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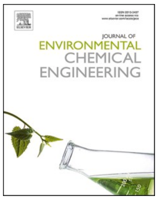

Recovery of rare earth elements from acid mine drainage: A review of the extraction methods

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ABSTRACT

Acid mine drainage (AMD) poses severe environmental pollution problems due to its high acidity, toxic metals and sulphate content. Current methods to tackle the problem are inadequate and those that work are costly. However, AMD contain the rare earth elements (REEs) which remain very important due to the growing increase in their demand because of their critical and indispensable use in many high-tech industries today. The growing demand of the REEs should be met by an increase in supply. The recovery of REEs from AMD is an important development that would cushion REEs supply challenges, thus requires significant consideration. There are several techniques that have been used to recover metal ions from wastewater including AMD. This paper gives a review of typical treatment techniques, innovative developments and examples of the various technologies used for the recovery of REEs from different process solutions, which could be applied in the recovery of REEs from AMD. These techniques include chemical precipitation, solvent extraction, cloud point extraction, ion flotation, ion-exchange, adsorption, molecular recognition technology, magnetic separation and membrane filtration . It is clear from the literature surveyed that chemical precipitation, solvent extraction, ion-exchange and adsorption are the most studied techniques for the recovery of REEs from solutions. Precipitation, ion flotation and adsorption processes show significant potential in their application to recover REEs from AMD. However, the complex AMD chemistry with high concentration of heavy metals require development of integrated process flowsheets incorporating the removal of heavy metals prior to precipitation, ion flotation or adsorption to increase the purity of the REE product stream. On the other hand, these flowsheets should be developed with economic feasibility considerations. Whereas solvent extraction is the preferred method for recovery of rare-earth ions from concentrated aqueous waste streams and pregnant leaching solutions, this method is not recommended for removal of rare-earth ions from diluted aqueous waste streams such as AMD because of the unavoidable contamination of the aqueous phase by organic solvents. Ion-exchange resins and chelating resins also show potential. However, despite ion-exchange being a cheap process, the slow kinetics, large volumes of AMD and the potential of resin poisoning from the impurities in AMD make the process challenging. This necessitates research into developing IX resin suitable for AMD chemistry. In addition, there is recognized prospect of the application of magnetic separation, ionic liquids and cloud point extraction in the recovery of REEs from dilute solutions, although these technologies have not been tested in treating huge volumes of process solutions.

1. Introduction

The mining industry is of considerable importance to the world's economy. The industry provides enormous mineral and metal products, both for industrial and household consumption. Metals play an integral role not only in modern societies, but have historically been associated with industrial development and improvements in the living standards of societies [138]. However, the mining and mineral processing industries not only process large quantities of materials, but also generate large volumes of wastes. The industrial revolution has led to many of the world's current environmental problems such as the wastes generated from mining and mineral processing, climate change, air pollution as well as toxins in rivers and soils. This is due to the increase in the demand of metals which results in an increase in mining activities and

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associated waste generation. The wastes generated from the mining operations include, but not limited to tailings, sludges, slimes, flue dust and mine waters, etc. Of importance is the mine impacted water, commonly called acid mine drainage (AMD). The AMD is recognized as one of the most significant environmental challenges facing the world due to the toxic nature of the water [39]. This means that the removal of the metals and other contaminants from the affected water becomes a necessity.

The two important aspects of the treatment of AMD are economic and environmental. On the economic front, the capital costs for AMD treatment plants can range from ~$100,000 (U.S.) for small passive treatment systems to millions of dollars for large chemical treatment plants [16]. The high capital costs coupled with the other running costs has led to a paradigm shift in research and development where AMD is concerned. The focus is not just acid neutralization for environmental protection but the recovery of valuable products [120]. These products include metals, sulphuric acid as well as water. The AMD is also known to contain valuable metals such as the rare earth elements (REEs).

The REEs are a group of 17 elements which have similar physiochemical properties. These are the 15 lanthanides from Lanthanum to Lutetium and two other elements, scandium and yttrium. The REEs are classified as heavy rare earth elements (HREEs), light rare earth elements (LREEs) or middle rare-earth elements (MREEs). Table 1 is a summary of the classification of REEs including some of their properties. These elements have unique physical and chemical properties which make them find extensive applications in different technologies, summarized in Fig. 1. The metals find application in products such as hybrid vehicles, wind turbines, military applications and advanced electronics such as cell phones [130,38,80].

Although relatively abundant in the earth's crust, REEs rarely occur in a concentrated form which makes it economically challenging to process them. The total worldwide production of REEs in 2016 and 2017 were 129,000 and 130,000 tons, respectively [51]. To date, China alone accounts for 80% of the total production [148,51]. With the limited exports of REEs from China and the extensive global demand for green and sustainable products in energy, military, and manufacturing industries, the demand for these metals is only expected to increase. In addition, the world has entered the era of the 4th industrial revolution (4IR) whose success depends on the access to the critical elements and REEs, the basis of our digital world.

Fig. 2 shows the trends in the global rare earth oxide (REO) production and demand. It is estimated that the demand will reach 210,000 metric tons by 2025 [3]. To meet this demand, there is a need to increase production by establishing alternative sources of REEs. One potential source of REEs is AMD. For example, it has been estimated that coal mine drainage outflows in the Appalachian Basin in Pennsylvania, USA generates a total of about 538 metric tons of REEs per year in a dissolved state, with ~83% of that from low pH (<5) discharges [125].

Table 1
Properties and classification of REEs [47,97,103,144].

Element	Ionic radius (Å)	Atomic radius (Å)	Classification A	Classification B
La	1.045	187	LREEs	LREEs
Ce	1.01	182	LREEs	LREEs
Pr	0.997	182	LREEs	LREEs
Nd	0.983	181	LREEs	LREEs
Pm	0.97	181	LREEs	LREEs
Sm	0.958	180	LREEs	MREEs
Eu	0.947	204	LREEs	MREEs
Gd	0.938	179	HREEs	MREEs
Tb	0.923	178	HREEs	HREEs
Dy	0.912	177	HREEs	HREEs
Ho	0.901	176	HREEs	HREEs
Er	0.89	175	HREEs	HREEs
Tm	0.88	174	HREEs	HREEs
Yb	0.868	192	HREEs	HREEs
Lu	0.861	174	HREEs	HREEs
Sc	0.745	162	HREEs	HREEs
Y	0.9	180	HREEs	HREEs

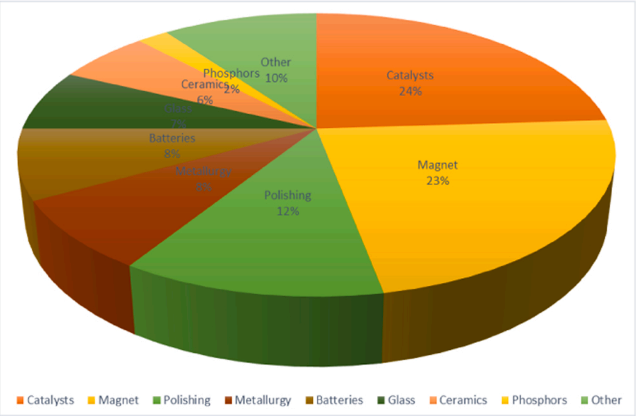

Fig. 1. : Estimated REEs demand by application [148].

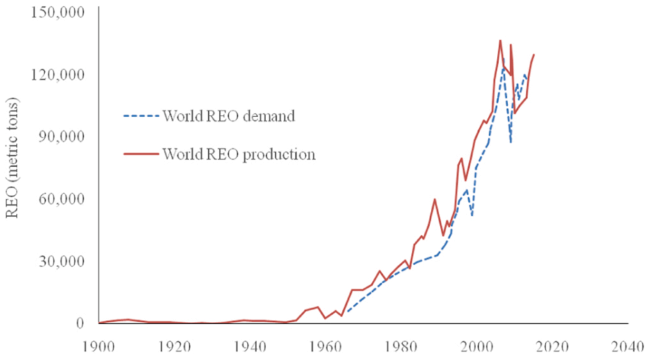

Fig. 2. Global REO production and demand [148].

This paper presents a critical review on the progress of the enrichment or recovery techniques of REEs from wastewater such as brines, seawater and metallurgical effluents. The focus is on the possible application of these techniques to recover REEs from AMD. The paper begins with the evaluation of the chemistry of REEs in acidic waters and an extensive review of the various recovery techniques that have been or can be used to recover REEs from wastewater. The evaluated process techniques are discussed in the context of the complex and diverse AMD solution chemistry. The review concludes with the prospects and sustainability of the REEs resources.

2. Chemistry of rare earth elements in wastewater

The last two decades have seen numerous publications on the geochemistry of REEs in different waters [137,12,33,55,54,82,34,86]. The concentration and distribution of these metals in the water systems are determined by several factors. These include the REEs source, chemical composition of water, including pH and concentration of available ligands, aqueous processes such as adsorption and desorption and fractionation during water-rock or water-colloid interaction [137,29].

Noack et al. [86] presents comprehensive studies on the distribution of REEs in ocean, groundwater, rivers and lakes and reported concentrations of around 5, 53, 71, 170 pmol/L (all parts per trillion concentration levels), respectively. However, the REEs concentration reported in AMD is 1–4 orders of magnitude above natural waters [125,8]. Table 2 shows the concentration of REEs from different water sources. The concentration of REEs in AMD is higher compared to natural waters,

Table 2
The REEs concentration (μg/L) in acid mine drainage and other water sources.

Species	Mpumalanga South Africa[79]	Jaintia Hills coal fields, India[146]	The Sitai Coal mine, China [113]	Metalliferous Hills, Italy[100]	Odiel River, Spain[28]	Mississippi River, USA[43]	Zhujiang River, China[70]	Coalfields, USA [22]
pH	2.10	2.60	3.61	3.10	3.25			2.7–7.3
La	845	316	7.77	185	13.2	0.0039	0.035	0.005–140
Ce	5510	1108	19.4	390	36.2	0.0073	0.075	0.01–370
Pr	–	148	2.78	45.8	–	0.0014	0.012	–
Nd	1310	303	12.9	172	19.7	0.0073	0.053	0.006–260
Sm	–	154	2.98	34.8	4.85	0.0021	0.037	0.005–79
Eu	–	37.1	0.87	8.65	1.09	0.0007	0.015	–
Gd	–	168	3.78	40.2	5.78	0.0036	0.031	0.005–110
Tb	–	28.5	0.70	5.00	0.83	0.0005	0.006	–
Dy	–	132	4.06	23.7	4.96	0.0045	0.028	0.002–99
Ho	69	35.5	0.87	4.18	0.9	0.0012	0.006	–
Er	–	56.8	2.43	10.5	2.2	0.0041	0.023	–
Tm	–	12.3	0.34	1.21	0.3	0.0006	0.006	–
Yb	–	51.2	1.99	7.07	1.73	0.0039	0.023	–
Lu	–	10.4	0.31	0.94	0.26	0.0007	0.005	–
Sc	112	–	–	–	–	–	–	1.0–36
Y	2050	–	–	–	–	–	–	0.11–530
Total REEs	9896	2561	61.21	928.96	92.01	0.0418	0.355	0.355

with lanthanum, cerium and yttrium up to parts per million (ppm) levels. A strong correlation between acidity and REEs concentration has been reported [118,139,55,7]. Below a pH of 5 in the water-sulphate (SO_4^{2-}) media, REEs concentration increases due to complexation with the sulphate ligand forming a stable $REESO_4^+$ complex, which is the dominant complex in acidic waters [8,55]. The sulphate complexation inhibits the sorption of REEs and stabilizes them in solution. Strong complexation with the carbonate (CO_3^{2-}) and the bicarbonate complex $(Ln(CO_3))^{2-}$ is understood to account for the decrease in REEs concentration at a pH above 5 due to the tendency of the REE-carbonate complexes to be adsorbed by metal (e.g. Al, Fe, Mn) hydroxide colloids [72]. Fig. 3A and B shows the variations of the relative abundance of La^{3+} aqueous species in natural water (A) and acid water (B).

3. Explored techniques for the recovery of rare earth elements from dilute solutions

The REEs concentration in the leach solution produced from leaching of both primary and secondary materials is several orders of magnitude higher than in wastewater. The high REEs concentration makes the whole REEs recovery process economically viable. However, the recovery of these metals from wastewater necessitates the need to use methods that would fit the low REEs concentrations. This section reviews some of the process techniques that have been used to recover REEs not only from AMD but different dilute wastewater, their challenges and the innovative improvements that have been made.

There are numerous technologies that have been explored to remove or recover metals from industrial waste streams. These techniques include precipitation, solvent extraction, ion exchange, adsorption, molecular recognition technology, magnetic separation, membrane filtration, flotation, electrodialysis, reverse osmosis and nanofiltration. The efficiency of these processes largely depends on the concentration of the metals in solution and the solution chemistry e.g., the pH, ionic strength, redox condition, viscosity, complexation, etc., [102,85]. This section discusses the applications and limitations of these techniques in the enrichment of REEs from AMD.

3.1. Chemical precipitation

Chemical precipitation is by far the most common technology used in removing dissolved metal ions from solutions such as wastewater. The metal ions are removed by transforming them into insoluble compounds which are then removed by physical means. Chemical precipitation has found wide application because of its simplicity. REEs can be recovered from weakly acidic wastewater (pH 1–4) by fractional precipitation. This method entails the removal of part of the REEs from solution by the addition of a chemical reagent to form a new, less soluble compound. Double salt, oxalate, phosphate, and hydroxide precipitation methods have been used to recover REEs from different process solutions.

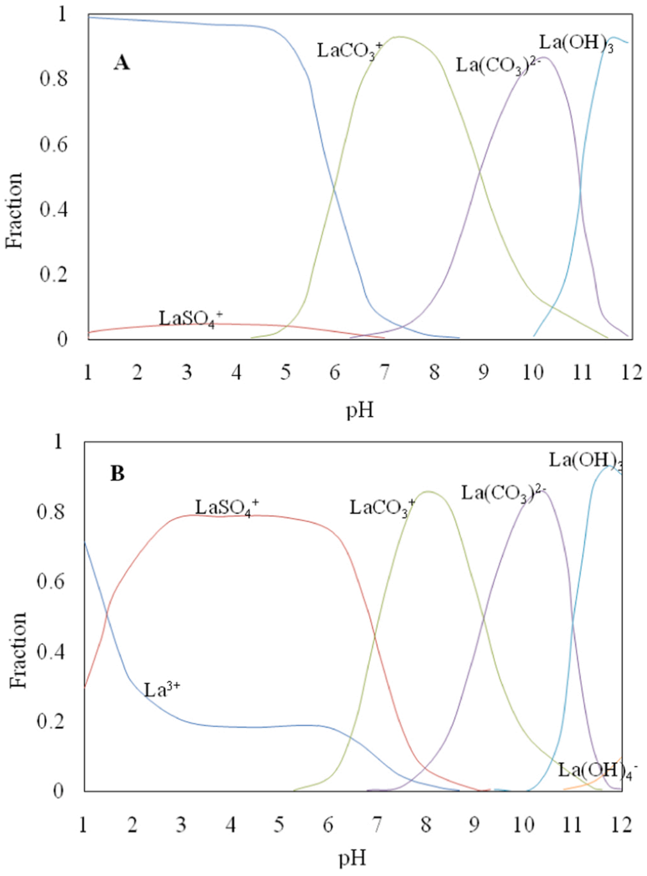

Fig. 3. Variation of the relative abundance of La^{3+} aqueous species with pH in: A) natural water of a regular weathering profile ([Total Inorganic Carbon]= 1 mM; [SO_4^{2-}]= 0.01 mM]; B) acid mine water ([Total Inorganic Carbon]= 0.01 mM; [SO_4^{2-}]= 1 mM]).
Redrawn from Ayora et al. [8].

3.1.1. Double salt precipitation

One of the most widely used methods to separate REEs from acidic solutions is by precipitation as double sulphate hydrates through the addition of metal sulphate salt. This can be represented by Eq. 1 [11,41]. Double salt precipitation of REEs is generally confined to crude separation of the REEs mixture into LREEs, MREEs, and HREEs. The elements lanthanum, cerium, praseodymium, neodymium and samarium form sparingly soluble double sulphates whereas those of holmium, erbium, thulium, ytterbium, lutetium, and yttrium are soluble. Europium, gadolinium, and dysprosium form double sulphates of intermediate solubility.

$$M^{+} + REE^{3+} + SO_4^{2-} + nH_2O \rightarrow MREE(SO_4)_2^{2}.nH_2O \tag{1}$$

M^+: Na^+ and K^+, NH_4^+

In the early REEs industry, Xu [143] used double salt precipitation to separate trivalent REEs from thorium. Table 3 shows the recoveries that were obtained. The REEs recovery was 99.7% with very minimal co-precipitation of impurities. Iron was the major impurity in the solution and the mass balance calculations showed that all the iron remains in the solution. Kul et al. [67] conducted decontamination experiments of the REEs from the REEs solution containing thorium, iron, aluminium and manganese and 23 g/L REEs by rapid precipitation at 50 °C using Na_2SO_4. The precipitation reactions were conducted at elevated temperatures because as the temperature rises, the solubility of the double sulphates fall. At such conditions, the double salt is almost insoluble in saturated solutions of the alkali sulphate [95]. From the test work, it was observed that the total REEs double sulphates content was $>$ 90%. A total of 0.7% of impurities co-precipitated.

Although the concentration of REEs in the studies conducted by Xu [143] and Kul et al. [67] was higher (23–35 g/L), Kim et al. [61] separated REEs from the iron-REEs sulphate solution containing 23.39 mg/mL neodymium and of 8.67 mg/mL dysprosium. The precipitation was conducted at 60°, 3 hours reaction time and 7 equivalents sodium sulphate. Neodymium was easily precipitated as a neodymium-sulphate salt. On the other hand, excessive sodium sulphate was needed for the precipitation of dysprosium sulphate salt. Qi [101] concluded that to completely precipitate REEs, the double salt dosage of 2–3 times that of the stoichiometric requirement is necessary. In the context of AMD, double salt precipitation is a selective technique with preference for the REEs over iron, aluminium and manganese, which are some of the major impurities contained in AMD. However, challenges remain in the application of this technique to recover REEs from wastewaters. These include the low REEs concentrations of the wastewaters coupled with the high energy requirement (temperatures between 50 and 90 °C) and the excess salt sulphate required to complete the precipitation reactions.

3.1.2. Oxalate precipitation

Oxalate precipitation is another method for REEs precipitation owing to the strong affinity of the oxalate ion for REEs and their low solubility. REEs-oxalate complexation has been reported to form hydrated REEs salts according to Eq. 2 [20,56].

$$2REE^{3+} + 3OX^{2-} + nH_2O \rightarrow REE_2OX_3^{3}.nH_2O \tag{2}$$

The formation of REEs-oxalate complexes was reported as early as the 1950 s [23,32]. Oxalate precipitation has long been used as a pre-concentration step in REEs analytical chemistry. For example, the oxalate gravimetric method is used as a pre-concentration method of REEs from dilute solutions were oxalic acid is spiked into a weak acidic solution containing REEs, resulting in colored REEs oxalate precipitate as $REE_2(C_2O_4)_3.nH_2O$ [1]. Kuroda et al.[69] and Osseo-Asare [57] employed an oxalate precipitation step to isolate lanthanides from a sulphuric acid leach solution. Chi and Xu [20] developed a solution chemistry approach to study the REEs precipitation from a solution containing 12 mM/L total REEs using oxalic acid. An experimental optimal pH of 2, to obtain more than 95% recovery and purity of REEs precipitate was reported. Josso et al. [56] studied the precipitation of REEs from a low concentration leach solution (0.1–0.5 g/L) and high concentration of impurities. The formation of REEs-oxalate was reported to be favoured in the order MREEs $>$ LREEs $>$HREEs. An optimal pH range of 1.1–2.0 was recommended.

Table 3
REEs recoveries by double salt precipitation from a sulphate leach solution based on [143].

	REE	ThO_2	Fe	P_2O_5	$[H^+]$ (mol/L)
Leach solution (g/L)	35	0.15	21	10	1.5
Double salt (%)	42–45	0.1–0.2	0.2	0.3	
Filtrate (g/L)	0.1	0.02–0.04	21–22	11	1.5
Recovery (%)	99.7	73.3–86.6	0	0	

The decision to choose oxalate precipitation, however, largely depends on the concentration of REEs and possible interfering elements i.e., aluminium, chromium, iron, titanium and zirconium [14]. The total oxalic acid needed for precipitation consists of three parts, stoichiometric requirement, excess acid to achieve complete precipitation and complexation of non-REEs impure ions [101]. Only the first two parts are involved in the precipitation of pure REEs. Chi and Xu [20] deduced the formula to estimate the consumption of oxalic acid by non-REEs elements like aluminium, iron, magnesium and calcium. It was concluded that the stoichiometric amount only accounts for 60% of the oxalic acid with the other 40% being consumed by precipitating non-REEs impurities. Oxalic acid being an expensive reagent, the application of oxalate precipitation to recover REEs from AMD, with low REEs concentration, but with high impurity concentration, could prove to be uneconomical [10]. Another disadvantage of oxalate precipitation is the release of carbon dioxide in a series of reactions during the calcination of $(REE)_2(C_2O_4)_3,nH_2O$ to produce the rare earth oxides, Eq. 3, which could raise environmental concerns.

$$2REE_2(C_2O_4)8H_2O \xrightarrow{650-800^{\circ}C} 2REE_2O_3 + CO_2 + 8H_2O \tag{3}$$

3.1.3. Phosphate precipitation

Another technique used for the recovery of REEs from aqueous solution is phosphate precipitation. This is due to the strong affinity of lanthanides and yttrium for the phosphate conjugate compared to the sulphate. The addition of the phosphate ions to the REEs-containing solution is expected to trigger the precipitation of REEs as phosphates according to Eq. 4;

$$REE(SO_4)_n^{3-2n} + PO_4^{3-} \rightarrow REEPO_4 + nSO_4^{2-} \tag{4}$$

Volkovich et al. [132] conducted precipitation studies by dosing lithium phosphate to a solution containing REEs which gave essentially complete precipitation of $LnPO_4$. Chávez Vela [18] recovered REEs from AMD containing 130 mg/L of REEs using phosphate precipitation. In another study, Beltrami et al. [10] obtained 95% recovery of REEs from a solution containing 250 mg/L of REEs and high concentration of iron (32, 300 mg/L). It was demonstrated from this study that it is possible to obtain purified REEs starting from industrial solutions, like AMD, which are usually discarded.

Two of the predominant heavy metal elements contained in most AMD solutions are iron and aluminium. Although iron can be transformed from one oxidation state to the other and subsequently removed by different techniques, aluminium is very similar to REE ions. Due to the similarities, aluminium is expected to compete with the precipitation of REEs during phosphate precipitation which is in accordance to the reported pKs values for REE-phosphates and aluminium phosphate. These are presented in Table 4. This could result in co-precipitation of impurities with the REEs and thereby reducing the purity of the final product and increasing the cost of subsequent purification stages [10,18, 76]. There is thus a need to have an aluminium scrubbing step to make

Table 4
pKs values of $Al(PO_4)_s$ and some of the $REE(PO_4)_s$.

Metal	pKs ($MPO_{4\ (s)}$)
Al^{3+}	18.3 (T = 37 °C, I=0.15 mol L^{-1})
La^{3+}	22.43 (T = 25 °C, I=0.5 mol L^{-1})
Ce^{3+}	26.3 (T = 25 °C, I=0 mol L^{-1})
Gd^{3+}	25.6 (T = 25 °C, I=0 mol L^{-1})

the process feasible. The other factor is the cost of phosphoric acid, which is an expensive reagent. However, disodium phosphate (Na_2HPO_4) can be used as a cheaper option to provide the phosphate ions required for precipitation.

3.1.4. Hydroxide precipitation

Hydroxide precipitation is another technique that has been tested in the recovery of REEs from solution. A hydrometallurgical process route was developed for the conversion of REEs borosilicate containing 43.12 wt% lanthanum oxide, 9.37 wt% yttrium oxide and 4.60 wt% gadolinium oxide to REEs hydroxide using sodium hydroxide [53]. The recoveries of 99.4% lanthanum, 100% yttrium and 100% gadolinium were obtained. Khawassek et al. [59] recovered REEs from effluent solutions containing 135 ppm of REEs using ammonium hydroxide at pH 9.3. However, the precipitate only contained 16.2 wt% REEs with the bulk of it being iron. To improve the REEs product purity, the cake was re-dissolved in hydrochloric acid followed by double salt precipitation and a REEs precipitate purity of 73.5 was obtained. The reduced precipitate purity was due to the sorption of the REEs on the iron(III) oxyhydroxide precipitate. Quinn et al. [102] studied the distribution coefficients for REEs in an aqueous solution containing oxyhydroxide precipitates of iron, aluminium, gallium and indium. It was observed from the study that the sorption of yttrium on the iron (III) oxyhydroxide precipitates is intermediate to that of lanthanum and cerium. Li et al. [73] recycled REEs from industrial wastewater with flowerlike nano-magnesium hydroxide. More than 99% of REEs were successfully taken up by the magnesium hydroxide nanoparticles. To avoid the sorption of REEs on the iron (III) oxyhydroxide particles, Ma et al. [79] removed iron by precipitation at pH 3.5 prior to REEs hydroxide precipitation at pH 5.

3.1.5. Summary

The behavior of the REEs and other cations during the precipitation process depends strongly on the solution chemistry, available ligands (i.e., OH^-, SO_4^{2-}, NH_4^+, CO_3^{2-}, and PO_4^{3-}), and concentration of elements. The review shows that all the reviewed precipitation techniques can be used to separate REEs from the bulk of heavy metals contained in the AMD. However, challenges remain. For example, a common observation in RE recovery by oxalic acid precipitation requires excess use of oxalic acid. The exact reason for this excess requirement of oxalic acid is not clear and thus require further research explaining the oxalic acid consumption with respect to the AMD solution chemistry. In the hydroxide precipitation, the Al contained in the AMD would be co-precipitated with the REEs. Solving the problem of REEs product stream contamination require developing of integrated process flowsheets, coupling precipitation with other techniques.

3.2. Solvent Extraction

Solvent extraction (SX) has generally been accepted as the most appropriate commercial technology for separation of REEs because of its ability to handle larger volumes of pregnant liquor and the high loading capacity of the extractants used ~ 180 g REEs/L [141,41]. The three major classes of extractants used to separate REEs include the cation exchangers or acidic extractants, solvation extractants or neutral extractants and anion exchangers or basic extractants (Xie, 2014). The chelating extractants have also been used to a lesser extent [108]. Table 5 summarizes the common extractants used in the extraction of REEs.

3.2.1. Carboxylic acids

The carboxylic acids such as naphthenic (cyclohex-3-ene-1-carboxylic acid), versatic acid (neo-decanoic), cekanoic (6-Methylheptanoic acid), and neo-heptanoic (4,4-Dimethylpentanoic acid) have been investigated to recover REEs from different solutions [9,66,98]. The mechanism of extraction of REEs using such acid extractants can be represented by Eq. 5 [127];

$$REE^{3+} + 3(HL)_2 \rightarrow REE(HL_2)_3 + 3H^+ \tag{5}$$

where $(HL)_2$ is a dimer molecule of the extractant in non-polar diluents like kerosene, and $REE(HL_2)_3$ is a REE complex.

Singh et al. [121] studied the extraction of REEs including yttrium from a chloride medium with cekanoic, naphthenic, neo-heptanoic and Versatic 10 acids in dodecane. The extraction order for REEs was found to be La<Ce<Pr<Nd<Sm<Gd<Dy<Ho for all these acids. Perston and Du Preez [50] concluded that the extraction of yttrium differs for these reagents with yttrium being extracted with the MREEs (La <Ce <Nd<Gd< Y < Ho <Yb) whereas it is extracted by naphthenic acid with the LREEs (La < Ce < Y <Nd<Gd< Ho <Yb). Although naphthenic acid has widely been used for separating yttrium from the lanthanides in China, the extractant composition changes with its use and its high solubility in water leads to reagent losses [25]. This has led to the development of alternative carboxylic acids, such as sec-nonylphenoxy acetic acid (CA-100) and sec-octylphenoxy acetic acid (CA-12) which have much lower aqueous solubilities than naphthenic acids [141]. CA-100 was tested for the extraction of scandium, yttrium and lanthanum from acid chloride solutions and the results indicated that it can extract the REEs at lower pH values than versatic acid. The extraction behavior of yttrium was observed to closely resemble that of HREEs [135].

3.2.2. Organophosphorous extractants

Various types of acidic or neutral organophosphorous extractants have been used to recover REEs from mineral acidic media. These include 2-ethylhexyl phosphoric acid (D2EHPA), mono(2-ethylhexyl) ester (P507/PC88A), di(2-ethylhexyl) phosphoric acid (P_2O_4) and tributyl phosphate (TBP) [93,105,40]. A continuous solvent extraction process for the separation of the MREEs (Sm, Eu, Gd, and Tb) and the LREEs fractions (La, Ce, Pr, and Nd) from a nitrate acidic solution is described by Preston et al.[99]. A 15% v/v of D2EHPA in Shellsol AB was used to extract MREEs in an 8-stage counter-current circuit. The recoveries of the MREEs to the strip liquors was 95–100% with the losses of the LREEs reported at< 4%. Rabie [104] also used D2EHPA to separate samarium, europium, and gadolinium from the other REEs in a mixed nitrate-chloride leachate and reported a 78% recovery. In China, the main extractant used to separate REEs from each other is mono

Table 5
Solvent extractants used to recover/separate REEs [89].

Category of extractant	Name of extractant	Target REEs
Carboxylic acid	cyclohex-3-ene-1-carboxylic acid 6-Methylheptanoic acid 4,4-Dimethylpentanoic acid, neo-decanoic	Y, Ce, Pr, LREEs
Organophosphorus	D2EHPA, 2-ethylhexyl, 2-ethylhexyl, tributyl phosphate	La, Ce, Pr, Eu, Tb, Tm, Yb,Lu, Nd, Ho, Gd, Sm, Dy, Er
Amines	Primene 8 l-R, Primene JM-T, and N-benzylheptadecylamine	Eu, Pr, Ce, Y, Tm

(2-ethylhexyl) ester (P507) [40]. The separation factors of LREEs are higher as compared to the HREEs. In another study, Ganji et al. [37] carried out an investigation to evaluate and compare the separation of REEs including lanthanum, gadolinium, neodymium and dysprosium from nitric acid solution using D2EHPA, Cyanex272 (bis(2,4,4-trimethylpentyl) phosphinic acid) and a mixture system of D2EHPA and Cyanex272. A mixture of D2EHPA and Cyanex272 gave the best separation results owing to the higher separation factors of Dy/Nd (720.05) and Dy/Gd (3640.27) as well as lower extraction efficiencies of Gd (64.54%), La (30.07%) and Nd (26.47%) from Dy (99.92%). Cyanex 272 was reported to have the lowest separation factors. The solvent extraction of several REEs from sulphate medium using Cyanex reagents group has also been investigated. However, the Cyanex reagents group is strongly affected by the low REEs extractability and their low loading capacity resulting from the low lipophilicity of the coordination compounds formed during the extraction process [11]. More so, Cyanex 272 has higher selectivity of other metal species including iron and aluminium.

3.2.3. *Amines*

Amines are solvents that are entirely made up of bulky organic cations and different types of inorganic anions. Amine based extractants are one of the most useful nitrogen-containing extractants for the REEs. These include primary amines, secondary amines, tertiary and quaternary ammonium salts [1]. Organic amines with molecular weight of around 250–600 are suitable for the extraction of REEs because they are insoluble in water. They are known to form stable salts in strong acidic solutions and their anion exchange ability follow the order of ClO_4^- > NO_3^- > HSO_4^- > F^-. Li et al. [74] used amine N1923 to separate REEs from a sulphuric acid matrix solution contaminated with iron and thorium. REEs were isolated from iron and thorium with the extraction efficiency of the REEs decreasing with an increase in the REEs atomic number. Secondary amines e.g., N235 have also been reported to extract REEs efficiently in the presence of salting-out agents [1]. Rice and Stone [107] investigated several other amines in the solvent extraction of REEs. Favorable results were obtained using sulphate solutions. However, extractions from chloride, nitrate, and perchlorate solutions were reported as negligible. The most effective separations were obtained with the amines Primene 8 l-R, Primene JM-T, and N-benzylheptadecylamine.

3.2.4. *Ionic liquids - green solvents*

Green chemistry is the design of chemical processes and products that reduces or eliminates the use and generation of hazardous substances [5]. Ionic liquids (ILs), also considered as green solvents, have been studied as potential solvents or carriers of metal ions in liquid-liquid separation. The increased interest in the use of ILs is due to their unique properties such as non-volatility, non-flammability, and wide temperature range for the liquid phase. Although the greenness of IL has been questioned because of possible hydrolysis resulting in the formation of toxic HF or partial loss to the aqueous phase, they are still an important solvent in metal processing. Various fields of ILs applications are presented in Fig. 4 with wastewater being the area of interest. Few studies have been conducted on the application of ILs to enrich the REEs from different process solution. Mohapatra et al. [83] developed diglycolamide-based IL to extract Eu^{3+} under acidic conditions and obtained 98% recovery. Zhu et al. [149] developed a novel IL-based synergistic extraction system utilizing the ionic liquid tricaprylmethylammonium nitrate ([A336][NO_3]) and the commercial extractant di (2-ethylhexyl) 2-ethylhexyl phosphonate (DEHEHP) for the extraction of rare earth nitrates. The maximum synergistic enhancement coefficient of 3.44 was attained.

Green chemistry technologies like the use of ionic liquids also show immerse potential for the recovery of REEs from process solutions. Considering that AMD is an environmental concern and the production of further hazardous substances or waste should be restricted, the use of amines and ionic liquids to recover REEs from AMD should be explored.

3.2.5. *Summary*

Solvent extraction of REEs has been extensively researched and is a widely used technique for separation of individual REEs. The use of cation exchangers, solvation extractants, and anion exchangers, for separating rare earths has been studied. Commercially, D2EHPA, HEHEHP, Versatic 10, TBP, and Aliquat 336 are the widely used commercial extractants to separate rare earth elements. Although solvent extraction has its merits such as low energy consumption, regeneration of solvents, ease of REEs stripping with weak acids, high selectivity even in a matrix of other impurities, limitations of its use to recover REEs from AMD still exists. This arises from the use of organic volatile, combustible, and toxic solvents. Often, traces of solvent components are carried into effluent streams, which necessitate environmental abatement. More so, organic solvents can be expensive because of the large volumes of solvents used. As such, this technique cannot be used to recover REEs from such huge, dilute solutions. In addition, the high sulphate concentration of the AMD is expected to reduce the extraction efficiencies due to the masking of the metals by anionic sulphate-REEs complexes formed in solution. An alternative to conventional solvents is ionic liquids. Ionic liquids are very good solvents for both inorganic

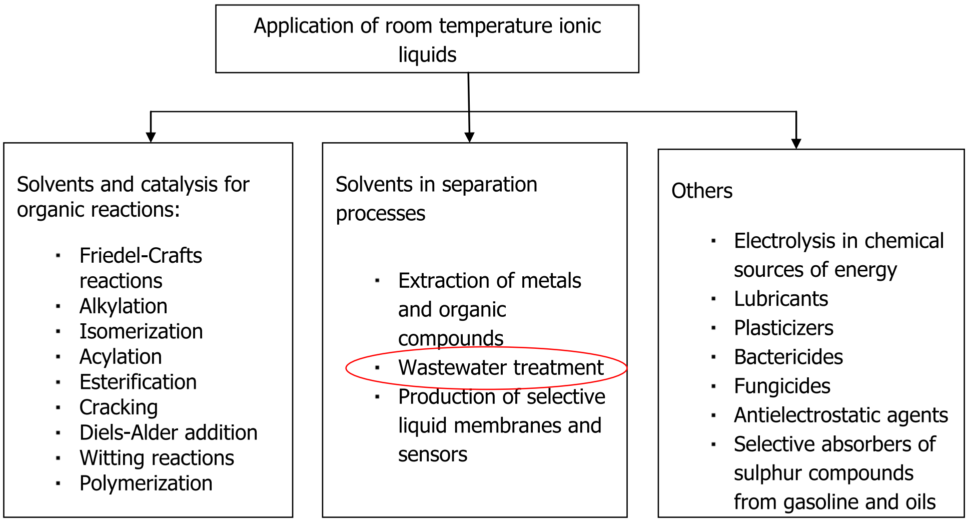

Fig. 4. Schemes of ILs applications[112].

and organic compounds (from small, simple molecules to complex polymers). However, although successfully applied to recover REEs from different process solutions, there application in wastewater treatment, and specifically recovery of metal value from AMD remains largely unknow and thus requires considerable attention.

3.3. *Cloud point extraction*

Cloud point extraction (CPE) is a liquid-liquid extraction technique which is based on the fact that most of the nonionic surfactant can form micelles in aqueous solutions and become turbid when they are heated beyond cloud point temperature (CPT). Above this CPT, the micelle phase disengages into small volumes of surfactant rich phase and a dilute aqueous phase, in which the surfactant concentration is close to the critical micelle concentration (CMC). The metals which solubilize in the hydrophobic core of the micelles are separated and concentrated in small volumes. Fig. 5 shows the overall schematic process for CPE.

CPE has become widely utilized for separation and pre-concentration of trace metal ions prior to analysis in analytical chemistry [42]. The metals in ionic or hydrophobic chelates resulting from different chemical reactions can be concentrated using this method. CPE has been applied to trace REEs analysis. Table 6 is the list of the extraction system of CPE along with subsequent detection technique. Silva et al. [119] developed a low-cost methodology for the determination of Er(III)−2-(3,5-dichloro-2-pyridylazo) − 5-dimethylaminophenol as a chelating agent and PONPE-7.5 as a nonionic surfactant. The proposed procedure was successfully applied to determine erbium in synthetic samples. Similar techniques have been developed for pre-concentration of dysprosium prior to its spectrophotometric determination in urine [90]. Recently, a cloud point extraction and separation of scandium and yttrium (III) was investigated using Triton X-114 with and without 8-hydroquiloline (HQ) as an added chelate agent [140]. The effects of various parameters including aqueous phase pH, HQ concentration, Triton X-114 concentration, heating temperature and incubation time were investigated. It was observed that there was a different extraction and separation behavior of scandium and yttrium with and without the HQ chelate. It was also demonstrated that CPE extraction is an excellent method to separate scandium and yttrium.

3.3.1. *Summary*

The CPE is a simple, cheap and rapid concentration technique that has scored considerable success in analytical chemistry. It uses water and avoids the use of large amounts of expensive toxic and flammable solvents. With the need for a green chemistry approach, the use of CPE in the extraction of REEs from wastewater and particularly AMD should be exploited. The high selectivity and the fact that it can concentrate trace elements from nano scale make it even more attractive for possible application in metal recovery from wastewater. In addition, its fast reaction kinetics means that huge volumes can be treated per specific time as compared to solvent extraction which requires multiple loading and extraction stages. However, the energy required to reach the CPT could increase the overall cost of the process.

3.4. *Ion flotation*

Flotation has been established as the most significant method for the concentration and dressing of ores and minerals. From the principles of mineral flotation comes ion flotation which is finding its way as a separation technique of dilute aqueous solutions, with interest in metal ions recovery. Just like in mineral flotation, ion flotation involves the removal of surface-inactive ions from the aqueous solutions with addition of surfactants (also termed as collectors) followed by air bubbling through the solution. It is another form of co-precipitation of metal ions [81]. The schematic for general ion flotation process is given in Fig. 6.

Ion flotation has several advantages for treating dilute solutions including low energy requirements, low residual concentration of metals, rapid operation, small space requirements and that it can be applied to a variety of metals at various concentration levels and produces minimal sludge [94]. Hogan et al. [45] studied the ion flotation of lanthanum, cadmium and caesium from water. The elements were tested at collector to colloidal ratios of 2, 5 and 10. The maximum removal efficiency for the metals when floated individually was 46.2%, 99.8% and 98.6% for caesium, cadmium and lanthanum, respectively. Ion flotation of yttrium (III) and ytterbium (III) cations from dilute aqueous solutions in the presence of chloride ions using sodium dodecyl sulphate as a collector was studied by Lobacheva et al. [78]. The distribution and recovery coefficients of the two metals as a function of aqueous phase

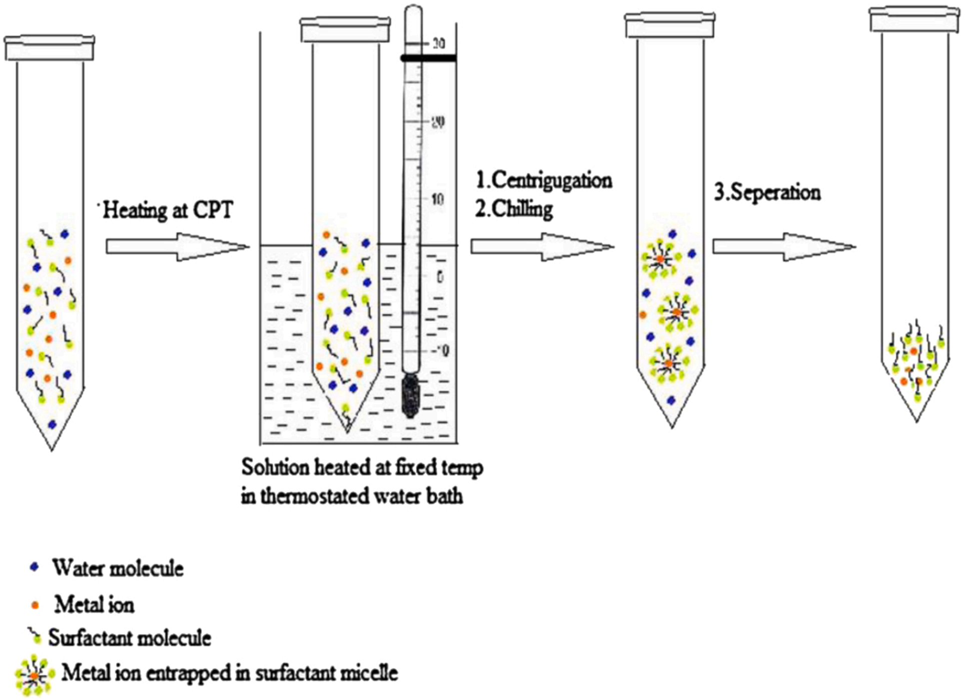

Fig. 5. Schematic of the overall process of cloud point extraction [115].

Table 6
Application of CPE for trace REEs analysis [1].

Analyte	Surfactant	Complexant	Enrichment factor	Detection	Limit of detection	Sample
REEs	Trixton X-114	8-HQ	7.9–9.2	ICP-OES	41.4 (Yb) – 448 (Gd) ng/L	Tea leaves and mushroom
REEs	Trixton X-114	No complexant	5.4–8.1	–	69.0 (Sc) – 509.5 (Sm) ng/L	Tea leaves and mushroom
REEs	Trixton X-114	TTA	9.14	ICP-OES	2 (Pr) – 103 (Lu) mg/L	River water
Dy, Er, Eu, Gd, Ho, La, Lu, Pr, Sm, Tb, Tm, and Yb	PONPE-7.5	PAN	70	NAA	0.27 (Yb) – 3.07 (Eu) ng/g	–
Eu(III)	Trixton x-114	Alizarin red S	22	FAAS	6 ng/L	Water
REEs	Trixton X-114	(*i*-pr) DGA	140	ICP-MS	0.2 – 30 ng/L	Soil

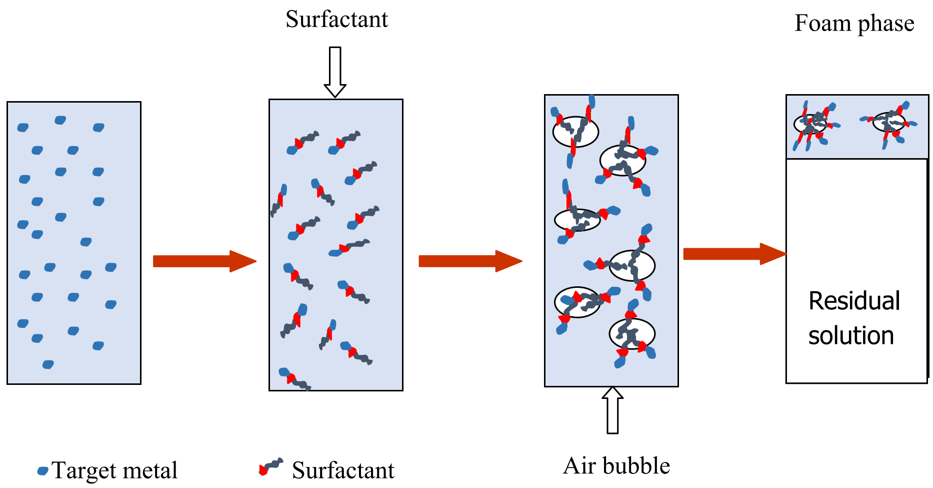

Fig. 6. Schematic of the overall process of ion flotation [17].

pH at different sodium chloride concentration were determined. Maximum separation coefficient of 50 was observed with the chloride concentration of 0.01 M at pH 7.8. Golloch [1] also reported a process that was used for flotation of trace REEs using $Fe(OH)_3$ as a precipitant, with oleic acid applied as the surfactant at pH 8–9.

3.4.1. *Summary*

Ion flotation has several advantages including high efficiencies, rapidity and possibility of recovery of both organic and inorganic species, depending on the surfactant used. However, the floatability is affected by various factors such as pH, flotation time, air flowrate, collector to metal ratio, froth concentration and ionic strength [114]. The complex chemistry of the AMD also means close attention should be paid to selectivity of the processs. The ionic strength of the AMD solution would also impact on separation as an increase in the ionic strength decreases the separation efficiency.

3.5. *Ion-exchange*

Ion exchange (IX) is a technique that removes metal ions from solution by exchanging them with weakly bound ions in a resin. Ion exchange resins consists of two main types, i.e., cation exchange resins, that exchange positively charged ions while anion exchange resins exchange negatively charged ions. Resins are usually made from the polystyrene polymer backbone and differ only by their specific functional groups. IX has become an attractive alternative for separations and recovery of metals from dilute solutions because of its simplicity. Although this method simplifies the separation process and makes it possible to separate mixtures with complex matrices, IX usually exhibit poor selectivity and slow kinetics (Smith et al., 2017). IX methods have been used for the recovery of several metal ions, including REEs from different process solutions. The first application of this method in REEs enrichment was in the separation of fission products obtained from nuclear reactors [124]. This was followed by many other investigations employing a large variety of ion exchangers including the organic or resins and inorganic or zeolites exchangers [91,111,133,4,63]. The IX resins are normally classified as cationic, anionic and chelating having sulphonic or carboxyl groups, amine groups and organic groups, respectively. Table 7 summarizes some of the resins that have been used for the extraction and pre-concentration of REEs from different solution using IX.

3.5.1. *Cation-exchange resins*

The REEs are separated on columns filled with cation-exchange resin. In the cation exchange process, the polystyrene sulphonic cation exchangers are most often used and REE cations are exchanged with H^+, ammonium ion or other cations derived from the ion exchange phase [63]. Rychkov et al. [111] conducted a comparative study of IX of REEs, ferric iron and aluminium of industrial uranium leaching solutions using a strongly acidic gel sulphonated polystyrene cation exchange resins at pH 1.5–2.0. Although poor selectivity was observed, they recommended that the resin can be used for pre-concentration of REEs from industrial solutions of complex composition. Khawassek et al. [60] studied the equilibrium and kinetic characteristics of REEs adsorption process using a strong acid macro reticular resin Dowex 50 × 8 at pH 1.25. A saturation capacity of 80 mg REEs/g resin was obtained.

3.5.2. *Anion exchange resins*

Anion exchange has been shown to be an effective way to separate metal ions. Impressive separations of metal ions can be achieved by

Table 7
REEs extraction and pre-concentration using ion exchange.

Resin	Extraction process	Ref
Tulsion CH-96 and T-PAR (cation-exchange resin)	HREEs like Tb, Dy, Ho, Y, Er, Yb and Lu from phosphoric acid	[68]
IR-120 P (cation-exchange resin)	Recovery of REEs from chloride medium	[96]
Dowex I-X8 (anionic-exchange resin)	Extraction of all REEs at different proportions of nitric acid and acetone	[4]
Bio-Rad AG 50 W-X2 (cation-exchange resin)	Determining the stability constants for the mono- and difluoro-complexes of REEs	[116]
Amberlite XAD-4 (cation-exchange resin)	The pre-concentration and separation of La(III), Nd(III) and Sm (III) from chloride solution	[24]
D152 resin (anionic-exchange resin)	The sorption of REEs ions from HAC–NaAC buffer solution	[142]
XAD-4 (chelation IX)	Adsorption of La(III), Nd(III) and Sm(III)	[58]
Tertiary pyridine resin (anion-exchange resin)	The separation method of REEs from methanol and nitric acid mixed solution	[126]
Ion-imprinted polymers; template: Sc-8-hydroxyquino-line complex (chelation IX)	Pre-concentration of REEs from different ores and sea water	[77]
2,6-diacetylpyridine functionalized Amberlite XAD-4 (cation-exchange resin)	Extraction and pre-concentration of REEs from sea water	[145]
Dowex 50 × 8 (cation-exchange resin)	Study the kinetic characteristics of the REEs adsorption process from El-Erediya chloride liqueurs have been determined	[60]
Polystyrene sulphonic acid purotite C-100 (cation-exchange resin)	Recovery of REEs from Uranium Mining Solutions	[111]

manipulating the solution chemistry using mixed solvents [133]. For example, Alstad and Brunfelt [4] studied the adsorption of REEs on an anion exchange resin from nitric acid-acetone mixtures and established that this was a powerful system for separating the REEs elements. The adsorption of the REEs from a nitric acid-methanol was studied by Faris and Warton [31]. Adsorption measurements were made at room temperature using the column elution technique and employing emission spectrographic analysis. The system proved efficient for macro separation of extremely pure REEs and for fractionation of crude REEs mixtures. The simplicity of operations of such systems is attractive for the enrichment of trace elements.

3.5.3. *Chelating resins*

Chelating resins are usually used to collect trace elements from dilute solutions like seawater. For example, the adsorption properties of chelating IX resins containing a mixed sulphonic/phosphonic, aminophonic or amino diacetic acid functional groups were investigated for separating REEs from hydrometallurgical solutions [91]. A selectivity preference of iron and thorium over REEs and aluminium was observed. An analytical method for the pre-concentration of REEs in seawater was developed by Waqar et al. [136] using an indigenously synthesized chelating resin. The method was based on immobilization of fluorinated β-diketone group on solid support styrene divinyl benzene. More than 95% of the REEs and specifically lanthanum, cerium, neodymium, samarium, europium, gadolinium, dysprosium, erbium, ytterbium and lutetium were obtained with a pre-concentration factor of 200 times. Contrary to the cation and anion exchangers, chelating ion exchangers show varying degrees of affinity and selectivity with respect to REEs. Their properties largely depend on the nature of the functional group and much less on the beads size and other physicochemical properties.

3.5.4. *Summary*

The IX resins are becoming attractive to extract metal ions from dilute solutions since the extractant is attached to the solid phase which simplifies the separation process. This technique offers advantages such as simple designs, applicable to dilute feeds, can achieve a high concentration factor, and has virtually no loss of separation media to the environment. Although IX can be exploited to recover REEs from wastewater like AMD, the downside is that the method exhibit slow kinetics and depending on the separation agent used, selectivity can be limited [123]. The slow reaction kinetics would be a bottleneck in the application of IX to recover REEs from AMD considering the huge volumes that have to be treated. In addition, there is a risk of resin poisoning with some cationic impurities which are in large concentrations such as iron and aluminium. This would lead to a decrease in sorption capacity and/or selectivity [44]. Kołodyńska and Hubicki [63] also point out the disadvantage of ion exchange separation of mixtures of REEs on the polystyrene-sulphonic cation exchangers as being the lack of a universal eluant. This would mean application of different eluants to recover different elements. The limitations of IX in metal recovery from complex solutions such as AMD necessitates investigations to understand the process kinetics with respect to the complex solution chemistry.

3.6. *Adsorption*

Adsorption has been used as a recovery technique or as a pre-concentration step of metal ions from low-concentration sources. It is one of the major industrial separation techniques used in the purification of effluent media. It is a mass transfer operation through which a solid material can selectively remove dissolved components from an aqueous solution by attracting the dissolved solute to its surface. This technique has long been recognized as one of the promising extraction methods due to its environmental friendliness, wide-range availability, scalability and simplicity of operation as compared to solvent extraction or ion exchange [147]. The adsorption technique has been tested to recover REEs from different aqueous solutions, including brines, seawater and other metallurgical effluents [128,147]. A wide range of sorbents have shown high affinities towards a variety of REEs with good capacities, rapid kinetics and economics. These include the oxides of Fe and Mn [6], magnetic nanoparticles [128,27], silica based sorbents [134,13,87], polymer adsorbents [106] and nanofiber adsorbents [46]. Royer [110] provides an extensive review on the removal and recovery of REEs from mine waters. Table 8 is a summary of some of the adsorbents that have been used to recover REEs from different solutions.

Functionalized magnetic nanoparticles are excellent candidates for the selective extraction of trace metal elements from wastewater. Magnetic nanoparticles are a class of nanoparticles that can be manipulated

Table 8
Summary of some adsorbents used to recover REEs.

REEs	Adsorbent	Ref
La, Nd, Sm, Gd, Tb	Poly (amidoxime-hydroxamic acid) and poly (N-methyl amidoxime -N-Methyl hydroxamic acid) resins	[2]
Eu	Silica doped with acyl-hydroxypyrazole derivatives	[13]
Eu	Di(2-thylhexly) phosphoric acid-immobilized magnetic GMZ bentonite	[19]
Eu, Gd, Tb, Dy	Acrylic acid (AAc) grafted on polyethylene (PE) film	[21]
La, Gd, Eu	Magnetic (Fe_3O_4)and non magnetic (SiO2 and TiO2) decorated with TMS-EDTA	[27]
Tm	Bis(2,4,4-trimethylpentyl) monothiophosphinic acid	[52]
Er	Ion Imprinted Polymer Solid Phase	[106]
Dy, Y, Tm, Yb	Amberlite XAD-7 impregnated with organophosphorous extractant	[117]
Nd	Carboxymethyl chitosan adsorbents entrapped by silica	[134]
La	2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester-grafted magnetic silica nanocomposites	[140]
Nd, Dy	Silica gel modified with diglycolamic acid.	[87]

using magnetic fields. They consist of two parts, a magnetic material, often iron, nickel or cobalt and a chemical component that has functionality. The particles have been tested on their application in the recovery of REEs from different solutions. Elsaidi et al. [30] presented a proof-of-concept study for the efficient extraction of selected REEs from brine solutions using magnetic metal-organic framework (MOF). The process was proven to be efficient with REEs recoveries of 99% within the first 5 min. Dupont et al. [27] selectively recovered REEs from an aqueous solution by EDTA-functionalized magnetic nanoparticles with a high selective adsorption of nanoparticles (100–400 mg/g). Another effective route for the fabrication of magnetic particles for high adsorption capacity and selectivity towards metal ions, with excellent acid resistant property and long service life was provided by Wu et al. [140]. The magnetic material was first coated with silica, and then a silane-coupling agent (3-chloropropyltryethosysilane) was used for grating 2-ethylhexyl phosphonic acid mono-2-ethylhexyl (P507) on the surface of the magnetic silica nanocomposite. The maximum adsorption capacity of La(III) was 55.9 mg/g at an optimized pH of 5.5 and the La (III) adsorption was found to follow the second order kinetic equation. Galhoum et al. [35] recovered ytterbium, dysprosium and neodymium using hybrid chitosan-magnetic nano-based particles functionalized by diethylenetriamine (DETA). The maximum sorption capacity of 50 mg/g of the REEs was obtained with the sorbent being recycled five times before 6% of the sorption capacity could be lost.

Silica gel is a widely used solid material due to its well-established particle size, high surface area and high mechanical and chemical thermal stability. Modified silica has found increasing utilization in metal recovery from dilute solutions. The silica is modified by impregnation with organic ligands onto the surface or by grafting through the spacer. Adsorption of REEs on silica gel sorbents has been used as a pre-concentration step in analytical chemistry. For example, silica gel loaded with 1-phenyl-3methyl-4-benzoylpyrazol-5-one (PMBP) was used for pre-concentration of REEs prior to their determination using inductive coupled plasma atomic emission spectroscopy (ICP-AES) [75]. In a pH range of 5–8, the REEs were separated from a matrix of other elements and retained on the column packed with modified silica gel. The metals were eluted using 2 molar nitric acid. This mechanism is represented by Fig. 7.

Callura et al. [15] conducted selective adsorption tests of REEs from aqueous brine solutions onto functionalized silica particles with three different ligands – phosphonoacetic acid (PAA), (*N,N* bisphosphono (methyl) glycine (BPG)) and diethylenetriaminepentaacetic dianhydride (DTPADA). Maximum REEs removal from 0.5 molar sodium hydroxide solution was achieved at pH 7 for PAA, pH 2 for DTPADA and in both acidic and basic conditions for BPG functionalized materials. Apart from the use of magnetic nanoparticles to adsorb REEs, Dupont et al. [27] also used nonmagnetic nanoparticles (SiO_2 and TiO_2) surface coated with N-[(3-trimethoxysilyl) propyl] ethyl diamine triacetic acid (TMS-EDTA). The general adsorption capacity of the nanoparticles was still between 100 and 400 mg/g. Other studies have been conducted on the recovery of REEs using silica based sorbents [134,13,87].

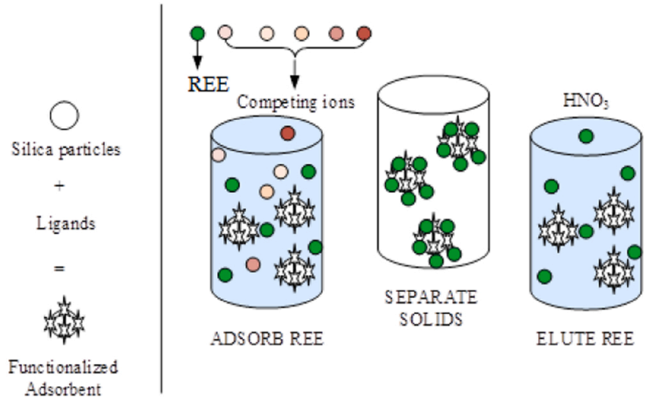

Fig. 7. Mechanism of adsorption of REEs on silica sorbent, separation and elution [15].

Polymer adsorbents address some of the shortcomings of silica based adsorbents like instability at extremely low pH and the presence of residual silanol groups [94]. Polymer adsorbents can either be biopolymers [65], chemical modified biopolymers, imprinted polymers [26] or cellulose and chitosan polymers [36].

In a study by Kondo and Kamio [64], individual REEs were separated using polymeric microcapsule membrane containing acidic organophophorous compounds as an extractant. It was established that the adsorption and elution was achieved by selecting pH values of the feed solution with each REEs being separated with a purity of more than 95%. Roosen and Binnemans [109] 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 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 of 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 showed that separation of the rare-earth ions is feasible with DTPA-chitosan/silica, without the need for using the solutions of chelating agents as eluents.

3.6.1. *Summary*

Although extensive research has been undertaken to recover REEs using adsorption, there is no adsorbent material in practical use [122]. The requirements for practical adsorbents include high selectivity for REEs, absorbability at low pH, easy desorption of the metal ions, high adsorption and desorption rates, high adsorption capacity, durability against repeated use, low-cost, and high mechanical strength [87]. Even if there is little published information in open literature on the recovery of REEs from AMD using adsorption, a great deal of work has been done on effluent treatment. The reviewed literature shows that this is a promising technique which can be used to recover REEs from AMD. However, studies should be conducted to evaluate the effect of impurities on the adsorption of REEs from AMD.

3.7. *Molecular recognition technology*

During the past two decades, a breakthrough in achieving extremely high selectivity in metal separations has been made through the introduction of molecular recognition principles in designing separation systems that employ pre-designed metal-selective ligands [48]. Molecular Recognition Technology (MRT), a green chemistry process, is used for the separation and recovery of a variety of metals from a complex matrix with minimal generation of waste. MRT is based on the noble prize winning chemistry work of Pedersen [92] who synthesized a large number of cyclic polymers and observed that they had outstanding selectivity for specific alkali metals. The technique is based on selective recognition of specific metal ion guests by supported ligand hosts, allowing highly selective individual separation and recovery of metals from complex matrices present in industrial feed solutions [123]. MRT column systems operate on a 4-step cycle basis. A complete system cycle sequence consists of the following [49].

1. Loading phase – The target ion is loaded onto the appropriate selective SuperLig® product which has been charged into the column (s).
2. Pre - elution wash phase – Any remaining feed solution is washed out of the column.
3. Elution phase – The target ion is eluted from the SuperLig® product in the column, forming a high purity product solution.

4. Post – elution wash phase – Any remaining eluant is washed out the column. The cycle then begins again as above.

MRT has been tested for the recovery of platinum group metals (PGMs) and REEs [49]. Ucore Rare Metals Inc [129] used a three step MRT to produce HREEs concentrate consisting of 99% of REEs from a pregnant leach solution (PLS). In step 1, scandium and cerium were separated from REEs group, in step 2 the LREEs and yttrium (Y, La, Pr, Nd) were separated and in step 3, individual members in the LREEs and HREEs are separated from each other.

Many conventional solvents are toxic, flammable and corrosive and usually require huge capital and operating costs. Elimination of solvents in chemical processes is one of the most active areas of research. The fact that no solvents are used in MRT is a huge advantage as compared to other solvent based extraction processes. Although MRT has only been tested to recover REEs from pregnant leach liquor, its potential application to recover REEs from AMD should be explored as it has shown selectivity in the recovery of metals as well as low capital and operating costs [123].

3.8. *Magnetic separation*

Magnetic separation is a process used to separate materials from those that are less or nonmagnetic. It is a well-established method used in ore processing, food industry, biomedical diagnostic, etc. The method of magnetic separation of REEs is on the difference in the magnetic predisposition of REEs. Some REEs ions are strongly paramagnetic e.g., Dy, Ho which means that they move towards the magnet while the others are diamagnetic e.g., Sc, Y. Kolczyk et al. [62] determined the efficiency of the separation of aqueous solutions of holmium from the other REEs. The distribution of ions in the solution took place in a steady magnetic field generated by a set of neodymium magnets. The results obtained showed that holmium could be extracted using this method. Smith et al. [123] reports a patent where magnetic segregation method was used to recover REEs from the geothermal fluids. The method involves the collection of the hot geothermal brine in a heat exchanger followed by cooling the hot fluid down. As the fluid cools down, the REEs in the brine condense out of the fluid, forming a condensate. The condensate is then accelerated by applying a physical force (gravity or centrifuge), followed by applying a magnetic force simultaneously. Due to combinations of both physical and magnetic forces, the components of condensate segregate differently. The segregated REEs can be collected and removed from the condensate. The process can be optimized by varying the duration, intensity, time and constancy of the two forces for the segregation of the REEs from other components of the condensates. For example, the magnetic separation can be modulated so that a scalar amount of force varies by either applying the forces simultaneously or one beginning first followed by another over varying periods of time.

3.8.1. *Summary*

Magnetic separation is a promising technique which could be employed to recover REEs from AMD. However, the solution chemistry of AMD means that some other paramagnetic impurities would be recovered together with the REEs. This would mean having a purification stage prior to magnetic separation to remove other magnetic species. Furthermore, studies conducted on magnetic separation of the REEs report that it is an expensive and complicated technique and changes are necessary to improve the economic viability of the technique before it can be considered for application on a commercial scale.

3.9. *Membrane filtration*

Filtration membranes are microporous barriers of polymeric, ceramic or metallic materials which are used to separate solutes, colloids or fine particulate from solution. Several types of membranes are employed in water treatment including microfiltration, ultrafiltration, reverse osmosis and nano filtration. Membrane filtration technologies have not only shown great promise for heavy metal removal but can also be applied to recover REEs. The process efficiency primarily depends on the pore sizes of the membrane with the smaller pores achieving higher separation efficiency [131]. The downside of using smaller pore size membrane filters is that it results in a restricted fluid flow. As such, a high-pressure process is required to improve the diffusion and results in an increase in the operational costs. Membrane filtration processes, including, electrodialysis, reverse osmosis [71], nanofiltration [84] and membrane electrolysis [88] have all been investigated to recover REEs from wastewater.

3.9.1. *Summary*

Although the membrane filtration technique can remove toxic metal ions including REEs from wastewater with high efficiency, its challenges such as high costs, membrane fouling, process complexity and low permeate flux have limited its application. There is the need to find cost effective membrane filters for this technology to be economical viable for metal recovery/removal.

4. Conclusion and prospects

AMD could be a source of REEs although the potential of this waste stream for REEs recovery remains largely unexplored. This review focused on technologies which would enable the recovery of REEs not only from dilute wastewater but from AMD as well. The drive is to translate these technologies, which would normally remove metal ions from wastewater for water purification, into products that feed into the circular economy. The technologies that have traditionally been used to remove or recover REEs from process solutions where they are either in low or high concentrations have been screened. However, several limitations remain to be solved before applying the discussed methods to recover REEs recovery from AMD. The REEs precipitation from AMD remains a challenge due to the high concentration of impurities and low concentrations of REEs. Alternative processes like complexation of impurities to facilitate selective precipitation of REEs should be investigated. Adsorption and ion-exchange, albeit being slow processes remain the most viable process techniques that can be used to recover REEs from AMD. The emerging technologies like molecular recognition technology, magnetic separation, ionic liquids and cloud point extraction should also be given significant attention. Furthermore, potential application of combined technologies should also be investigated for possible application.

Table 9 summarises the advantages and disadvantages of the techniques reviewed. To our knowledge, based on the latest advances in REEs extraction technology, REEs removal from contaminated water and their recovery from secondary sources, future research should be focused on.

1) the development of a low-cost process to remove and recover REEs from AMD addressing the challenges outlined in Table 9
2) the production of high-purity REE from AMD using integrated flowsheets
3) the life cycle assessment (LCA) for sustainability of the process techniques

The successful application of these technologies in REEs recovery from wastewater would bridge the gap between supply and demand of REEs by addressing potential REEs materials supply challenges.

CRediT authorship contribution statement

Brian Mwewa: Conceptualization, Methodology, Software, Data curation, Visualization, Investigation, Validation, Writing – original draft preparation. **Margreth Tadie**: Writing – review & editing. **Elias**

Table 9
Summary of the advantages and disadvantages of the various process methods for enrichment of REEs.

Removal method	Advantages	Disadvantages
Chemical precipitation	Low capital cost Simple operation Able to remove most metals	High cost of precipitating agents Might lead to production of excess sludge which poses disposal concerns
Solvent extraction	Can handle huge volumes High selectivity depending on extractant used	Expensive process due to cost of extractants Not economical in the treatment of dilute waste solutions
Cloud point extraction	High selectivity High metal upgrade	Not tested for matric of solutions
Ion flotation	Simple and inexpensive Low sludge generated Low cost	Low flotation efficiency for complex, high ionic strength aqueous systems
Ion exchange	High metal selectivity Metals can be removed and reused	Slow kinetics Resin poisoning Fouling
Adsorption	Cheap and simple process Easy desorption of metals Environmentally friendly	Performance is largely dependent on type of adsorbent
Molecular recognition technology	High selectivity Green chemistry procedure	Expensive process
Magnetic separation	Low cost	Nonmagnetic materials cannot be extracted using this method
Membrane filtration	Efficient separation process Low solid generation	Membrane fouling Process complexity

Matinde: Writing – review & editing. **Sehliselo Ndlovu**: Writing – review & editing. **Geoffrey S. Simate**: Writing – review & editing.

Declaration of Competing Interest

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

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