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Rare earth elements removal techniques from water/wastewater: a review

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ABSTRACT

The rare-earth elements (REEs) remain very important due to the growing increase in their demand and for their critical and indispensable use in many high-tech industries today. This growing demand for REEs has led to an increased environmental exposure and water pollution from numerous REEs commercial products and as a result, the recovery of REEs is a significant issue that requires appropriate consideration. There are diverse and various strategic techniques available to remove metal ions from aqueous solutions, but nanofiber adsorbent appears to be quite innovative due to their outstanding characteristics such as cost effectiveness, flexibility, high surface area, porosity, and the portable nature which makes them a better choice for potential adsorbent applications. This review presents a brief view on several typical removal techniques, new developments and applicable examples of the various technologies used for the removal of rare earth elements from water/wastewater solutions. The review highlights these developments with a particular focus on innovative physicochemical removal processes like adsorption as the process techniques most widely used.

Keywords: Rare-earth elements; Removal techniques; Adsorption; Ion exchange; Solvent extraction; Nanofibre

1. Introduction

Rare-earth elements (REEs) are surface active elements which play an essential role in metallurgy, such as alloying and purification of metals [1], and may be found in over 250 different minerals. REEs have widespread use and importance for industrial applications due to their metallurgical, optical and electronic properties. The increase in industrial usage, economic and environmental benefits of the REEs have resulted in an increased demand and price. This growing demand for the REEs have also led to an increased environmental impact and water pollution from numerous REE commercial products and rare earth (RE) metal mines. Water pollution from the addition of RE metals from industrial activities is increasing greatly and also becoming a global concern because mining, mineral processing and metallurgical operations are generating effluents containing RE metals [2]. Therefore, the recovery of REEs is an important concern that requires appropriate attention and this has led to the advancement of techniques and processes for the recovery of the metallic ions from various sources.

The developed processes have indeed accelerated the advancement of knowledge in REE removal. Precipitation is considered an easy method of recovering REEs, but its disadvantages, such as the large amount of chemical reagents required, its ineffectiveness for low concentrations of metals and sludge generation make it less attractive [3]. Solvent extraction (SX) is well-established for recovery of metals from various effluents and many types of extractant have

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been studied for the extraction of RE metals [4,5], but the available extractants also extract other base metals, making it difficult to obtain the required RE metal purity. Ion-exchange and chelating resins are other appropriate methods for concentrating and separating metals ions from dilute effluents by playing with the affinity of specific functional groups towards REEs [6–10].

The adsorption process, being a surface occurrence is another key interest recognised as promising, efficient and most widely used fundamental approach in hydrometallurgy and wastewater treatment processes [11–13] due to being economically viable, simple, technically feasible and socially acceptable [14]. The adsorption process offers flexibility in design and operation and in many cases will produce high-quality treated effluent. Various adsorbents are being investigated for metal ion removal [15], especially the use of polymeric nanofibers to remove metal ions from different sources [16–18] because nanofibers have interesting structural characteristics, such as high surface area to volume ratio, low basis weight, high porosity and interconnectivity, good structural stability and controllable thickness of the electrospun scaffold which are suited for adsorption of metals.

This review will discuss different prospects for RE elements (REEs) removal technologies and the advancement and revolution of these techniques with focus on electrospun nanofibers which have unique properties and are emerging as a better choice for potential adsorbent applications. The review also evaluates the advantages and disadvantages of each process and it is hoped that this work will provide researchers with greater clarity on the available process for the removal of RE metals and provide industrial end-users with emerging technologies and further strengthen the engagement between research and application process.

2. Rare earth elements

REEs denote a group of 17 chemically similar metallic elements, including scandium, yttrium, and the lanthanoids [19]. The REE electronic configuration is constituted of an inner shell with electrons in the $4f^n$ orbital, shielded by an outer shell composed of electrons in orbitals $5s^2$, $5p^6$, $5d^{1-10}$ and $6s^2$ [20]. The interesting properties that have allowed their application are largely due to the unique 4f electrons [21]. The REEs have highly localized electronic states and very predictable electronic transitions that are weakly influenced by the coordination environment or crystal field. The REEs physicochemical properties are very close because of their close electronic configurations, and their most thermodynamically stable form is the trivalent, M(III) form [20].

Traditionally, the REs elements are divided into two groups of light REEs group (LREEs) containing elements from lanthanum to europium (Z from 57 to 63) and the heavy REEs group (HREEs) which contain elements from gadolinium to lutetium (Z from 64 to 71). Yttrium, the lightest REE, is usually grouped with the HREEs where it share similar chemically and physically properties [22]. Despite the name, REEs are not actually rare in geologic abundance, especially the LREEs, which are extracted in a more common and easier way than the HREEs. The problem certainly is not their absolute concentration (10–500 ppm by weight) but the difficulty to find economically exploitable deposits [23]. The only elements, that are really scarce (upper crust abundance ≤1 ppm) and difficult to find, are europium, lutetium and thulium [23]. In absolute terms, the REEs are more abundant than many of the platinum group metals (e.g., platinum and palladium) and have similar abundances to tin, zinc, and tungsten.

REEs' economics are as complex as their chemistry and worldwide demand for REEs has had a general upward trend for many decades. The result of an analysis of 14 raw materials defined as critical at a European Union level with respect to the politico-economic stability of the producing country, their geographical concentration, their substitution potential, and their rate of recycling showed that REEs (15 lanthanides plus yttrium and scandium) were included on this list from the 41 raw materials analysed [24,25]. Therefore, REEs' demand will continue to grow and depending on price and availability, global demand could increase to 160–200,000 t.p.a. by 2020 and magnet-based applications will continue to grow at the highest rate. The REEs have made their way into many aspects of modern life and are crucial to current standards of living and technology. They are extensively used in astronavigation, catalysts for petroleum refining, high-strength permanent magnets, metallurgical industries, photoelectronic and are also vital in nuclear energy programs [26].

The main commercial sources of REs are bastnesite (La, Ce)FCO_3, monazite, (Ce, La, Y, Th)PO_4 and xenotime, YPO_4. Over 90% of the world's economically recoverable REEs are found in primary mineral deposits in bastnaesite ores located in China and at Mountain Pass in California (USA) while, monazite deposits in Australia, Brazil, China, India, Malaysia, Russia and South Africa, are the second largest concentrations of REEs [27]. Four RE metals, viz. cerium, lanthanum, neodymium and yttrium, constitute more than 85% of the global production and the recoveries for each of these metals are possible, even though it still remains a challenge [28]. The concentrations of REEs are generally at subparts per trillion range (sub-ng L^{-1}) levels making their determinations at such low levels to be achieved only by using highly sensitive techniques that affords excellent sensitivity [29,30]. The ever-increasing demand for RE metals and their compounds are crucial due to a broad and rapidly expanding range of applications that rely upon their chemical, catalytic, electrical, magnetic and optical properties which has equally led to the development of technologies and processes for the separation of the metallic ions from various sources.

3. Rare earth elements removal technologies

The recovery of REEs can involve many different processes depending on the concentration of valuable or toxic metals, the composition of the solution and the economics of the process and target metals [10]. REEs recovery from solid waste or minerals may involve pyro-metallurgy [20], an energy intensive process, using high temperatures to chemically convert feed materials and separate them so that the valuable metals can be recovered [31,32] or alternatively, hydrometallurgy (chemical leaching or bioleaching) which is the most common chemical extraction method of separating individual REEs from the mineral concentrate [33,34]. The hydrometallurgical processes include a wide range of technologies such as adsorption [12], ion exchange [35], ionic imprinted polymers [36], chemical precipitation [37], electrocoagulation (EC) [38], flotation [39], electrodialysis (ED) [40], reverse osmosis (RO) [41], membrane filtration [42], nanofiltration (NF) [43], membrane electrolysis (ME) [44] and SX [45,46] which are available for the removal or extraction of metals from leachates or waste streams with varying levels of success [47–50]. Some of these methods can be applicable in research settings and in an industrial-scale. Several of these treatment technologies are briefly described in the following sections with some of their advantages and disadvantages also enumerated.

3.1. Chemical precipitation

This is a widely used process for metal recovery using hydroxide, carbonate, or sulphide treatment or some combinations of these treatments [37]. Precipitation is a simple, inexpensive and effective process for removal of RE metals from aqueous solutions and can be accomplished by the addition of coagulants such as lime, iron salts or alum followed by pH adjustment, addition of a chemical precipitant and flocculation. The formed precipitates can then be separated from water by sedimentation or filtration. The simplicity of the process, convenience and safe operations and inexpensive equipment requirement make it a popular method for metal removal from contaminated wastewater. Inspite of these advantages, chemical precipitation requires a lot of chemicals to decrease metals to an acceptable level for discharge. Other drawbacks include excessive sludge productions which require additional treatment, slow metal precipitation kinetics, poor settling, increased cost of sludge disposal and the long-term environmental impacts of sludge disposal [51].

Hydrometallurgical process for extraction of lanthanum, yttrium and gadolinium from spent optical glass containing 43.12 wt.% lanthanum oxide, 9.37 wt.% yttrium oxide and 4.60 wt.% gadolinium oxide using sodium hydroxide followed by hydrochloric acid leaching of the residual solids was reported by Jiang et al. [52] and the recovery of 99.4% lanthanum, 100% yttrium and 100% gadolinium was obtained from the glass. The results from the investigation of the effects of process parameters showed that increase in NaOH concentration and HCl concentration, conversion temperature, liquid-to-solid ratio and conversion time accelerated the REE leachability. Quinn et al. [53] obtained the distribution coefficients for yttrium (Y) and the REEs (YREEs) in aqueous solutions containing freshly precipitated hydroxides of trivalent cations (Fe^{3+}, Al^{3+}, Ga^{3+} and In^{3+}). The study observed that the sorption of Y on Fe(III) hydroxide precipitates is intermediate to that of La and Ce and the behaviour of Y was rationalised from the propensities of different YREEs for covalent versus ionic interactions.

3.2. Electrocoagulation

EC is a promising electrochemical treatment technique that does not involve the addition of chemicals or regeneration [38]. EC involves the electrochemical production of destabilization agents which bring about charge neutralization for pollutant removal and it has been widely used for water or wastewater treatment. A variety of electrodes can be used for the treatment of wastewater, and they include iron or steel, zinc, aluminium, magnesium or combination of them. Electrochemically generated metallic ions from these electrodes can undergo hydrolysis near the anode to produce series of activated intermediates capable of destabilizing the finely dispersed particles present in the water/wastewater to be treated. The destabilized particles then aggregate to form flocs [54].

The generation of metal ions takes place at the anode while hydrogen gas is released from the cathode. The hydrogen gas also assists the flocculated particles to float out of the water. This process sometimes is called electro-flocculation. The advantages of EC include compact treatment facility, relatively low cost, high particulate removal efficiency and possibility of complete automation while its major disadvantage is the high operating costs. The EC process is based on the continuous in-situ production of a coagulant in the contaminated water.

Murthy and Parmar [55] studied the removal of strontium (up to 100 mg/L) from synthetic wastewater by EC. Stainless steel and aluminium electrodes were used and removal efficiencies were compared with respect to EC time, current density, amount of electrolyte added, solution pH, distance between electrodes, temperature and initial concentration of strontium. The study reported the optimum operating variables values were 50 min of process time, 8 mA/cm^2 current density and solution pH 5 for which around 93% and 77% removal efficiency was achieved using stainless steel and aluminium electrodes, respectively. A pseudo-second-order kinetic model fitted the data better than the pseudo-first-order model.

3.3. Flotation

Ion flotation is an alternative separation technology for recovering and removing metal ions from dilute aqueous solutions. The process of ion flotation is based on imparting the ionic metal species in waste water hydrophobic by use of surface active agents (surfactants) and subsequent removal of these hydrophobic species by air bubbles [39]. This method has several advantages for treating diluted wastes such as low energy requirements, low residual concentration of metals, rapid operation, small space requirements, flexibility in applying the method to a variety of metals at various levels and production of small volumes of sludge that are highly enriched with the desired elements. All of these factors reduce the cost of processing but the separation efficiency depends very much on ionic strength. The trend of research also shifted from flotation alone to a combination of flotation and other physicochemical treatment methods such as adsorption and membrane filtration [56].

Industrial wastewater is a complex mixture; therefore, decreased efficiency drawback due to ionic strength remains the main reason holding back their wider applications. The 1-hydroxy 2-naphthylhydroximic acid was synthesized as the REEs collector under the guidance of the isomerism principle, and applied to flotation of REEs from Baotou Mineral Processing Plant. The results showed that the reagent can effectively separate the REEs; the grade and recovery of RE minerals in rough concentrate with 10.95% RE ores feed are 37.02% and 80.10%, respectively, which was a good expectation for the 1-hydroxy 2-naphthylhydroximic acid as the RE minerals collector [57].

3.4. Membrane filtration

Membrane filtration is a molecular sieving technique which retains particles whose sizes are greater than the pore size. Size-exclusion membranes such as microfiltration, ultrafiltration, ED, NF and RO membrane base their separation on size discrimination for heavy metal removal. The efficiency of membrane filtration technique primarily depends on the pore size of the membrane. A higher efficiency can be achieved with smaller membrane pore size [42]. However, small pore size will result in restricted diffusion of feed. Hence, high pressure is required to improve diffusion through the membrane which will increase the operational cost due to the consumption of energy.

Membrane filtration technology can remove toxic metal ions with high efficiency, but its challenges such as high cost, membrane fouling, process complexity and low permeate flux have limited their use in heavy metal removal. Samarium, a REE, was removed from aqueous solution by polyelectrolyte-enhanced ultrafiltration process using poly (acrylic acid) (PAA) with average molecular weight 100,000 Da using a tangential cell system. Polyether sulfone membrane with molecular weight cut-off of 5,000 Da and an effective filtration area of 50 cm^2 were used (PES-5). The obtained results showed that the permeate flux increased linearly with increasing transmembrane pressure and the increase in the concentration of PAA, also increased the Sm(III) ions retention to 80%. A better retention was observed at 2×10^{-4} mol L^{-1} PAA concentration and 3 bar transmembrane pressure [58].

3.4.1. Electrodialysis

ED is a membrane separation technique where ionized species in solution are transported, through an ion-exchange membrane, under the influence of an electric field. When a solution containing ionic species is introduced into the cell compartments, anions migrate towards the anode and cations migrate towards the cathode crossing anion-exchange and cation-exchange membranes, respectively. An alternate disposition of the membranes, separating the cell compartments, allows the ions that are able to cross the anion-exchange membrane to be stopped by the cation-exchange membrane and vice versa [40].

ED is not as economically competitive as other membrane separations because of the ion-exchange membranes (especially bipolar membranes), high cost of electrodes and the relatively short life time of membranes when working in high-density electrical fields due to the formation of metal hydroxides, which clog the membrane [59]. It is more suitable for a metal concentration of less than 20 mg/L which becomes a major limitation for the process. Continuous processes such as ED and filled cell ED are otherwise also called continuous electrodeionization. The advantages include the ability to produce a highly concentrated stream for recovery and the rejection of undesirable impurities from water. Since ED is a membrane process, careful operation and clean feed are required besides periodic maintenance to prevent any damage to the stack.

Feasibility study was done on recovering waste acid (hydrochloric and sulfuric acid) by vacuum membrane distillation (VMD) and diffusion dialysis (DD) in RE metallurgy [60]. Results showed that up to 80% of free hydrochloric acid can be recovered from RE chloride solutions by VMD. Furthermore, more pure hydrochloric solution can be recovered in the permeate side, due to cut-off rate for RE ion usually above 98%. Sulfuric acid can also be recovered from RE sulphate solutions by DD. The recovery rate of sulfuric acid can be controlled between 70% and 80% in the actual practice.

3.4.2. Reverse osmosis

RO is a process in which heavy metals in wastewater are separated by filtering through a semipermeable membrane allowing the fluid that is being purified to pass through it, while rejecting the contaminants at a pressure greater than osmotic pressure caused by the dissolved solids in wastewater [41]. Pressure is the major parameter that affects the extent of heavy metal removal by RO instead of pH, and the higher the pressure, the higher the metal removal efficiencies, and thus the higher the energy consumption. Generally and in comparison with other membrane filtration, RO is more effective for metal removal from inorganic solution due to the rejection percentage of over 97% with a metal concentration range from 21 to 200 mg/L. Other advantages of using RO include a high water flux rate, high salt rejection, resistance to biological attack, mechanical strength, chemical stability and the ability to withstand high temperatures. RO has been developed with a membrane pore size down to 10^{-4} μm.

The limitations is that the small pores of the membrane make it more prone to fouling due to the suspended solids or oxidized compounds such as chlorine oxides thereby increasing the operational costs. Furthermore, a relatively clean feed that is free from any suspended particles is required to avoid membrane blockage because, even a small oxidised compounds such as chloride oxides can block the small pores of RO membranes [61]. Hence, membranes have to be replaced frequently to achieve good performance, which thus incur additional cost. Currently the available RO membranes are sensitive to chlorine, pH and oxidants and are liable to fouling by submicron particulates, extensive feed pretreatment and high transmembrane pressure that are required result in high energy costs [59].

The maximum pore size of RO is typically 1°A and since the pore size is smaller than hydrated metal ionic size, RO becomes the most efficient membrane filtration technique for the removal of dissolved metal ions which does not require any membrane modification. RO also requires high pressure to facilitate the diffusion of water due to their very small pore size but it may not always be economically feasible for the removal of RE metals due to the high energy needed to provide the necessary pressure for the diffusion of water across the RO membrane. Lawrence et al. [62] determined the fate of REEs, which include Gadolinium (Gd), which was measured accurately at very low concentrations (Terbium (Tb) is measured at 7 fmol/kg during the study) and production of purified recycled water from effluent. Whereas, coagulation and microfiltration showed negligible removal, the major removal step occurred across the RO membrane where anthropogenic Gd (the amount of Gd attributable to MRI contrast agents) was reduced from 0.39 nmol/kg to 0.59 pmol/kg, a reduction of 99.85%. The RO concentrate had anthropogenic Gd concentrations of 2.6 nmol/kg, which was an increase in concentration in line with the characteristics design of the plant.

3.4.3. Nanofiltration

NF membranes require pore sizes and the smallest membrane pore size used is approximately 10°A. The process has the advantage of a high rejection of organic molecules compared with ultra-filtration (UF) process and a low operating pressure compared with RO [43]. NF membranes have an anionic surface charge in their structure, which can also attract metal cations to their surface. Hence, NF is more efficient in removing dissolved solids than UF. An important feature of NF membranes is their ability to separate ions from water and separating these ionic species depends strongly on the membrane charge and pore size. A highly charged membrane is better able to exclude coions (ions of the same charge as the membrane) of the membrane structure and similarly, a membrane with smaller pores is better able to retain ionic species. Therefore, apart from the consideration of the characteristics of the solute to be removed, the knowledge of the surface and pore characteristics of a NF membrane also allow for predictions of the membrane separation behaviour [63]. Its advantage includes being well-defined and a 95% high metal ion removal efficiency while its limitations include very high capital cost, preconditioning and high water rejection.

Murthy and Choudhary [64] investigated the application of commercial NF to treat REE (neodymium) containing water. Their experimental results indicated that the rate of Nd(III) rejection increased with an increase in the applied pressure and feed flow rate; and decreased with an increased feed solution concentration of Nd(III) from 10 to 80 mg/L. Rejection of Nd(III) ions using NF membrane was widely influenced by solution pH due to the charged nature of the membrane which changed with the variation in pH while the use of a surfactant (sodium dodecyl sulphate) in aqueous solution resulted in its adsorption on the membrane surface, thereby changing membrane characteristics, and in turn influencing the rejection. This induced complexation step increased the rejection to a greater extent by forming [Nd-EDTA]- complex thereby increasing its molecular weight and thus increasing rejection of Nd(III) ions from 86.74% to 99.36%.

3.4.4. Membrane electrolysis

ME is a chemical process driven by an electrolytic potential and can be applied to remove metallic impurities from metal finishing wastewater. ME can be employed to treat plating wastewater with a metal concentration of higher than 2,000 mg/L or less than 10 mg/L while the major drawback is its high energy consumption. There are two types of cathodes used: a conventional metal cathode (electrowinning) and a high surface area cathode. When the electrical potential is applied across an ion-exchange membrane, reduction–oxidation reaction takes place at the electrodes [44].

Oishi et al. [65], proposed and studied a process for separation and recovery of RE metals from wastes which utilizes molten salt electrolysis and an alloy diaphragm. The diaphragm functioned as a bipolar electrode and enabled selective permeation of RE ions. The results indicated that dysprosium (Dy) and neodymium (Nd) permeated from the anolyte to the catholyte and the selectivity was confirmed during the alloying step which indicated a high possibility of separation of Dy from La and Fe. The expected advantages of this process are that RE metals were effectively separated from impurities such as iron-group metals and that the selectivity for each RE metal could be controllable by adjusting the electrolytic conditions such as melt and alloy compositions and potential of the alloy diaphragm.

3.5. Solvent extraction

SX is a widely used separation technique due to effective extraction ability and separation selectivity, and it separates complexes based on solubility differences between two immiscible liquids in contact with each other which are usually water and an organic solvent. The extractions are from an aqueous phase into an organic phase and the extractants solvate, exchange or chelate the metal ion. Though SX has long been used to remove ions from water, the finite aqueous solubility of the extractants, solvents and modifiers, and their loss through phase disengagement, remain important problems. In addition, due to the large volume of organic phase that would be required, SX cannot be applied to dilute metal ion solutions [45]. SX is inefficient because the procedures are usually time-consuming, labour-intensive and the requirement of large volume of solvent used in the process [49].

All the three major classes of extractant, namely, anion exchangers (or basic extractants), cation exchangers (or acidic extractants) and solvation extractants (or neutral extractants) have been utilized for separating REs. SX has come to be one of the most important separation processes in hydrometallurgical processing of REs. Studies into SX of individual REE have been extensively carried out with the use of various extractants in different media, though, only a relatively few investigations are practical for industrial application. SX was largely accepted as the most applicable commercial technology for separating REs due to the need to be able to handle larger volumes of dilute pregnant liquors [66]. Many types of extractant have been investigated for the extraction of RE metals, including di-(2-ethylhexyl) phosphoric acid (HDEHP) [67], Ethyl-bis-triazinylpyridine (Et-BTP) [68] and Cyanex 272 and Cyanex 921 /Cyanex 923 [69].

Naganawa et al. [70] developed a new extractant containing the glycol amic acid group which was selective for extraction of RE metals. Thereafter, several researchers [70–74] have carried out recovery of REEs from aqueous solutions using the new extractants and in these investigations, extractants containing glycol amic acid showed effective and selective extraction of RE metals from mixtures of diverse metals. Narita and Tanaka [75] synthesised *N*-*N*′-dimethyl-*N*,*N*′-dioctyl diglycol amide (MODGA) for separation of rare elements from base metals and reported that MODGA preferentially extracted RE metal cations over those of the base metals. However, Van Nguyen et al. [76] pointed out the disadvantages of SX which include loss of extractant, emulsion and third-phase formation, phase separation and use of inflammable diluents.

Abreu and Morais [48] studied the separation of REEs from heavy REE concentrate through SX. Seven extractants, three organophosphorus acids, a mixture (neutral ester) and three amines were studied. The organophosphorus extractants were investigated in hydrochloric and sulphuric media whereas the amines performance was assessed in a sulphuric medium. The study established that for the extractants investigated, 2-ethylhexyl mono (2-ethylhexyl) ester phosphonic acid (IONQUEST 801) [77] is the most indicated for the separation of heavy REE because it has lower affinity with the REE compared with the affinity of DEPHA/REE, which makes the strip of the REE from Ionquest 801 easier than from di-2-ethylhexyl phosphoric acid (D2EHPA). Moreover, the number of stages necessary for the stripping of the REE from IONQUEST 801 is much lower than that observed when DEPHA is employed.

Ganji et al. [78] also conducted an investigation to evaluate and compare the performance of D2EHPA, Cyanex272 (bis(2,4,4-trimethylpentyl) phosphinic acid) and a mixture system of D2EHPA and Cyanex272 in the separation of REEs including lanthanum, gadolinium, neodymium and dysprosium from nitric acid solution. The results showed that Cyane272 had the lowest separation factors in the separation of Dy, La, Nd and Gd from each other. It was found that the mixture system of D2EHPA and Cyanex272 had the best performance in the separation of REEs investigated owing to the higher separation factors of Dy/Nd (720.05) and Dy/Gd (3,640.27) as well as lower extraction efficiencies Gd (64.54%), La (30.07%) and Nd (26.47%) from Dy (99.92%).

3.6. Ion exchange

Before the advent of industrial scale SX in the 1960s, ion-exchange technology was the only practical way to separate the REs in large quantities [35]. Ion exchange was used to obtain small quantities of high purity RE product from electronics or analytical applications [66]. Ion-exchange materials can be synthetic or natural. Organic materials, specifically polymeric materials, have had more development and have been widely studied due to their greater versatility. These materials are more commonly known as ion exchange resins.

Ion-exchange resins have become attractive alternatives for separations from dilute solutions since the extractant is bound to a solid phase, simplifying the separation process. Though this makes it suitable for separations of mixtures with complex matrices and also environmentally safe but they can exhibit poor metal ion selectivity and kinetics [79]. In ion-exchange process, metal ions from dilute solutions are exchanged with ions held by electrostatic forces on the exchange resin. The advantages include high removal capacity, and the process is less dependent on pH of water while disadvantages include high cost and partial removal of certain ions. It also requires high-tech operation and maintenance, while regeneration creates a sludge disposal problem and sometimes, ions are difficult to remove from the resin [38].

The use of ion-exchange resins in specific applications entails more consideration of chemical and physical factors. For example, resin retention capacity will be influenced by the chemical nature of the ligand group functionality, cross-linking degree, cross-linking reagent, distance between functional groups and support chain. On the other hand, physical properties are also important, for example, the swelling ability and mechanical properties present a large dependence on the cross-linking degree because, highly cross-linked materials are harder, and in many cases, are more mechanically stable. However, if the swelling capacity is lower, causing the diffusion of metal ions in such materials to be slow may result in a decrease in the process rate and will finally affect its applicability. Resins with a low cross-linking degree possess good diffusion, major swelling and a jelly-like appearance but possess a poor mechanical stability [80].

However, this process is technologically simple and permits efficient removal of even traces of impurities from solutions [81]. Resins also have certain ligands that can selectively bond with certain metal cations, making ion exchange easier to use and less time-consuming. Waqar et al. [82] developed an analytical method for the preconcentration of REEs in seawater using an indigenously synthesized chelating resin for the preconcentration of (REEs) based on immobilization of fluorinated β-diketone group on solid support styrene divinyl benzene. Percentage recoveries of La, Ce, Nd, Sm, Eu, Gd, Dy, Er, Yb and Lu were ≥ 95%, a preconcentration factor of 200 times, and relative standard deviations < 5% were achieved.

Raju and Subramanian [83] also developed a novel grafted polymer for selective extraction and sequential separation of lanthanides, thorium and uranium from high acidic wastes by grafting Merrifield chloromethylated (MCM) resin with octyl(phenyl)-*N*,*N*-diisobutylcarbamoyl-methylphosphine oxide (CMPO) (MCM-CMPO). The resin showed very high sorption capacity values of 0.960 mmol g^{-1} for U(VI), 0.984 mmol g^{-1} for Th(IV), 0.488 mmol g^{-1} for La(III) and 0.502 mmol g^{-1} for Nd(III) under optimum HNO_3 medium, respectively. The grafted polymer showed good durability and reusability even up to 20 cycles. The polymer also showed good selectivity and sensitivity towards analytes down to ppb levels.

3.7. Biosorption

Biosorption is the binding of chemical species to biopolymers. It can also be defined as the ability of biological materials to accumulate heavy metals from wastewater through physicochemical or metabolically mediated pathways of uptake. In biosorption, either live or dead microorganisms or their derivatives complex metal ions through the action of ligands or functional groups located on the outer surface of the cell [84]. Biosorption represents a biotechnological innovation as well as a cost-effective means for the recovery of RE metals from aqueous solutions. A variety of biomaterials, such as activated carbon, algae, bacteria, fungi, resin and yeasts, have been reported to serve as potential adsorbents for the recovery of REEs [49].

The major advantages of biosorption over conventional treatment methods include low cost, minimization of chemical or biological sludge, high metal binding capacity, high efficiency, no additional nutrient requirement and regeneration of biosorbent. The initial incentives for biosorption development in industrial process are the fast kinetics of adsorption and desorption, and the nongeneration of secondary residues. Biosorption process performance is comparable with the ion-exchange treatment and has provided a substitute treatment of industrial effluents from the traditional physicochemical methods. Biosorption could be used in situ and with proper design, it may not need any industrial process operations and can be integrated with many systems [85].

The mechanisms of the process involved in metal accumulation on biosorption sites are numerous and complicated. As shown in Fig. 1, metal binding can proceed through electrostatic interaction, ion-exchange, precipitation, and surface complexation, which can occur individually or combined [86]. The important factors that influence the biosorption processes include pH, temperature, biosorbent dosage, initial metal concentration, agitation rate and contact period [49]. Batch experiments usually focus on a range of these factors to evaluate the full biosorption potential of REE.

Das et al. [87] used biosorbents of animal (fish scales) and plant origin (neem saw dust) to recover lanthanum(III) from aqueous environments. Maximum La(III) uptake was reported to be 200.0 mg/g in the case of fish scales (FS) and 160.2 mg/g in the case of neem sawdust (NS) under optimum conditions. Analysis confirmed a major involvement of the participation of amide, amines, alkines, aliphatic compounds and alkyl groups during La(III) biosorption and a maximum adsorption efficiency and recovery of La(II) from ceramic industrial effluent using FS were 88.5% and 84.6%. Regeneration studies suggested that the FS could be successfully reused up to 6 cycles and could serve as potential agent for the recovery of lanthanum from industrial effluent. Biosorption of neodymium by microorganisms was reported by Palmieri et al. [88] and maximum biosorption was obtained using the microalgae *Monoraphidium* sp. (1,511 mg/g cell), followed by Bakers' yeast (313 mg/g cell), *Penicillium* sp. (178 mg/g cell) and activated carbon (61 mg/g cell).

3.8. Adsorption

Adsorption is an alternative treatment technique for recovering valuable elements or toxic metals from wastewaters [89]. Adsorption is a mass transfer process where a substance is transferred from the liquid phase to the surface of a solid, and becomes bound by either physical or chemical interactions which results in the transfer of metals from the aqueous phase to the solid phase [12]. The adsorption process advantages make it a promising alternative to costly removal methods for the separation and removal of various metals from polluted water. Studies on the treatment of effluents containing toxic metals have shown adsorption to be a highly effective technique which could be used for the removal of REEs from aqueous environments [90,91].

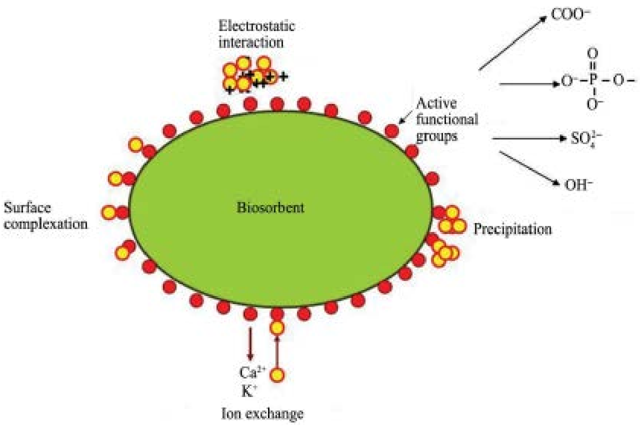

Fig. 1. Mechanisms of biosorption of REEs [49]. Reprinted with permission from Elsevier.

Adsorption process is recognised as one of the most efficient, promising and widely used fundamental approach in hydrometallurgy and wastewater treatment processes [11–13] even from low-concentration sources [92]. The adsorption process offers flexibility in design and operation and in many cases will produce high-quality treated effluent. In addition, adsorption is sometimes reversible and adsorbents can be regenerated by suitable desorption process [41,93]. In practice, adsorption commonly involves passing a fluid over a bed of adsorbent particles, onto which components (sorbate) are sorbed. The process continues until the sorbent is saturated and the adsorbate components can no longer be removed from solution effectively. The sorbent may be disposed of or regenerated. Regeneration is commonly carried out by passing a solvent (often strong acid) through the used adsorbent, releasing sorbed components into a regenerant solution which is collected. The sorbent material may then be reused. Regeneration also recovers the metals so they can be disposed of properly or purified for reuse [94]. Regeneration of the sorbent is important in cyclic processes when the used sorbents are expensive while kinetic parameters are used to determine the rate of the sorption process [95].

In the processes of adsorption, adsorbents with porous structure and enormous surface areas are significant. Small pores, such as micropores (pore size < 2 nm) and mesopores (2 nm < pore size < 50 nm), result in high porosity and surface area which are responsible for adsorption [96]. Adsorption capacity is an essential parameter for the estimation of process costs. In adsorption technology, it is widely known that two adsorbent materials (even for the same pollutant) cannot be compared without maintaining similar experimental conditions. Some of the considerations which strongly influence the whole procedure are (1) the adsorbent's dosage; (2) agitation speed; (3) contact time; (4) initial pollutant concentration; (5) ionic strength of solution; (6) temperature; (7) the pH solution and (8) volume of adsorbate. It is clear that if any of the aforementioned conditions vary, the experiment will not be the same and consequently no comparison will be correct. Having the above in mind, the only comparisons that can be realised are those for adsorbent/adsorbate systems of the same study [97].

Several adsorbents including activated carbon, zeolites, bentonite, peat, sawdust and biomaterials have been studied for the adsorption of REEs from aqueous solutions [98,99]. The adsorbent must have good mechanical properties such as strength and resistance to attrition and it must have good kinetic properties, that is, it must be capable of transferring adsorbing molecules rapidly to the adsorption sites. In most applications, the adsorbent must be regenerated after use and therefore it is desirable that regeneration can be carried out efficiently and without damage to mechanical and adsorptive properties. The raw materials and methods for producing adsorbents must ultimately be inexpensive for adsorption to compete successfully on economic grounds with alternative separation processes [100–102].

A number of different materials with increasing complexity have been tested for REEs. Many of these adsorbents are reported to have low selectivity and poor removal efficiencies for low concentrations of metal ions. Also, the slow removal rates often fail to meet pollution control requirements [103]. Thus, the need arises for exploring alternative adsorbents, with better metal removal efficiency for low aqueous concentrations initiating the research to exploit the unusual and unique properties of nanomaterials. Several adsorbent materials and their adsorption capacities are discussed latter.

3.8.1. Magnetic nanoparticle adsorbent

Functionalized magnetic nanoparticles are excellent candidates for the selective extraction of metal traces from wastewater streams or industrial effluents [104]. These adsorbents can act towards metal ions as a kind of "nano-sponges" and can easily be retrieved from solution with a magnet. After the adsorbed ions are stripped, the nanoparticles can be reused, making this a promising sustainable green technology.

Magnetic (Fe_3O_4) and nonmagnetic (TiO_2 and SiO_2) nanoparticles were coated with EDTA-silane (Fig. 2) and their adsorption capacity and selectivity towards rare-earth ions were investigated [105]. The high adsorption capacities (100–400 mg/g) of these nanoparticles were due to their small diameter (10–20 nm) and high surface area (85–140 m^2/g), combined with a large coverage of *N*-[(3-trimethoxysilyl) propyl] ethylenediamine triacetic acid (TMS-EDTA). It was found that the selectivity towards smaller rare-earth ions increased in the same order as the density of the EDTA-silane on the surface, namely Fe_3O_4 (TMS-EDTA) < TiO_2 (TMS-EDTA) < SiO_2 (TMS-EDTA), SiO_2 and TiO_2 nanoparticles which could hold larger quantities of TMS-EDTA on their surface and therefore adsorb more rare-earth ions, even though their removal from solution was more tedious.

Wu et al. [106] provided an effective route for the fabrication of magnetic material with high adsorption capacity and selectivity towards metal ions, excellent acid resistance property and long service life. Silica was firstly coated on the magnetic particles, and then silane-coupling agent (3-chloropropyltryethosysilane) was used for grating 2-ethylhexyl phosphonic acid mono-2-ethylhexyl (P507), an organophosphorous acid extractant, on the surface of magnetic silica nanocomposite. The adsorption behaviour of La (III) with P507 functionalized magnetic silica nanocomposite was therefore systematically investigated. The optimal pH used was 5.5 with the maximum of adsorption capacity of 55.9 mg/g. After ten times adsorption–desorption cycles, no obvious decrease in adsorption/desorption capacity was found. The P=O functional groups were confirmed to be involved in the coordination.

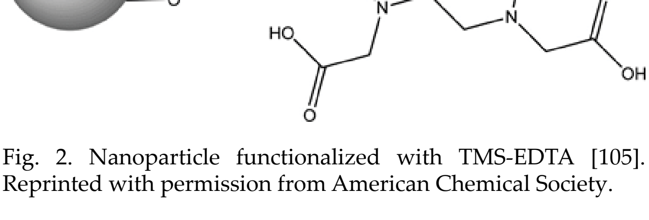

Fig. 2. Nanoparticle functionalized with TMS-EDTA [105]. Reprinted with permission from American Chemical Society.

The recovery of three RE (RE) metals ions Yb(III), Dy(III) and Nd(III), belonging to heavy, mild and light REs, respectively, was also investigated using hybrid chitosan-magnetic nano-based particles functionalized by diethylenetriamine (DETA) by Galhoum et al. [20]. The nanometric size of sorbent particles (30–50 nm) minimized the contribution of resistance to intraparticle diffusion on the control of uptake kinetics. Maximum sorption capacities were 50 mg g^{-1}, irrespective of the REEs and the sorbent could be recycled for five sorption/desorption cycles with less than 6% loss in sorption performance.

3.8.2. Silica-based sorbents

There is an increasing utilisation of mechanically stable synthetic matrices as solid supports for adsorption. Silica gels in particular lend themselves to be modified as such supports. The surfaces are modified either by impregnation of the organic ligands directly onto the surface or by covalent grafting through spacer units for metal ion extraction purposes [107]. Silica gel is a widely used solid material due to its well-established particle size and high surface area, well-defined porosity and high mechanical, chemical and thermal stability [108]. Silica gels as a solid support material have some advantages such as nondeforming, good mechanical strength and heat-stability. Chelating agents could be loaded easily onto the silica gel with high stability or be bonded chemically to the support for a higher and better stability [109]. The immobilization of extraction ligands on silica supports has some advantages over immobilization on organic polymer supports such as short time for equilibration, higher sorption capacities, excellent swelling resistance in different solvents and easy modification of the surfaces to obtain a specific modified support which will depend on the synthetic method used.

Silica gel loaded with 1-phenyl-3-methyl-4-benzoylpyrazol-5-one (PMBP) was prepared and used for the preconcentration of trace amounts of REEs in water samples prior to their determination by inductively coupled plasma atomic emission spectrometry (ICP-AES) [110]. REEs (La, Eu, Yb and Y) were quantitatively retained on the column packed with modified silica gel in the pH range 5–8 and separated from the matrix, and then recovered by eluting with 2.0 mol L^{-1} HNO_3. The adsorption capacity of modified silica gel for La, Eu, Yb and Y was 0.208, 0.249, 0.239 and 0.224 mmol g^{-1}, respectively. This method has been effectively applied for the determination of La, Eu, Yb and Y in geological and environmental samples with satisfactory results. Similar successful and satisfactory results were obtained by Berijani et al. [111] when functionalized nanoporous silica (SBA-15) using *N*′-[(2-hydroxy phenyl) methylene] benzohydrazide (BBH) was utilized as a selective sorbent for the separation, preconcentration and determination of dysprosium (Dy) in natural water. The extraction recovery was 96.5, analytical curve was linear in the range 0.2–1,000 μg L^{-1} and the detection limit was 0.05 ng mL^{-1}. The sorbent exhibited very high adsorption capacity and a fast rate of equilibrium for sorption of Dy ions.

3.8.3. Polymer adsorbents

The development of polymer-based sorbents addressed the two limitations of silica-based sorbents such as instability at extreme pH and the presence of residual silanol groups. Porous polymeric sorbents became an alternative class of materials to overcome some of the shortcomings of previous sorbents. The traditional polymeric sorbent is macroporous polystyrene-divinylbenzene (PS-DVB), the hydrophobic structure of which has a specific surface area of up to 800 m^2/g [112]. Previously, resins were organized by classifying them based on the mechanisms by which metal ions interact with the ligands when bound to the support. The mechanisms identified are according to the properties of the metal ions and the ionic radius, polarizability and coordinate geometry. Polymeric supports have been developed for the complexation of various metals and have received attention by their application for metal recovery from dilute solutions. Different functional groups can be immobilized on the polymer due to the applicability of organic reactions on a solid phase and the success of the functionalization relies largely on the choice of a suitable solvent used to swell the material [79].

The introduction of chelating polymers has allowed the synthesis of ion-selective adsorbent which offers an enhanced selectivity for the removal and concentration of metal ions. Stripping of the metal ions from the ligand is important to polymer-based processes; regeneration and reuse of the polymers are also important to the economics of the application. Cross-linked polymers with functional groups capable of binding metal ions also offer potential advantages such as ease of operation, regeneration and reuse and environmental compatibility. These properties are important to the separation of toxic heavy metals from waste solutions and water in the environment [113]. An understanding of selectivity in the immobilized ligand-metal ion interaction is important to these applications.

In a study on separation of RE metals with a polymeric microcapsule membrane containing acidic organophosphorus compound as an extractant by Kondo and Kamio [114]. La, Ce and Pr as light RE, Sm, Eu and Gd as middle RE, Ho and Er as heavy RE and Y were chosen as sample elements of lanthanoid ions. It was found that adsorption and elution of lanthanoids were achieved by selecting pHs of the feed aqueous solution and each lanthanoid was separated in more than 95% purity. Another study by Roosen and Binnemans [115] investigated the functionalization of chitosan with ethylenediaminetetraacetic acid (EDTA) or diethylenetriaminepentaacetic acid (DTPA) groups to obtain a material that was much less soluble in acidic aqueous solutions than the native chitosan for efficient binding of rare-earth (lanthanide) ions. It was shown that adjustment of the pH of the aqueous feed solution allowed the selectivity of adsorption for rare-earth ions mixtures containing two different ions. After stripping of the metal content, the modified chitosans could be reused for new adsorption experiments. The experiments show that separation of the rare-earth ions is feasible with DTPA-chitosan/silica, without the need for using solutions of chelating agents as eluents.

For increasing adsorption efficiency, surface modifications of synthetic and seminatural polymers by using functional groups of carboxylic, sulfonic, amide and amine have been abundantly developed [116–123]. Several polymer-supported ligands used in REEs separations include: EDTA and DTPA [105,124], 8-hydroxyquinoline (8-HQ) [125,126], hydroxamic acid [127,128], tetramethylmalonamide (TMMA) [129,130], 2,6-diacetylpyridine [131], phosphorus ligands [106] and o-vanillinsemicarbazone (OVSC) [132]. Selectivity can be increased with ligands that can coordinate or chelate with the target metal ion. The grafting of amino and carboxylic acid groups on cellulose increased La(III) sorption efficiency of cellulose and maximum sorption capacity increased from 38 mg La g^{-1} (0.273 mmol/g) for cellulose to 101 (0.727 mmol/g) and 170 mg La g^{-1} (1.22 mmol/g) for amino derivative (PAC) and amino-carboxylic derivative (PCMC) [10].

Macro porous cross-linked polystyrene functionalised with iminodiacetic and aminomethylphosphonic acid groups was used in the sorption of La(III) metal [9] while Calix[4] arene-o-vanillinsemicarbazone was immobilised on a polymeric matrix and used for the preconcentration and separation of lanthanum(III) and cerium(III) [7]. Cellulose and chitosan intrinsic sorption properties for Nd(III) and their efficiency for metal recovery was improved by the grafting of aspartic acid which allowed increased sorption capacities due to the specific reactivity of carboxylate groups [15]

3.8.4. Nanofiber adsorbents

Polymer nanofibers are an exciting novel class of material having diameter in the range of nanometre [133]. Fibres with diameters below 100 nm are generally classified as nanofibers and provide a connection between the nanoscale world and the macroscale world, since the diameters are in the nanometre range and the lengths are in kilometres [134]. The diameters of polymeric nanofibers are not visible under optical microscopes because they are smaller than the wave length of light, but can only be viewed under the electron microscopes [135]. Polymer nanofibers, with diameters in the nanometre range, possess larger surface areas per unit mass and permit easier addition of surface modifications comparable to polymer microfibers. Nanofibers adsorbents have high adsorption capacity; the operation is simple, and the adsorption process is rapid. There is an emergent and growing interest in the application of these nanomaterials as adsorbents [136].

Electrospun nanofibers could be collected as single fibres, nonwoven mats, uniaxially aligned arrays or multilayered films by modifying the electrospinning setup. In addition to controlling macroscopic organization of nanofibers, electrospinning allows the manoeuvre of the secondary structures of individual fibres as well as increasing the structural complexity [137]. Nanofibers possess unique properties that distinguish them from other nonwoven fibres, such as high surface area per unit mass, high porosity, layer thinness, high permeability, low basis weight, cost effectiveness and superior directional strength. It is these unique properties of nanofibers that make them a promising material for a variety of applications from medical to consumer products and industrial to high-tech applications [138]. Electrospun polymeric nanofibers have a vast potential for deposition and support of other materials on their surfaces due to the high surface area, high porosity and high interfibres connections [139]. A variety of new fibre materials have been developed and have found industrial applications based on their excellent mechanical properties and/ or special functions. To date, a variety of synthetic and natural polymers have been electrospun [140], and some applied to adsorption of metals. Nanofibers provide an attractive solution to the removal of toxic metals from water [141].

In recent years, the use of electrospun polymeric nanofibers for adsorption of heavy metals has increased [142–154] and the applications of electrospun nanofibers as adsorbent are summarised [133]. The functionalised electrospun nanofibers have a great prospect when functionalised via incorporation of functional materials into the fibres, or via surface chemistry or coating techniques, and may be able to remove small molecules or metal ions from a solution [138]. Different schemes can be used to produce nanofibers bearing different functional groups and the functionalisation of a preformed nanofiber only requires setting the conditions for the functionalisation reaction, since the base fibre is the same. The approaches to the preparation of functional fibres are essentially of three different types, namely by (1) pre-electrospinning-synthesis of a functional polymer followed by spinning into a fibre or by (2) blending and coelectrospinning by special spinning techniques or by (3) postfunctionalisation-fibre preparation followed by introduction of functional groups [155]. Generally, the polymer support can be modified either chemically (by covalent bonding of the ligand to the matrix) or physically (by direct blending of a chelant into the matrix) [156,157].

The research and development of nanofiber for adsorption is still emerging and more approaches are expected to increase the knowledge in this new area especially for removal of REEs from aqueous solution. Polydopamine (PDA) membrane was prepared by coating PDA on nanofibrous mats and used for adsorption of La (III) ions [158] as illustrated in Fig. 3. The nanofibrous mats were fabricated with blended solution of polyacrylonitrile (PAN) and polysulfone (PSF) in *N*,*N*′-dimethyl acetamide by electrospinning. It was shown that the maximum equilibrium uptake capacity of La (III) on PDA membrane was 59.5 mg/g (0.43 mmol/g) and the experimental data was well fitted to Langmuir isotherm equation. The adsorbed La^{3+} on PDA membranes could be desorbed in 0.01 M phosphoric acid aqueous solution and the membrane can be regenerated in 0.1 M aqueous ammonia successfully without significant influence on its adsorption capacity.

Micronanostructured p-sulfonatocalix[8]arene (calix8) complex membranes prepared by electrostatic adsorbing anionic calix8 onto the cationic nanofibrous mats with micronanostructure were utilized as an affinity membrane for the selective adsorption of lanthanum(III) ions [159]. The as-prepared nanofibrous calix8 complex membranes were tested for selective adsorption of La(III) ions in aqueous solution and results showed very high adsorption capacity and selectivity for La^{3+} from other metal ions such as Fe^{3+}, Al^{3+}, Cu^{2+}, Ca^{2+}, Mg^{2+} and K^{+}. The adsorption capacity was 155.1 mg g^{-1} for La(III) ions and the resultant membranes could be desorbed and regenerated successfully without affecting significantly their adsorption capacity.

3.9. Ionic imprinted polymers

Ionic recognition is a concept with important fundamental and technological implications which is a technique widely used for the preparation of polymeric materials that are capable of high molecular recognition. The polymers which are prepared based on molecular imprinting will have the shape and chemical memory of the target molecule. They are easy to prepare, stable, inexpensive and also able to recognize target molecule selectively [160]. Ion-imprinted polymers (IIPs) are polymeric materials which on leaching, the imprinted ion can rebind, sense or transport (when cast as membranes) selectively the target analyte in presence of closely related inorganic ions [36]. In the past years, there has been a rapid increase in number of publications concerning metal-imprinted polymers [161].

The ability of an imprinted sorbent to adsorb La^{3+} ions was assessed by batch adsorption technique. A straw-supported ion imprinted polymer sorbent was prepared by surface imprinting technique combined with activators generated by electron transfer for atom transfer radical polymerization (AGET ATRP). The maximum sorption amount was 125 mg/g, and the sorption equilibrium could be reached within several minutes. The imprinted sorbent was repeatedly used for ten times without any significant loss in the initial binding affinity [162].

Garcia et al. [163] synthesized different polymers using ionic-imprinting technique as a model for actinides/

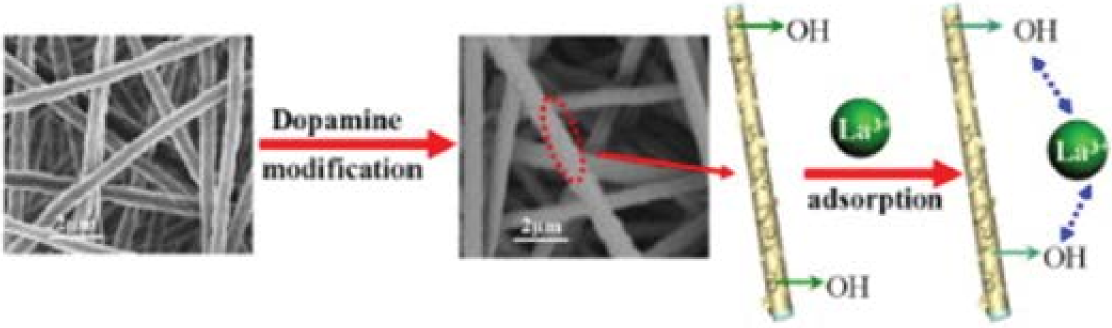

Fig. 3. Schematic of polydopamine fabrication, preparation and adsorption of Lanthanum (III) ions [158]. Reprinted with permission from Elsevier.

Table 1
Summary of the main advantages and disadvantages of the various physicochemical methods for treatment of rare earth metal in water/wastewater

Removal technologies	Advantages	Disadvantages
Chemical precipitation	Simple and safe operation	Increased operational cost of sludge disposal
	Low capital cost	Excessive sludge productions
	Most metals can be removed	Slow metal precipitation kinetics
Electrocoagulation	High particulate removal efficiency	Sacrificial anodes need to be replaced periodically
	Relatively low cost	Sludge production
	Compact treatment facility	High operating cost
Flotation	Low sludge generation	Treatments are required to improve the removal efficiency
	Low cost and low energy requirements	Decreased efficiency due to ionic strength
Membrane filtration	High separation selectivity and efficiency	Process complexity and low permeate flux
	Small space requirement	High operational cost
	Low solid waste generation	Membrane fouling
Solvent extraction	Recover metal ions from high concentrations of the target metal ions	Extractants also extract other base metals
	Separates complexes based on solubility differences	Time consuming and labour-intensive
Ion exchange	Metal selective	Not all ion exchange resin is suitable for metal removal
	High regeneration of materials	Regeneration creates a sludge disposal problem
	Less time consuming	High capital cost
	High removal capacity	Partial removal of certain ions
Biosorption	Use of inexpensive biosorbents	Potential for biological process improvement is limited
	Regeneration of biosorbent and low operating cost	Separation of biosorbents is difficult after adsorption
	Selectivity and efficiency	Early saturation
	High metal binding capacity	
Adsorption with new adsorbents	Easy desorption of the metal ions	Performance depends on type of adsorbent
	Easy operating conditions	Production of waste products
	High metal binding capacities	
	Low-cost	
Ionic imprinted polymers	Stable and easy to prepare	Polydispersity nature of the recognition sites
	Inexpensive	Difficult to characterize
	Metal selective	

lanthanides separation in order to separate lanthanides by liquid–solid extraction. The materials were based on acrylic acid, vinylpyridine, or a diethylene triamine pentaacetic acid derivative. The influence of the structure of cross-linking agents and the use of monomeric complexing agent were studied and a significant increase in the selectivity of complexation was achieved when the material was prepared in the presence of the target ion. The summary of the main advantages and disadvantages of the various physicochemical methods discussed for the recovery of RE metal are presented in Table 1, but no specific treatment has been found to be entirely effective and applicable for RE metal removal.

It is important to note that several other factors such as the overall treatment performance of each method compared with other techniques, the initial metal concentration, environmental impact of the process, plant flexibility and reliability, in addition to the economic parameter such as the operational costs and capital investment are taken into consideration in selecting the most suitable removal treatment method.

4. Conclusion and prospects

REEs have unique properties and are essentially valuable in many high-technology applications such as catalysts for petroleum refining, high-strength permanent magnets, metal and glass additives and phosphors used in electronic displays. REEs comprise the 15 elements of the lanthanide series as well as yttrium, and may be found in over 250 different minerals. This review presents a combined survey and significant developments of the various approaches (chemical precipitation, coagulation–flocculation, flotation, SX, ion exchange, adsorption, membrane processes, filtration, RO and electrochemical techniques) for the removal of REEs from aqueous solutions as well as diverse other sources with emphasis on the current progress in the use of electrospun nanofibers. The adsorption process is considered a promising fundamental alternative to other removal methods for the separation and removal of metal in hydrometallurgy and wastewater treatment processes. The adsorption process is acknowledged as efficient, economically viable, technically feasible, and an extensively used approach. Electrospun nanofibers with unique properties such as high surface area per unit mass, high porosity, layer thinness, high permeability, low basis weight and cost effectiveness, are emerging as a good choice for potential adsorbent applications for RE metals.

Acknowledgments

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