHPA and separation using a polymer inclusion membrane with D2EHPA immobilized within a PVC matrix. The final indium concentration in aqueous solution from the solvent extraction process (97 mg/L, 83% recovery) was slightly lower than that from the membrane separation method (110 mg/L, 100% recovery). The latter method offered additional advantages such as high reusability, lower cost, minimal environmental pollution, and simple operation.

In turn, Kim et al. [75] designed an electrodialysis system using cation-exchange (Neosepta CMX) and bipolar (Neosepta BP-1) membranes to electrically desorb indium ions from the inorganic adsorbent VSB-5 (99 mg In/g). They found that chemical indium desorption reached 80% at pH 2 or lower, while electrical desorption reached 60% at a pH of 4 or lower, under comparable equilibrium duration times. However, electrochemical desorption ultimately showed higher efficiency than the chemical process at the same pH.

4.3. Liquid Membranes

Liquid membranes combine the solvent extraction and stripping stages into a single process. The simplest configuration (Figure 7c) typically consists of aqueous solutions as the feed and stripping phases, separated by an organic liquid phase (membrane) [76]. These systems are characterized by non-equilibrium mass transfer, meaning that metal ion separation is not limited by equilibrium conditions, as in traditional solvent extraction. There are various examples of using liquid membranes for indium separation within different module designs.

Kondo et al. [77] investigated indium separation from gallium using a supported liquid membrane containing diisostearylphosphoric acid as a carrier (in n-heptane diluent), impregnated into a porous tetrafluoroethylene film. An acidic nitrate feed solution was used as the feed, and concentrated nitric acid was employed as the stripping solution. They found that the extraction rate was limited by the interfacial reaction between $In(OH)^{2+}$ and the extractant. The permeation process was constrained by film diffusion in the aqueous feed solution and the interfacial reaction. Indium was selectively separated from gallium ions, with a separation factor ranging from 15 to 22. Further studies [78] focused on the separation and concentration of indium ions using an emulsion liquid membrane with the same mobile carrier. It was found that the stability of the membrane depended on the concentration of the emulsifier (Span 80), temperature, and agitation rate. Indium was

quantitatively extracted within 20 min, but the reaction was limited by the same factors as in the previous module system.

In turn, Dang et al. [79] studied two separation systems: (i) traditional solvent extraction and (ii) a hydrophobic hollow-fiber module system with an organic phase composed of D2EHPA extractant (in Isopar L diluent, with n-dodecanol as a modifier) and HCl solution as the stripping agent. The membrane system showed slightly higher indium recovery, almost achieving complete indium recovery (80% for solvent extraction), due to the larger contact area between the organic and aqueous phases within the strip dispersion. Further, Huang et al. [80] developed a method for indium recovery from LCDs using ultrasound-assisted leaching (in H_2SO_4), followed by supported liquid membrane extraction. In the second stage, they used a similar hollow-fiber membrane system as in the previous study [79]. The efficiencies of supported liquid membrane extractions were 80 $\pm$ 2% and were only slightly dependent on the D2EHPA fraction (5–20%) and HCl concentration (2–6 M). The overall recovery rate of indium from waste LCDs was close to 80%, and the indium purity of the final product solution was almost 100%.

5. Conclusions

Indium remains an essential metal for advanced technologies, particularly in the production of electronic devices and photovoltaic panels. Given its critical role in these fields, the demand for indium is expected to increase in the coming years. However, both natural and secondary sources contain only trace amounts of recoverable indium, requiring the development and application of specialized separation methods. Various techniques for indium recovery have been explored in research works. Methods such as solvent extraction, ion-exchange, and membrane processes have shown promising results in selectively separating indium from complex aqueous solutions. Among the most efficient techniques, solvent extraction using D2EHPA has demonstrated high recovery rates, while ion-exchange resins and membrane-based methods offer advantages in terms of reusability, reduced chemical consumption, and consequently, lower environmental impact. Despite these advancements, each method has limitations, particularly in selectively separating indium from impurities (especially Fe^{3+} and Sn^{2+}). However, these challenges can be overcome through proper conditioning of the feed solution (e.g., reducing Fe^{3+} to Fe^{2+}) or by optimizing the conditions during the selective stripping stage (e.g., for Sn^{2+}).

It is important to note that each of the discussed techniques has inherent operational and technical limitations that must be considered when designing recovery processes (Table 6). Nevertheless, further research and development are necessary to enhance the selectivity, efficiency, and scalability of these methods. In this regard, membrane-based methods appear to be the most promising for further development due to their simplicity and significantly reduced use of organic reagents. However, combining these methods or developing hybrid systems could offer more effective solutions for large-scale indium recovery, contributing to sustainable resource management and meeting the growing demand for this critical metal in technological applications.

A crucial step in evaluating the effectiveness of indium separation methods is testing them on real leachates obtained from the processing of actual waste materials (ITO, LCD, CIG/CIGS, etc.). Such solutions are based on different acids and contain multiple metal ions at varying concentrations, reflecting realistic industrial conditions. This approach allows for assessment of both the selectivity and robustness of the chosen method in complex systems. Experiments with synthetic solutions, while useful for preliminary parameter optimization, do not fully capture challenges arising from competing ions or chemical variability in real leachates.

Table 6. Assessment of indium separation strategies.

Method	Advantages	Disadvantages
Solvent Extraction	Selective separation of target metal, versatile for many systems, adaptable to different conditions, scalable from lab to industry, low cost with simple equipment, high efficiency, easy phase separation, allows for continuous operation, enables purification to high-purity products, fast extraction kinetics	Uses flammable/toxic organic solvents, requires large solvent volumes, potential solvent loss or contamination, sometimes slow for certain systems, can generate hazardous waste, sensitive to emulsion formation, requires careful control of pH and temperature, limited effectiveness for very dilute solutions
Ion exchange	High selectivity for specific ions, efficient even at low concentrations, allows for continuous operation, can achieve high purity products, reversible and regenerable resins, adaptable to different pH and temperature conditions, minimal use of hazardous solvents, easy scale-up from lab to industrial processes, rapid kinetics in many systems	High cost of resins, limited capacity (requires frequent regeneration), sensitive to fouling and clogging, not applicable for very concentrated solutions, performance affected by competing ions, requires careful pH and temperature control, disposal of spent resin can be challenging
Membranes	High selectivity for target ions, operates at ambient conditions, minimal chemical consumption, continuous operation possible, scalable from lab to industrial scale, can concentrate and/or purify solutions, environmentally friendly with low waste generation, adaptable to different feed compositions	Membrane fouling, scaling or clogging from particulates, limited chemical/thermal stability, high initial investment, gradual loss of selectivity or permeability, sensitivity to extreme pH or oxidizing agents, frequent maintenance and cleaning needed, not always effective for very dilute solutions, limited lifetime, reducing efficiency, potential incompatibility with viscous or high-concentration feeds, high membrane cost

An additional important aspect in the recovery of indium is the choice of the final product, whether as the pure metal or as a chemical compound. This decision depends on market price, industrial demand, and the intended application of the recovered material. The selected form of indium directly influences the choice of recovery method. For instance, producing metallic indium typically involves processes such as electrodeposition or thermal reduction in chemical compound, while indium compounds may be obtained through controlled precipitation or crystallization. Therefore, aligning the recovery strategy with the desired product ensures both economic viability and technical efficiency of the overall process.

The next stage involves extending the methods beyond the laboratory, allowing for assessment of their efficiency and stability under conditions that more closely reflect industrial practice. This stage requires optimization of operational parameters to ensure high selectivity and efficient separation while maintaining technological and economic feasibility, as well as minimizing environmental impact by promoting a closed-loop hydrometallurgical recycling. It also allows for the identification of potential limitations, such as loss of selectivity, contamination, or mass transfer issues at the pilot scale, which may not be evident under laboratory conditions.

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