Review

Polymer-Based Extracting Materials in the Green Recycling of Rare Earth Elements: A Review

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ABSTRACT: Rare earth elements (REEs) are becoming increasingly important in the development of modern and green energy technologies with the demand for REEs predicted to grow in the foreseeable future. The importance of REEs lies in their unique physiochemical properties, which cannot be reproduced using other elements. REEs are sourced through mining, with global exploration of additional commercially viable mining sites still ongoing. However, there is a growing need for recycling of REEs due to the current supply of REEs not matching the growing demand, the environmental impact of REE mining and processing (the so-called "balance problem"), and the generation of large volumes of harmful electronic waste (e-waste). Industrial REE processing is mainly carried out by hydrometallurgy processes, particularly solvent extraction (SX) and ion exchange (IX) technologies. However, these methods have a significant environmental impact due to their intensive use of harmful and nonsustainable reagents. This Review highlights the development of approaches involving polymer-based extracting materials for REE manufacturing as more sustainable alternatives to current industrial REE processing methods. These materials include supported liquid membranes (SLMs), solvent impregnated resins (SIRs), macro and micro capsules, polymer inclusion membranes (PIMs), and micro polymer inclusion beads (μPIBs). Polymer-based extracting materials have the advantage of more economical regent usage while applying the same extractants used in commercial SX, enabling applications analogous to the current industrial process. These materials can be fabricated by a variety of methods in a diverse range of physical formats, with the advantages and disadvantages of each material type described and discussed in this Review along with their applications to REE processing, including e-waste recycling and mineral processing.
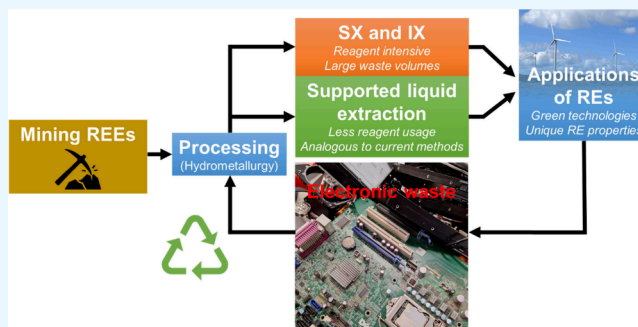
1. INTRODUCTION

1.1. Rare Earth Elements (REEs). Rare earth elements (REEs), as defined by the International Union of Pure and Applied Chemistry (IUPAC), predominantly consist of the lanthanides (Lns) La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu, but also include Sc and Y, elements commonly found alongside the lanthanides in mineral deposits.[1,2] Despite the misnomer that REEs are "rare", they are not especially so, the term first having been created in the 19th century when very few "rare earth" containing mineral deposits had been discovered.[2] Hence, when REEs were first isolated and studied, their abundance was genuinely rare when compared to the quantities of other known elements.[1,2] Despite retaining the title "rare", REEs are almost just as abundant in the earth's crust as some of the most common industrial metals, namely, Cr, Ni, Cu, Zn, Mo, and Sn.[3] This Review briefly outlines the importance and supply of REEs, the growing need for their recycling from end-of-life (EOL) electronic waste (e-waste), followed by a description of current industrial-scale processing methods (section 2), and finally alternative technologies (sections 3 and 4). These technologies involve the use of polymer-based materials incorporating extractant reagents, which are currently being developed and researched. This Review focuses on their applications to the recycling of REEs.

1.2. REEs in Technology. REE applications are set to grow rapidly in the near future due to their significant roles in the development of green technologies for sustainable global economies,[1,2,4−6] such as implementation in wind turbines as a means to generate energy, battery technologies to store it, efficient lighting to enable productive energy usage, screen displays, and electric vehicles (EVs).[5,7] REEs have also facilitated the miniaturization of technology products such as computers, lasers, and screen displays by enabling the

development of smaller and more efficient components.[2,4,7] Industrial processes also rely on REEs, which play important roles as catalysts and in polishing powders but also as additives in specialized metal alloys, glasses, and ceramics.[2,4] The properties of REEs arise largely from their Ln 4f electron orbitals, which are shielded by external 5s and 5p electron orbitals, enabling the REEs' unique magnetic (i.e., their unpaired 4f electrons responsible for strong paramagnetism) and optical (i.e., sharp emission and absorbance bands) properties.[2,8−10] These unique physiochemical properties cannot be replicated by other elements and have given rise to indispensable REE applications, which global society now heavily relies on.[1,2,4−6] Further applications of REEs are predicted to emerge over the coming decades, which will be accompanied by an increasing demand for higher purity and a wider range of REEs.[2,4,11,12]

1.3. Supply of REEs. Despite their relatively common abundance, finding suitable REE mineral deposits of economic value is still challenging, with extensive global REE mineral exploration still taking place today.[4,6,13,14] REEs first became well-known to the general public during the so-called REE crisis in 2010, when China began to restrict REE production and export through the introduction of export tariffs and quotas, enforcing environmental regulations, and no longer providing new mining licenses.[1,15,16] Importantly, at this stage, China accounted for over 95% of global REE production, having dominated the market since the mid-1990s.[15−17] Hence, global manufacturers no longer had access to the high volume of cheap REEs previously provided by China, causing REE market prices to spike significantly.[4,15,16,18]

Although China's export tariffs and quotas were eventually overturned and prices decreased in the following years, the so-called REE crisis prompted the global community to diversify its supply of REEs, with the critical REEs, namely, Y, Nd, Dy, Tb, and Eu, having now been highlighted as valuable and vulnerable resources, specifically for Europe, the U.S., and Japan.[1,15,16,18]

Current global REE production is considerable, presently measuring at hundreds of thousands of tons of annual rare earth oxide (REO) production and having already exceeded 100 000 t of REOs annually since the early 2000s.[19−21] Although there are hundreds of different REE minerals, only a few are of commercial value, specifically the phosphate minerals monazite ($(Ce, La, Y, Th) PO_4$), xenotime (YPO_4), and carbonate bastnäsite $(La, Ce, Y) F CO_3$.[22] Presently, the large majority of REE mining reserves and operations currently supplying REEs is in China. However, China's share in this production has decreased from over 95% of global production in 2010 to 58% in 2020,[17,20] as shown in Table 1. Other than China, significant global reserves have also been located in the

U.S., Canada, Australia, Russia, Brazil, India, Myanmar, Greenland, Madagascar, South Africa, Tanzania, Thailand, and Vietnam.[19,20] Since 2012, additional exploration in Australia, Canada, Greenland, and most recently Sweden and the U.S. has demonstrated that many more commercial REE mineral deposits are likely to be found.[13,23−25] The U.S., Australia, Myanmar, and Thailand are currently among the top 5 REO producers with a global share in 2020 of 16%, 9%, 13%, and 2%, respectively,[19,20] compared to having no REO production taking place in 2010,[17] demonstrating that the REE crisis has prompted additional exploration for REE minerals internationally.[14,26] The REO production of these countries in 2010 and 2020 is compared in Table 1.

Thus, although China is still currently the main global producer and holds a majority of currently known REE deposits,[19,20] a significant number of undiscovered REE mineral deposits are expected to be present around the globe, with even deep ocean deposits being considered viable.[1,4]

1.4. Environmental Impacts of REE Mining. There is a growing concern regarding increasing concentrations of REEs in the environment and the resulting implications for ecosystems and human health,[27−29] especially when considering the limited understanding of these implications compared to those of other industrial metals.[27,30] Currently, the main sources of environmental REE contamination are open cut mining, industrial processing effluents, and mine tailings,[2,29,31,32] with some REEs also having been detected leaching from urban and industrial e-waste disposal sites.[4] REE ores can also contain radioactive compounds, such as U or Th, which are also released into the environment from REE mining operations.[2,4,28] Increases in anthropogenic REE concentrations within areas surrounding mining operations and waterways downstream from these operations have already been detected, along with observed REE bioaccumulation in humans residing around and/or working at REE mining sites.[4,28,32,33] This has resulted in a number of studies of the bioaccumulation of REEs in human hair, blood, urine, brain, bone, liver, and lungs.[27,28] REE accumulation in humans has been linked to cytogenetic damage to sperm sex cells in humans, oxidative stress induced by redox active REEs, damaged respiratory tracts, and heart disease.[4,28,29,32,33] Exposure routes for REEs have been identified including contaminated soil, dust, water, and even food,[27,29] with crops like rice being particularly susceptible to REE accumulation.[4] The impact of high REE concentrations on plants and ecosystems is also becoming apparent, Thomas et al. having extensively studied the effect of La^{3+}, Ce^{3+}, and Y^{3+} on plant germination and biomass development, with concerns for plant health upon exposure to high REE concentrations.[34] The limited number of studies on environmental indicator species, along with a poor understanding of the toxicity thresholds for REEs, have also been widely highlighted with concern.[27−29] Thus, these large knowledge gaps provide a strong incentive to find alternative sources of REEs to reduce global dependence on REE mining and minimize generation of waste containing REEs.

1.5. Alternative REE Sources and the "Balance Problem". Various industrial waste products have been investigated as potential sources of REEs, including red mud from aluminum processing and phosphor gypsum from phosphorus production.[6,32,35] Fly ash from coal fired power stations can also contain commercially viable concentrations of

Table 1. U.S. Geological Survey of Global REE Production as REO in 2010 versus 2020[17,20]

country	2010 production (t)	% share	2020 production (t)	% share
China	130000	97	140000	58
U.S.		0	39000	16
Australia		0	21000	9
Myanmar		0	31000	13
Thailand		0	3600	2
other	3400	3	5400	2
total	133400	100	240000	100

Table 2. Reagent Classes and Molecular Formulas of Common Industrial REE Extractants Used in SX Processes[a]

reagent class	molecular formula	extractant
carboxylic acid	$(R_1 \cdot R_2 \cdot CH_3) \cdot C \cdot COOH$	versatic acids:
		$R_1 + R_2 = C_7$, Versatic 10;
		$R_1 + R_2 = C_6-C_8$, Versatic 911
	$(R_1 \cdot R_2 \cdot R_3 \cdot R_4) \cdot (CH_2)_n COOH$	naphthenic acids:
		R_1-R_4: varied alkyl groups
organophosphorus acids	$(R_1 \cdot R_2) \cdot POOH$	phosphoric acids:
		$R_1 = R_2 = C_4H_9CH(C_2H_5)CH_2O-$, di-2-ethylhexylphosphoric acid (D2EHPA)
		phosphonic acids:
		$R_1 = C_4H_9CH(C_2H_5)CH_2O-$, $R_2 = C_4H_9CH(C_2H_5)CH_2-$, 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (EHEHPA, HEHEHP, P507, PC88A)
		phosphinic acids:
		$R_1 = R_2 = C_4H_9CH(C_2H_5)CH_2-$, di-2-ethylhexylphosphinic acid (P227)
		$R_1 = R_2 = CH_3(CH_2)_3CH_2CH(CH_3)CH_2-$, di-2,4,4-trimethylpentylphosphinic acid (Cyanex 272)
	$(R_1 \cdot R_2) \cdot PSOH$	monothiophosphinic acids:
		$R_1 = R_2 = CH_3(CH_2)_3CH_2CH(CH_3)CH_2-$, di-2,4,4-trimethylpentyl-monothiophosphinic acid (Cyanex 302)
	$(R_1 \cdot R_2) \cdot PSSH$	dithiophosphinic acids:
		$R_1 = R_2 = CH_3(CH_2)_3CH_2CH(CH_3)CH_2-$, di-2,4,4-trimethylpentyl-dithiophosphinic acid (Cyanex 301)
chelating exchangers	$R_1 \cdot (CO) \cdot CH_2 \cdot (CO) \cdot R_2$	β-diketones:
		$R_1 = R-C_6H_5$, $R_2 = CH_3(CH_2)_5-$, R: alkyl group (LIX 54)
solvating extractants	$(R_1 \cdot R_2 \cdot R_3) \cdot PO$	phosphorus esters:
		$R_1 = R_2 = R_3 = CH_2(CH_2)_2CH_2O-$, tri-n-butyl-phosphate (TBP)
		$R_1 = R_2 = CH_2(CH_2)_2CH_2O-$, $R_3 = CH_2(CH_2)_2CH_2-$, dibutylbutylphosphonate (DBBP)
		phosphine oxides:
		$R_1 = R_2 = R_3 = CH_2(CH_2)_6CH_2-$, tri-n-octylphosphine oxide (TOPO, Cyanex 921, 923)
anion exchanger	$(R_1 \cdot R_2 \cdot R_3) \cdot NCH_3Cl$	primary amines:
		$R = (CH_3)_3C(CH)_2C(CH_3)_2)_4$ (Primene JMT, N1923)
		quaternary amines: $R_1 = R_2 = R_3 = C_8-C_{10}$ mixture (Aliquat 336, Adogen 464)

[a]Reproduced with permission from ref 2. Copyright 2015 Taylor and Francis Group.

REEs, with some coal deposits already containing high or even commercially viable REE concentrations.[4,36] REEs can also be produced as byproducts of U, Fe, and Ti mining operations, where REEs are secondary products after being enriched in the mine tailings or drainage.[32,35] Some REE mine tailings still contain commercially viable REO levels, including Mountain Pass (U.S.), which has tailings containing REO concentrations of 3–5%.[32] However, these sources alone are not sufficient to satisfy future REE demands, particularly regarding the critical REE supply.

Market pressure and increasing complications in REE supply chains have led researchers into the area of REE recycling from EOL e-waste, which is now a major topic within REE research.[12,15,36−38] Moreover, the volume of e-waste produced globally every year is increasing, with spent electronic devices such as mobile phones, computers, and laptops predominantly ending up in landfill, a trend which is predicted to grow significantly in the near future.[39,40] Rene et al. stated that in 2019 alone, global e-waste generation was 53.6 million metric tons, and that e-waste generation would increase by 33% over the next decade as the use of electronic devices increases.[40]

Despite increasing e-waste generation, there has been little improvement in the recycling of REEs from e-waste as reported by Binnemans et al. in 2013 that less than 1% of REEs were recycled.[15,38,41] The slow development of REE recycling projects is due to the presence of REEs in electronics at low concentrations and only in specific components, making them difficult to isolate from the bulk e-waste material.[12,37,38] Handling and environmental storage protocols are also a contributing factor to the high cost of e-waste recycling in developed nations.[40] Hence, until recently, the economic

benefit of recycling REEs has been marginal, but rising REE market prices are set to make REE recycling a much more economically viable venture.[4,37,38] The cumulative stockpile of viable REE e-waste resources (NiMH batteries, lamp phosphors, and REE permanent magnets (REPMs)) globally in 2020 was estimated by Mudali et al. to be 375 000 metric tons, of which 29 167 metric tons could be available REEs.[38] Thus, REE recycling projects in many developed countries are said to be approaching maturity and are set to be applied to industrial scale REE recycling in the near future.[38]

The development of REE recycling methods would have numerous advantages, the most important being the avoidance of "wasting" REEs, which could be used to service future technological demands, particularly critical REEs, such as Y, Nd, Dy, Tb, and Eu.[15,38,39] Second, recycling REEs would help solve the so-called balance problem.[15] The balance problem is unique to REEs and describes the disparity between the demand for specific critical REEs and the natural abundance of other REEs with which they occur, leading to the production of other REEs at a surplus.[15,42] This is currently most noticeable with Nd, one of the most commonly used REEs,[12] which is required for REPMs. However, to mine and process the required Nd, large amounts of La and Ce are produced in excess of global demand,[12,42] which could be avoided if Nd were recycled. Third, recycling REEs could have a lower environmental impact than mining and ore processing since REEs are already purified prior to their use in electronic components. As such, their recycling could be less chemically intensive and thus presents less of an environmental hazard. Recycling of e-waste would also reduce the environmental impact of harmful elements like REEs being released into the

environment after leaking from waste disposal sites[4,39,43] or being released from operational mining sites.[2,29,31,32]

There has been a significant amount of research into the leaching and digestion of REEs from EOL e-wastes,[4,37,38,44−46] focusing on the recovery of REPMs from computer hard drives, which have the highest recyclable REE content (viz., Pr, Nd, and Dy);[12,45,47,48] NiMH batteries as a source of La, but also Ce, Nd, Pr, and Y;[49,50] and fluorescent light tubes as a source of primarily Eu and Y, but also Tb, Gd, La, and Ce.[46,51−54] Other potential REE sources that could be recycled are glass polishing powders, catalysts, some small electrical components, and even some REE-containing glass materials.[15] However, less research interest exists in REE recovery from these sources since they are less widely available and can be more difficult to successfully remove REEs from.[38]

2. INDUSTRIAL PROCESSING OF REEs

2.1. Commercial Industrial Processing of REEs.
Currently, the most common and economically viable method for processing REEs is hydrometallurgy, where ores or e-waste are digested in strong acidic or alkaline solutions before processing.[37,38] Pyrometallurgy has also been widely applied to e-waste recycling,[38] but it is energy intensive[37] and emits significant quantities of toxic gases.[36] Hydrometallurgy techniques applied to commercial REE separation have varied over time and include selective oxidation, selective reduction, fractional crystallization, fractional precipitation, ion exchange (IX), and solvent extraction (SX), with IX and SX being the predominant separation techniques applied.[2,22]

SX is the most commonly used method because it can process larger volumes of material and is not very energy intensive,[2,37] thus making SX a more cost-effective method for separating REEs, even when the desired purity requires numerous separation stages as can be the case with industrial REE processing.[4,22]

2.2. Solvent Extraction (SX) of REEs.
Due to the diversity and complexity of REE ores, there are numerous commercial extraction methods, which have been developed for separating REEs, requiring a variety of different extractants, shown in Table 2.[22,55] The most common and widely used extractants are organophosphorus acid extractants such as di(2-ethylhexyl) phosphoric acid (D2EHPA) and 2-ethylhexyl-phosphonic acid mono-2-ethylhexyl ester (EHEHPA), carboxylic acids such as neodecanoic acid (Versatic 10) and naphthenic acid, solvating extractants such as tributyl phosphate (TBP), and quaternary ammonium anion exchange extractants such as Aliquat 336 (A336).[2,22,55] For high selectivity and thus greater purification capabilities, the acidic extractants, that is, the organophosphorus acids and carboxylic acids, are commonly used.[22,55] These acidic extractants form dimers in nonpolar solvents, and the SX process for the extraction of REEs can be described by eq 1.[22,55,56]

$$REE^{3+}{}_{(aq)} + 3H_2A_{2(org)} \rightleftharpoons REE(HA_2)_{3(org)} + 3H^+{}_{(aq)}$$
(1)
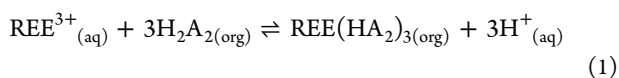
where REE is the rare earth element, H_2A_2 represents the organic acid dimer, and (aq) and (org) refer to the aqueous and organic phases, respectively.

Carboxylic acids are commercially applied to separating Y^{3+} from REEs, as the steric hindrance of the carboxylic acid affects the Y^{3+} extraction behavior.[55,56] For the separation of individual REEs, organophosphorus acids are recommended,

namely, D2EHPA and EHEHPA.[22,55] In particular, D2EHPA is capable of separating and purifying all REEs,[22,55] and it is therefore the most commonly used extractant for SX processing of REE mine ores. The application of D2EHPA in SX for EOL e-waste REE recycling has also been demonstrated to be effective, including for processing REPMs.[2,12,37]

Anion exchange extractants are also applied industrially, requiring the REEs to form an anionic complex with anions such as SO_4^-, Cl^-, SCN^-, or NO_3^- anions, although NO_3^- is most commonly used followed by SCN^-.[22] The extraction of REEs by anion exchange extractants is depicted by eq 2:[2,57]

$$REE^{3+}{}_{(aq)} + 3A^-{}_{(aq)} + R_4N{\cdot}A_{(org)} \rightleftharpoons (R_4N{\cdot}REE(A)_4)_{(org)}$$
(2)
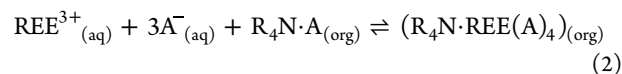
where REE is the rare earth element, and A^- is the anion of the anion exchanger $R_4N{\cdot}A$.

Anionic exchange extractants such as A336 usually favor lighter REEs in nitrate media and can be used to separate light REEs from heavy REEs.[2,22]

Solvating extractants require that the REEs form a neutral complex before extraction, with the most commonly applied system of TBP extraction from NO_3^- media, described by eq 3.[22]

$$REE^{3+}{}_{(aq)} + 3NO_3^-{}_{(aq)} + 3TBP_{(org)}$$
$$\rightleftharpoons REE(NO_3)_3(TBP)_{3(org)}$$
(3)
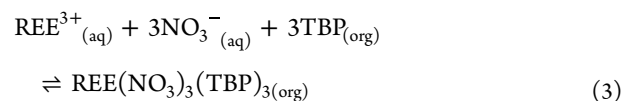
This extraction system has been applied to the separation of light REEs from heavy REEs.[2,22] The Cl^- anion can also be used with TBP but is characterized with distribution coefficients, which are lower than those in NO_3^- media.[22]

2.3. Ion Exchange (IX) Separation of REEs.
The use of ion exchange (IX) methods for the separation of REEs has a long history dating back to 1893,[2] but it was not until the addition of complexing agents, which form REE complexes capable of interacting with IX media, that IX methods had acquired sufficient separation factors for effective REE processing.[2] Ethylenediaminetetraacetic acid (EDTA) and hydroxyethylethylene-diaminetriacetic acid (HEDTA) are currently the most commonly used complexing agents in commercial IX separation systems, followed by diethylene-triaminepentaacetic acid (DTPA).[2,58] A wide range of commercial resins can be used for IX of REEs, particularly those functionalized with sulfonic acid, amino methyl-phosphonic acid, and quaternary ammonium groups.[58] The selectivity of the IX loading step is sufficient to separate REEs from other metals, but not from other REEs, which are later removed by selective elution.[58]

However, despite achieving high purities, IX methods have low productivity and are costly,[58−60] with dilution of the eluent also posing issues for the economics of IX separation processing.[2] As such, IX is only suitable for the production of small batches of very high purity REEs when the cost can be justified.[22,59] The application of IX is also not suitable for REE recycling purposes, where a high volume processing is required. Moreover, REEs in recyclable waste are already mostly isolated from other REEs, unlike those in ores. Instead, the main industrial method of commercial separation and purification of REEs in hydrometallurgy has been SX, both for mine ore processing and more recently for REE e-waste recycling.[22,37,38,40,46]

2.4. Environmental Impact of REE Processing. Despite their effective and proven track records in REE separation, mineral processing methods such as SX and IX are recognized as environmentally detrimental processes, intensively applying nonsustainable or toxic reagents, and producing large volumes of acidic, basic, or metal-contaminated wastes.[31,32,61] In the case of SX, this is due to the multiple separation stages required to purify REEs, using large volumes of fossil fuel-based organic solvents, which are nonsustainable, toxic to users, and have a significant environmental impact.[61,62] Moreover, the separation of REEs using IX produces large volumes of highly acidic waste and is also reagent intensive, requiring the use of expensive complexing agents.[59,60] Hence, globally there is significant interest in reducing nonsustainable and environmentally unfriendly reagent usage to minimize the impact of industrial processes on the environment.[61,62] This has led to the research and development of alternative and more sustainable technologies and methods for REE separation, which have the potential to replace some existing industrial SX and IX methods.

3. POROUS POLYMER SUPPORTS FOR REE SEPARATION

3.1. Supported Liquid Membranes. Liquid membrane technologies for the separation of REEs have been of interest to researchers and industry as they are user-friendly and efficient in reagent usage.[63,64] The main advantage of liquid membrane systems over conventional SX methods is their ability to simultaneously extract and back-extract the target chemical species involving facilitated transport (Figure 1),
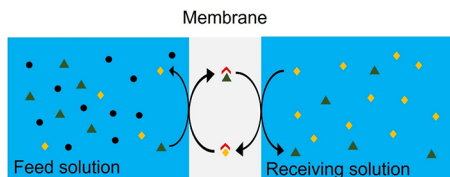

Figure 1. Schematic representation of facilitated transport across a liquid membrane. The target chemical species (▲) is selectively extracted from the feed solution by the extractant (red ∧), while other chemical species (●) remain in the feed solution. Once transported across the membrane, the target chemical species is back-extracted by a suitable stripping agent (yellow ♦).

which can be done continuously over long periods of time under suitable conditions.[41,63−65] Liquid membranes can also utilize the same extraction reagents as industrial SX methods, which enables the membrane separation systems to function analogously to industrial SX systems.[63,64]

Supported liquid membranes (SLMs) are a type of liquid membrane that has received considerable interest. An SLM consists of an organic phase contained within the pores of an inert porous membrane positioned between aqueous feed and receiving solutions (Figure 2).[63,66] The organic phase typically consists of an extractant (also known as carrier), like those applied in industrial SX,[63,65] dissolved in an organic solvent (diluent) such as kerosene, hexane, chloroform, toluene, *n*-decane, or even ionic liquids (ILs).[63,65] The supporting membrane is a microporous hydrophobic polymer membrane composed of poly(vinylidene fluoride) (PVDF), polypropylene (PP), or polytetrafluoroethylene (PTFE), and the organic
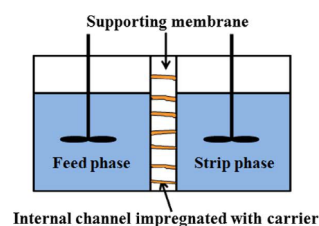

Figure 2. Schematic representation of a supported liquid membrane (SLM). Reproduced with permission from ref 63. Copyright 2018 Elsevier.

phase is retained within the membrane's porous structure by capillary forces.[63,66]

Although SLMs incorporate nonsustainable and toxic organic diluents and extractants similar to those used in SX, the advantage of SLMs is using these same reagents in lower volumes, reducing their environmental impact and thus making separation based on the use of SLMs a greener alternative to conventional SX.[63,66] In addition, SLMs can be used as hollow fiber supported liquid membranes (HFSLMs) and hollow fiber renewal liquid membranes (HFRLMs) (Figure 3), thus offering increased surface area for speeding up extraction and back-extraction.[63,67]
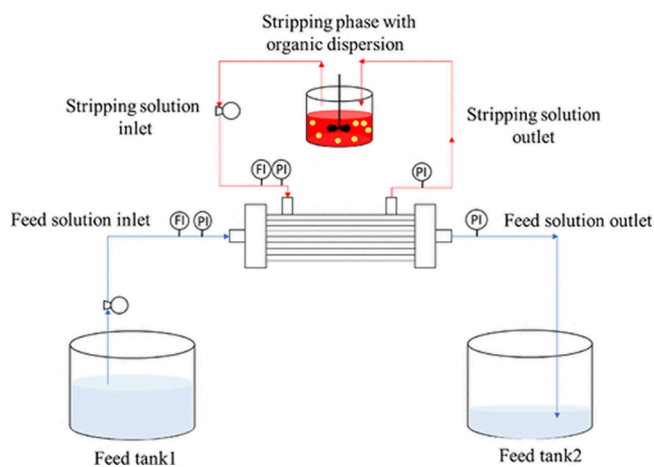

Figure 3. A schematic representation of an HFRLM setup. Reproduced with permission from ref 67. Copyright 2022 American Chemical Society.

The extraction of REEs by SLMs, HFSLMs, and HFRLMs uses the same extractants applied in industrial SX of REEs,[63,65] involving mainly D2EHPA,[67−69] Cyanex 272,[70,71] EHEHPA,[72] and TBP.[71,73] Some studies have used less common extractants such as trioctyl phosphine oxide (TOPO),[73] *N,N*-dioctyldiglycolamic acid (DODGAA),[74] Cyanex 923,[75] *N,N,N′,N′*-tetraoctyldiglycolamide (TODGA),[76,77] and dinonyl phenyl phosphoric acid (DNPPA).[78]

SLMs containing TODGA have been applied to the leaching of REEs from phosphate ores,[79] and the separation of Nd[3+] from monazite leachate using HFSLMs containing DNPPA.[78] SLMs have also been applied to REE recycling from e-waste, specifically for Y[3+] extraction from digests of fluorescent lamp phosphors using Cyanex 923,[75] and for the recovery of Nd[3+], Dy[3+], Tb[3+], and Pr[3+] from REPMs using D2EHPA[80] and TODGA.[76,77] The extraction of Pr[3+] and Nd[3+] from REPM e-waste using SLMs containing a synergistic extraction system of 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)-

imide ([C_6MIM][NTf_2]), TOPO, and TBP has also been investigated.[73] Additionally, the recovery of REEs from secondary sources such as coal fly ash using D2EHPA-containing SLMs has been studied.[81]

The main disadvantage of SLMs, HFSLMs, and HFRLMs is the instability of the membrane's liquid organic phase.[67] Although the liquid phase is contained inside the porous structure of the hydrophobic polymeric membrane support, it is vulnerable to leaching into the adjacent aqueous phases, as it is only retained within the pores by weak capillary forces.[65,66] This leads to the performance of the SLM and HFSLM decreasing over time and the leaching reagents contaminating the aqueous phases.[65,66] This loss of performance is partially addressed with HFRLMs, but the leaching of the organic phase remains an issue.[67]

Despite SLMs having demonstrated promise for REE extraction and the ability to separate REEs, the efficiency of membrane-based methods is limited by the comparatively small surface areas available for extraction and back-extraction, which could have significant ramifications when used in large-scale commercial extraction methods.

3.2. Polymer Particles Supporting and Encapsulating Extractants.
The development of effective bead or particle extractant materials is of interest to researchers and industry because of their high specific exposed surface area and the possibility of using separation systems such as fluidized bed reactors and extraction columns. Novel polymer-based particles for the extraction of REEs have been widely investigated, namely, ion imprinted polymer (IIP) particles,[82,83] polymer composite nanoparticles,[84] solvent impregnated resins (SIRs),[85,86] and extractant encapsulating polymer capsules.[87] Those which support liquid extractants are deemed by some to have significant advantages by virtue of the large range of extraction reagents, which can be encapsulated and supported inside a range of different base polymers, compared to the limited range of ligands that can be applied to functionalize polymers.[85−87] Thus, the encapsulation of a liquid extractant allows for a significant increase in the variety and flexibility of extraction capabilities, greater loading capacities, and simpler and cheaper fabrication.[85−87] In most cases, the extractants used are the same as those used in commercial SX, as they are relatively cheap, readily available, and their separation capabilities are well-characterized.[85−87]

3.2.1. Solvent Impregnated Resins. Solvent impregnated resins (SIRs) were first developed in 1971 by Warshawsky and Grinstead as a means of improving IX methods.[86,88] SIRs have the advantage of being very easy to produce because they utilize an already existing polymer framework such as commercially available IX resin beads, which are impregnated with commercially available liquid extractant, loaded up to 50 wt % of the SIR in some cases.[85,86] The basis of SIR applications as an alternative to SX is that they have the advantages of being suitable for use in both ion exchange and liquid−liquid extraction methods, possessing the selectivity of the liquid extractants they incorporate, and posing no risk of third phase formation.[86,88] SIRs are considered versatile due to the wide range of polymer supports and liquid extractants available, and offer utility by being cheaper to produce for a specific extraction system than it would be to develop new resin materials from scratch, which can be an expensive and time-consuming process.[85,86,88]

The polymer support usually consists of Amberlite or Lewaitit resin beads, which are composed of styrene (ST)-divinyl benzene (DVB) copolymer or acrylic beads.[58,85,86,88,89] A variety of other resin materials are also used, such as Merrifield or Diaion HP2MG (methacrylic ester copolymer) resins,[90,91] with custom-synthesized materials having also been reported.[92]

The polymer supports are washed in solvent, sometimes in combination with acid,[90,93] and are then impregnated with an extractant by mixing the beads and liquid extractant in a suitable solvent such as acetone,[93] toluene,[90] ethanol,[91] or methanol,[94] which is then evaporated. The resin beads, containing the extractant, are then washed with water.[85] Dry methods for preparing SIRs also exist, wherein the extractant is absorbed directly into the beads' porous structure before the excess extractant is removed by heating.[85]

The extractants used in SIRs for separation of REEs are those commonly used in industrial SX, namely, D2EHPA,[85,86,93−95] EHEHPA,[90,93,96,97] Cyanex 272,[96,98,99] A336,[95] P227,[100] Cyanex 923,[93] and TODGA.[94,101] Recently, Kovalenko et.al. demonstrated that SIRs containing *N,N*-dioctyl (diphenylphosphoryl) acetamide could be applied to the separation of Nd^{3+} and Fe^{3+} in nitric acid leachate of REPMs.[102] Extraction using IL impregnated resins has also been investigated, including ILs such as 1-octyl-3-methylimidazolium hexafluorophosphate ([C_8MIM][PF_6]),[91,103] trihexyl(tetradecyl) phosphonium mono-(2-ethylhexyl) 2-ethylhexyl phosphonate ([P_{66614}]-[EHEHP]), and trioctylmethylammonium bis(2,4,4-trimethylpentyl)phosphinate ([N_{1888}][BTMPP]).[104] Moreover, new extractants have also been synthesized and applied to SIRs, such as methylcarbamoylmethoxyacetic acid, known as "tripodal broom",[105] (2,3-dimethylbutyl)(2,4,4′-trimethylpentyl)phosphinic acid (INET-3),[106] and (2-diphenylphosphoryl)-4-ethylphenoxy)methyl)-diphenylphosphine oxide.[107]

It is well established that extractants leach from SIRs, thus reducing their performance over time and contaminating the adjacent aqueous phases in the same fashion as SLMs do.[58,85,86,88] One method for reducing extractant loss is to coat the SIRs with a protective barrier or semipermeable membrane as a means of stabilizing the loaded extractant.[85,86,88] This approach has seen limited application with SIRs,[88] but has been applied to SIRs fabricated for REE separation, that is, HP2MG beads with EHEHPA applied to the chromatographic separation of La^{3+} and Ce^{3+} from EOL car exhaust catalytic converters.[90] To stabilize the extractant, the beads were coated with poly(vinyl alcohol) (PVA) and cross-linked by glutaraldehyde or divinyl sulfone (Figure 4), which was found to significantly reduce the leaching of EHEHPA without significantly affecting SIR extraction performance.[90] This is a technique that has been used with
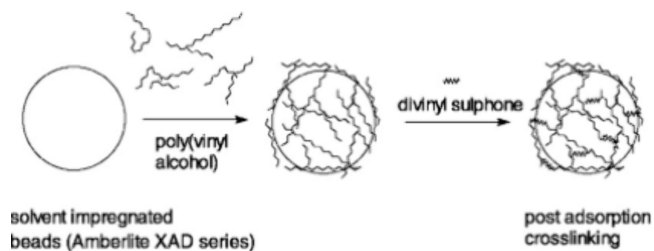

Figure 4. Schematic representation of the PVA protective coating of SIRs. Reproduced with permission from ref 108. Copyright 2004 Elsevier.

other SIR systems as a means of stabilizing the impregnated extractant, but this is the first account of it being used in a REE extraction system.[88,90]

3.2.2. Polymer Capsules. An alternative to using pre-existing polymer supports is to synthesize an inert polymer as part of the fabrication process. Polymer capsules are synthesized porous polymer beads that encapsulate an extractant inside their pores. The main method for fabricating polymer capsules and microcapsules as an extraction medium was first developed in the 1990s by Yoshizawa et al.[109−111] using ST and DVB as monomers and 2,2′-azobis-2,4-dimethylvaleronitrile (ADVN) as initiator. For REE extraction and separation, extractants commonly incorporated in polymer capsules are those utilized in industrial SX, for example, polymer capsules containing EHEHPA and in some cases D2EHPA (Table 4).

The polymer capsules can be synthesized using a dispersed phase containing monomers (DVB, ST,[112,113] polysulfone (PS),[114] or polyethersulfone (PES))[115] and initiator ((ADVN) or azobisisobutyronitrile (AIBN)) in a solvent, that is, toluene for St-DVB-based capsules and *N*-methyl-2-pyrrolidone (NMP) for PS and PES-based capsules.[112−115] The dispersed phase can also contain the extractant,[116,117] although in some methods the capsules are synthesized prior to loading them with extractant.[114] For ST-DVB-based polymer capsules or microcapsules, a reactor containing a continuous phase of deionized water with 2 wt % gum arabic is mixed and heated to 343 K under an inert atmosphere with the dispersed phase added to the reactor in one step.[116] For the PS- and PES-based methods, the dispersed phase is added to a room temperature continuous phase of deionized water via droplets (Figure 5) to produce polymer capsules of 1−2 mm diameter.[114,115,118]
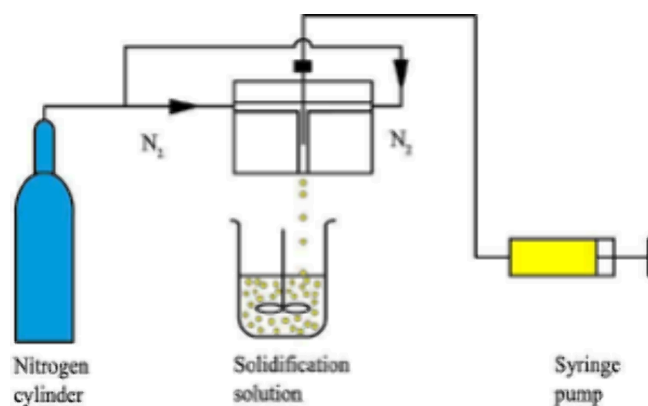

Figure 5. Schematic representation of a microcapsule fabrication apparatus using a coaxial microfluidic method. Reproduced with permission from ref 119. Copyright 2015 Elsevier.

The first report of a polymer capsule fabricated for REE extraction was that by Nishihama et al. in 2002,[112] wherein ST-DVB microcapsules containing P227 were fabricated for the separation of Pr^{3+}, Sm^{3+}, Er^{3+}, Nd^{3+}, and Y^{3+}. Since then, several publications have reported this technique and described the development of St-DVB-based microcapsules for the extraction and separation of REEs (Table 4).

Jing et al. and Wang et al. produced polymer capsules using PS as base polymer instead of ST-DVB, which was claimed to exhibit more favorable polymer properties, such as physical robustness, lower toxicity, and high resistance to strong acids,

bases, and heated environments.[114,118,119] These capsules were developed and characterized not only with EHEHPA as an extractant,[118,119] but also with the novel IL trialkylmethylammonium di(2-ethylhelxyl) orthophosphinate ([A336]-[P507]),[114] using La^{3+}, Sm^{3+}, and Er^{3+} as target REEs.

Yadav et al. produced a series of PES-based microporous capsules, made via a fabrication method similar to that used for PS capsules.[115,117,120,121] The justification for using PES over other polymers is that PES is a more environmentally friendly polymer with good chemical, mechanical, and thermal stability.[117]

To date, D2EHPA is the only extractant, which has been used in PES-based capsule fabrication, with these capsules being applied to extraction and separation of Y^{3+}, La^{3+}, Sm^{3+}, and Dy^{3+}.[115,117,120,121] One of the key focal points of the research on D2EHPA-based polymer capsules is the effect of additives (e.g., multiwalled carbon nanotubes (MWCNTs), LiCl, and PVA) on the porous structure of the capsules and the subsequent impact on both the extraction performance and the D2EHPA stability. The structural effects were observed using scanning electron microscopy (SEM) and were correlated to extraction results, with capsules fabricated with combining additives PVA and MWCNTs showing the greatest improvement in extraction performance, attributed to the formation of a finer and more uniform porous structure.[115,117,120,121]

The polymer capsules discussed here have been successfully applied in batch, column, and shallow bed reactor extraction methods, demonstrating the flexibility of the extraction materials in particle form (Table 3). However, it should be noted that like SIRs and SLMs, the extractants in polymer capsules are only retained by weak capillary forces, leading to extractant leaching,[115−117] which reduces the long-term reusability and effectiveness of these materials in addition to contaminating the adjacent aqueous phase.

4. NONPOROUS POLYMER SUPPORTS FOR REE SEPARATION

4.1. Polymer Inclusion Membranes. Polymer inclusion membranes (PIMs) are solvent-free liquid membranes, which have proven effective as an alternative to SX and SLM systems.[64,126,127] PIMs consist of a base polymer, an extractant, and a plasticizer/modifier (if necessary). Base polymers, such as poly(vinyl chloride) (PVC), poly(vinylidene fluoride) (PVDF), poly(vinylidene fluoride-*co*-hexafluoropropylene) (PVDF-HFP), or cellulose triacetate (CTA), provide the structure and mechanical stability of the PIM.[64,126,127] These base polymers are capable of retaining extractants such as those applied in industrial SX systems (Table 3) within the polymer's internal nanometer-size channels formed between the entangled polymer chains.[128] As such, PIMs have demonstrated superior extractant retention over their SLM counterparts.[64,128] In some cases, an additional reagent may be added to the membrane liquid phase, that is, a plasticizer, to improve extractant compatibility with the base polymer, thus ensuring that there is no precipitation or exudation of extractant from the PIM, while a modifier may be required to improve the solubility of the extracted adduct in the membrane liquid phase.[64,126,127] PIMs are formed mainly by solvent casting of a solution of the base polymer, extractant, and modifier/plasticizer in a volatile solvent, such as tetrahydrofuran (THF) or dichloromethane (DCM) for PVC- and PVDF-HFP-, or CTA-based PIMs, respectively.[64,126,127] This is achieved by dissolving the base polymer, extractant, and any

Table 3. Summary of Polymer Capsule Methods for Extraction and Separation of REEs[a]

extractant	polymer	target species	extraction study	ref
[A336][P507]	PS	La^{3+}, Sm^{3+}, Er^{3+}	developed and characterized polymer capsules for extraction and separation of La^{3+}, Sm^{3+}, and Er^{3+}	114
D2EHPA		Eu^{3+}	capsules packed into a column for the extraction and elution of Eu^{3+}	87
EHEHPA		La^{3+}, Sm^{3+}, Er^{3+}	developed and characterized polymer capsules for the extraction and separation of La^{3+}, Sm^{3+}, and Er^{3+}	118
		La^{3+}, Sm^{3+}, Er^{3+}	developed and characterized polymer capsules for the extraction and separation of La^{3+}, Sm^{3+}, and Er^{3+}	119
	DVB	La^{3+}, Sm^{3+}, Er^{3+}	modeled the extraction kinetics of selected REEs	122
		La^{3+}, Ce^{3+}	characterized polymer capsule extraction of La^{3+} and Ce^{3+} in a shallow bed reactor	123
		La^{3+}, Ce^{3+}, Pr^{3+}	shallow bed reactor extraction and separation of La^{3+}, Ce^{3+}, and Pr^{3+}	116
		Sm^{3+}, Eu^{3+}, Gd^{3+}	characterized the column separation of Sm^{3+}, Eu^{3+}, and Gd^{3+}	113
EHEHPA/ D2EHPA		Y^{3+}, La^{3+}, Ce^{3+}, Pr^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, Ho^{3+}, Er^{3+}	characterized REE extraction and applied polymer capsules to column separation	124
P227	ST-DVB	Pr^{3+}, Sm^{3+}, Er^{3+}, Nd^{3+}, Y^{3+}	characterized polymer capsules and their extraction of selected REEs	112
D2EHPA	PES	Y^{3+}, La^{3+}, Sm^{3+}	developed and characterized polymer capsule extraction of Y^{3+}, La^{3+}, and Sm^{3+}	115
		Dy^{3+}	developed and characterized polymer capsule extraction of Dy^{3+}	121
		Y^{3+}	developed and characterized polymer capsule extraction of Y^{3+}	117
		Y^{3+}	developed and characterized polymer capsule extraction of Y^{3+}	120
dibenzoylmethane	DVB	Gd^{3+}, Dy^{3+}	batch characterization of Gd^{3+} and Dy^{3+} extraction	125

[a]Abbreviations: Di-(2-ethylhexyl)phosphoric acid (D2EHPA), di(2-ethylhexyl) phosphinic acid (P227), divinylbenzene (DVB), 2-ethylhexyl hydrogen-2-ethylhexylphosphonate (EHEHPA), poly(ether sulfone) (PES), polysulfone (PS), styrene (ST), and trialkylmethylammonium di(2-ethylhelxyl) orthophosphinate ([A336][P507]).

required modifier/plasticizer in the solvent and then pouring the resulting PIM solution into a cast (e.g., a glass ring positioned on a glass plate). Once the solvent has evaporated, the PIM can then be simply peeled off and is ready to be used. A successful PIM is transparent, homogeneous, and mechanically durable (Figure 6).[64,126,127]
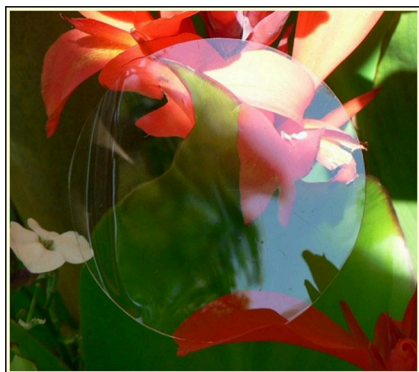

Figure 6. Image of an optically transparent and homogeneous PIM. Reproduced with permission from ref 64. Copyright 2017 John Wiley and Sons.

Most PIMs fabricated for REE separation are fabricated via the solvent casting method, when using PVC or CTA as their chosen base polymer.[129−131] However, more recently there has been significant research into the application of PVDF as a base polymer using N,N′-dimethylacetamide (DMAc) as solvent, whereby PIMs are fabricated by phase inversion.[132−137] This produces PIMs with highly porous structures, which can be asymmetric.[132] To the authors' knowledge, the effects of these structural differences compared to the solvent-cast PIMs have not yet been studied in more detail.

Although PIMs are solvent-free during application, the small amount of volatile solvent required in the solvent casting fabrication process is nonreusable and fossil fuel-based and

thus unsustainable. However, Carner et al. recently demonstrated that PVC- and PVDF-HFP-based PIMs could be successfully fabricated using the greener solvents 2-methyl THF and ethyl acetate, respectively.[138] As shown in Table 4, there is a significant number and wide variety of successful PIM compositions that have been applied to REE extraction, transport, and separation. However, as with SLMs, PIMs are limited by their surface area exposed to the feed and receiving solutions, which can impact the effectiveness of large-scale industrial separation processing. Moreover, to the best of the authors' knowledge, there are no studies applying PIMs to ore processing or the recycling of REEs from EOL e-waste.

4.2. Micro Polymer Inclusion Beads (μPIBs). Micro polymer inclusion beads (μPIBs) are a new form of polymer inclusion material consisting of the same base polymers, extractants, and modifiers/plasticizers as those used in PIMs, and are fabricated by a recently developed phase inversion microfluidic method.[147−149] The apparatus (Figure 7) used for this method is capable of fabricating μPIBs through the formation of droplets containing a THF solution of the base polymer, extractant, and modifier/plasticizer if required (the "μPIB solution"), which then undergo desolvation in an aqueous environment to precipitate the μPIBs.

A flow of μPIB solution is first merged with an aqueous NaCl "delivery solution" flow (generally 5−15 wt % NaCl, acidified to 0.1 M H$_2$SO$_4$ when applying acidic extractants[148,149]), causing it to segment before entering the desolvation column. The high salinity of the delivery solution slows the desolvation of THF, enabling the formation of uniform spherical μPIB solution droplets. Complete desolvation of these droplets then occurs under the lower salinity conditions of the solution in the desolvation column, resulting in the formation of μPIBs. The μPIBs can be fabricated to 50−120 μm diameter by manipulating the μPIB solution concentration, and their composition is similar to that of PIMs, although larger extractant mass fractions can be incorporated into μPIBs.[149] Like PIMs, μPIBs are a dense

Table 4. PIMs Applied to REE Extraction and Separation[a]

base polymer	extractant	REs	extraction study	ref
CTA	β-diketones	Sc^{3+}, Y^{3+}, La^{3+}, Pr^{3+}, Sm^{3+}, Tb^{3+}, Er^{3+}, Lu^{3+}	studied the pH effects on transport and flux of selected REEs through the PIM	139
	TODGA	Ce^{3+}	studied and modeled the extraction and transport of Ce^{3+}	140
		Ce^{3+}	PIMs formed as a hollow fiber and used to transport Ce^{3+}	141
		La^{3+}, Eu^{3+}, Lu^{3+}	studied the flux and separation factors of selected REEs via transport through the PIM	142
	noncyclic carriers	Ce^{3+}	synthesized noncyclic carriers, which were applied to PIMs used for the transport of Ce^{3+}	130
	EHEHPA, Versatic 10	Sc^{3+}	studied the separation of Sc^{3+} from other REEs	143
	amic carriers	Sc^{3+}	studied the separation of Sc^{3+} from other REEs	144
	Cyphos IL 104	La^{3+}	separated Ce^{3+} via selective transport in the presence of La^{3+}, Cu^{2+}, Co^{2+}, and Ni^{2+}	131
	D2EHPA and TBP	La^{3+}, Ce^{3+}	separated La^{3+} and Ce^{3+} via selective transport across the PIM	145
PVC	D2EHPA	La^{3+}, Gd^{3+}, Yb^{3+}	characterized the extraction of selected REEs from sulfuric acid solutions	129
	D2EHPA and Cyanex 272	Eu^{3+}	applied a combination of D2EHPA and Cyanex 272 for Eu^{3+} extraction from nitric acid solutions	146
PVDF	[A336][P507]	Lu^{3+}, Yb^{3+}	PIM applied to the separation of Yb^{3+} and Lu^{3+} by membrane transport	132
	Cyphos IL 104	Lu^{3+}, Yb^{3+}	PIM applied to the separation of Yb^{3+} and Lu^{3+} by membrane transport	133
	P227	La^{3+}, Sm^{3+}, Lu^{3+}	studied and characterized the extraction of selected REEs	134
		Lu^{3+}	studied extraction and transport of Lu^{3+} through the PIM	135
	Cyanex 272	Nd^{3+}, Dy^{3+}, Sm^{3+}	applied natural deep eutectic solvents to the phase inversion fabrication of PVDF-based PIMs containing Cyanex 272	136
PVDF-EVOH	Cyanex 272	Lu^{3+}	fabricated PIMs using new base polymer and characterized extraction of Lu^{3+}	137

[a]Abbreviations: Cellulose triacetate (CTA), di-2,4,4-trimethylpentylphosphinic acid (Cyanex 272), di-(2-ethylhexyl)phosphoric acid (D2EHPA), di(2-ethylhexyl) phosphinic acid (P227), 2-ethylhexyl hydrogen-2-ethylhexylphoshonate (EHEHPA), N,N,N',N'-tetraoctyl diglycolamide (TODGA), poly(vinyl chloride) (PVC), poly(vinylidene fluoride) (PVDF), tributyl phosphate (TBP), trialkylmethylammonium di(2-ethylhelxyl) orthophosphinate ([A336][P507]), and trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate (Cyphos IL 104).
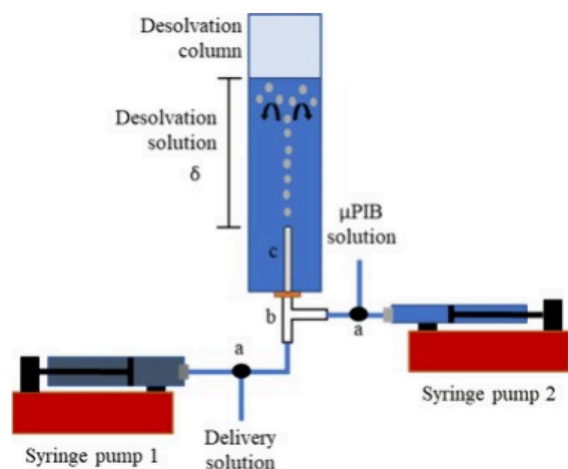

Figure 7. Schematic representation of the μPIBs fabrication apparatus. Reproduced with permission from ref 149. Copyright 2022 Elsevier.

and nonporous hydrophobic material. Thus, unlike the previously mentioned polymer capsules and SIRs, which encapsulate their extractant in their polymer porous structure, the extractant is held inside the μPIBs by the polymer matrix itself,[64,128] similarly to PIMs. Hence, the extractant is less prone to leaching from μPIBs compared to the other extractant-supporting polymer beads previously mentioned.

The application of μPIBs to the extraction and separation of REEs has been recently demonstrated by Croft et al. in the effective La^{3+} extraction from pH 2.5 H_2SO_4 solutions with PVC and PVDF-HFP-based μPIBs containing the extractant D2EHPA at 60 wt %.[149,150] PVC was found to be a superior base polymer compared to PVDF-HFP for D2EHPA μPIBs, demonstrating a higher initial mass transfer of La^{3+}.[150] PVC-based μPIBs were then applied to the separation of the critical REEs Nd^{3+} and Dy^{3+} from digested REPM e-waste, thus demonstrating the utility of this method for the separation of Nd^{3+} and Dy^{3+} from Fe^{3+}, Ni^{2+}, Co^{2+}, and boric acid in the digest, which also involved the selective back-extraction of Nd^{3+} and Dy^{3+} into 0.3 and 0.5 M H_2SO_4 stripping solutions, respectively.[151]

5. SUMMARY OF FUTURE TRENDS AND OPPORTUNITIES

The role of REEs in modern technology is predicted to increase, particularly due to applications in EVs, wind turbines, screen displays, and lighting, among many others. To satisfy this increasing demand, exploration for economically viable mineral deposits and expanding processing of REEs are taking place. However, the mining and processing of REEs are associated with a heavy environmental impact due to the release of REEs into the environment from mining operations and the reagent-intensive nature of REE processing. Hence, recycling of REEs from EOL e-waste is also becoming an area of interest, as the efficient recycling of REEs would solve the so-called "balance problem", reduce electronic waste generation, and reduce the environmental impact associated with REE mining and processing. Globally there is an increasing push toward developing methods for the recycling of REES from electronic waste, a trend that is likely to increase in the near future. This presents great opportunities for developed economies to begin implementing e-waste recycling and move toward establishing circular economies.

Although current processing techniques, namely, SX and IX, are effective, they are highly reagent intensive, using large volumes of fossil fuel-based solvents and producing large volumes of highly acidic or basic waste. Thus, to reduce the chemically intensive nature of REE processing, researchers have investigated polymer-based extracting materials for greener REE processing.

These materials have been demonstrated to be viable at the laboratory scale, and in many cases, the associated REE separation processes are chemically analogous to their SX counterpart methods, while being less reagent intensive in their application. These materials have been fabricated as membranes, hollow fibers, and beads/particles. The high versatility of liquid supported systems is demonstrated by the large range of commercial and novel extractants that can be applied and the wide range of base-polymers that can be used as a support. The application of SLMs has been most widely investigated for REE processing, including e-waste recycling, the separation of REEs from secondary sources, and mineral processing. SIRs have also shown promising e-waste recycling applications. Polymer capsule extraction materials have demonstrated effective REE extraction and separation performance with synthetic solutions but have not been applied to real-world solutions to the authors' best knowledge.

A significant challenge that faces porous polymer supported liquid materials is the stability of the supported liquid phase, which can leach from the polymer support over time and has significant implications for both the long-term reusability of these materials and the environmental impact of their use.

Nonporous polymer materials, namely, PIMs and μPIBs, developed with a wide range of extractants and base-polymers, have seen highly successful applications under laboratory conditions in the separation of REEs from REPM e-waste and have demonstrated high degrees of liquid phase stability. While all materials discussed in this Review have shown effective extraction and separation of REEs, current research efforts are focused on developing materials that are reusable, namely, through reducing loss of liquid extractant and maintaining extraction performance for prolonged periods of time. Future research will also need to apply these materials to the pilot-scale industrial processing of REEs to establish their competitiveness with currently used SX methods.

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Notes

LIST OF ABBREVIATIONS AND ACRONYMS

μPIBs = micro polymer inclusion beads
A336 = Aliquat 336
ADVN = 2,2′-azobis-2,4-dimethylvaleronitrile
AIBN = azobisisobutyronitrile
CTA = cellulose triacetate
D2EHPA = di(2-ethyl-hexyl)phosphoric acid
DCM = dichloromethane
DMAc = N,N'-dimethyl acetamide
DNPPA = dinonyl phenyl phosphoric acid
DODGAA = N,N-dioctyldiglycolamic acid
DTPA = diethylenetriaminepentaacetic acid
DVB = divinyl benzene
EDTA = ethylenediaminetetraacetic acid
EHEHPA = (2-ethylhexyl)phosphonic acid mono-2-ethyl-hexyl ester
EOL = end-of-life
EV = electric vehicle
e-waste = electronic waste
HEDTA = hydroxyethylenediaminetetraacetic acid
HFRLMs = hollow fiber renewal liquid membranes
HFSLMs = hollow fiber supported liquid membranes
IUPAC = International Union of Pure and Applied Chemistry
IX = ion exchange
NiMH = nickel metal hydride
PES = polyethersulfone
PIM = polymer inclusion membrane
PP = polypropylene
PS = polysulfone
PTFE = polytetrafluoroethylene
PVDF = poly(vinylidene fluoride)
PVDF-HFP = poly(vinylidene fluoride-co-hexafluoropropylene)
REE = rare earth element
REPM = rare earth permanent magnet
SIR = solvent impregnated resin
SLM = supported liquid membrane
ST = styrene
SX = solvent extraction
TBP = tributyl phosphate
TGA = thermogravimetric analysis
TODGA = N,N,N',N'-tetraoctyldiglycolamide
TOPO = trioctyl phosphine oxide

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