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Advances in the Development of Leaching Agents for Assisting Phytoremediation of Rare Earth Elements: A Review

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Rare earth elements (REE) are used to manufacture smart electronics. Conventional extraction of REE using concentrated ammonium salt elevates ammonia-N and REE levels and degrades water quality. The impact of leaching agents on the dissociation of REE from the ion-adsorption clay (IAC) is crucial for the success of *in-situ* mining by the leaching process. Furthermore, native plants may hyperaccumulate REE. The leaching of IAC with leaching agents may further enhance REE uptake. The objectives of this review are to discuss various chemicals that have been used for leaching REE from IAC and to elucidate the mechanisms of action during the leaching process. The transport and distribution of REE in the biomass of hyperaccumulators are elucidated. The outcome of this review may produce new knowledge on the suitability of various leaching agents, their REE-complex formations, and the effect of REE-complexation on hyperaccumulator uptake. This research may provide a safe method for in-situ leaching of REE from a mining site and the safe removal of toxic elements from soil with a delicate ecosystem.

Keywords: Hyperaccumulators*;* ligand; ion-adsorption clay; rare earth elements

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Rare earth elements (REE) are highly valued commodities due to their properties, making them important in the production and development of various sectors, such as energy, transportation, and electronics [1]. The discovery of REE occurred in Sweden towards the end of the 18th century [2]. According to the International Union of Pure and Applied Chemistry (IUPAC), REE consists of seventeen elements that include fifteen lanthanides (La-Lu), Yttrium (Y), and Scandium (Sc). Lanthanum (La), Cerium (Ce), Praseodymium (Pr), Neodymium (Nd) and Samarium (Sm) are classified as light rare earth elements (LREE) while Europium (Eu), Gadolinium (Gd), Terbium (Tb), Dysprosium (Dy), Holmium (Ho), Erbium (Er), Thulium (Tm), and Ytterbium (Yb) are heavy rare earth elements (HREE). Both Sc and Y are classified as REE because they occupy the same group (Group III) in the periodic table and exhibit partially similar chemical properties. Furthermore, Y is commonly grouped with the HREE due to its similarity in ionic radius and geochemical processes with Ho [3]. In contrast, Sc has a significantly smaller ionic radius and displays distinct chemical behavior compared to lanthanides, which is why it is often discussed separately in REE studies [4]. All REE usually form trivalent cations, although the divalent or the tetravalent oxidation state is known for most of its chemical compounds [5].

Malaysia has had a thriving tin mining industry and produced REE from its by-products (i.e., monazite and xenotime) [6]. Recently, ion-adsorption clay (IAC) has been of new interest in the REE mining industry due to its high REE content. Moreover, REE are weakly adhered to the IAC minerals (i.e., kaolinite, illite, and smectite) and can be easily extracted at low processing temperatures [7] by *in-situ* leaching technique using aqueous electrolytes, namely ammonium sulfate ($(NH_4)_2SO_4$) and sodium chloride (NaCl). The leaching process can be conducted without the need for excavation or vegetation damage [8]. However, the *in-situ* leaching of REE from IAC raises environmental concerns as it requires a high concentration of aqueous electrolytes. This leads to a growing interest in sustainable techniques like

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phytoremediation. In fact, leaching agents at a lower concentration may be used to enhance REE mobilization, allowing greater REE uptake by hyperaccumulator plants, and a sustainable recovery of REE through agromining. It offers an understanding of complex interactions between leaching agents, IAC, and REE bioavailability for improving uptake by hyperaccumulator. A new, more environmentally friendly approach for REE resource recovery can be achieved by reducing the overdependence on $(NH_4)_2SO_4$ and allowing natural restoration of its former mines.

This review elucidates the key chemical and physical characteristics of various leaching agents, their mechanisms in the *in-situ* leaching of REE from IAC, and their impact on the REE uptake and plant growth of hyperaccumulators. A combination of keywords such as "leaching agent," "rare earth elements", and "hyperaccumulator", was used in the literature search across several reputable databases, such as the Web of Science (https://www.webofscience.com/), Google Scholar (https://scholar.google.co.kr), and ScienceDirect (https://www.sciencedirect.com/). The search was limited to literature describing leaching agents and REE hyperaccumulators. High-cited and significantly advanced journal articles (Journal Citation Reports Q1 & Q2) were prioritized, while irrelevant references and spurious hits were eliminated. The protocol acknowledges potential areas for improvement in the review process, including: (1) the emergence of new publications after 2024; (2) the exclusion of certain older publications; and (3) a focus on literature published in English.

The Properties of REE

Table 1 shows the properties of REE based on their electronic configuration, ionic radius, and electronegativity. The increase in the atomic number from La to Lu leads to a unique reduction in the atomic radii of REE known as the lanthanide contraction. The increasing electrons in the 4f shell poorly shield the electrons in the outer shell (6s), causing them to be pulled closer to the nucleus. While most REE are trivalent, some can exist in other forms, such as Ce in the tetravalent form (Ce^{4+}), and Eu in divalent form (Eu^{2+}) [5]. The high and constant oxidation state of REE (+3 or +4) causes a slight but gradual increase in charge density. Hence, the electronegativity of REE is generally low, but will gradually increase with increasing atomic number. This trend gives REE a distinctive chemical property: LREE with a lower electronegativity tends to have a stronger ionic character, and *vice versa*. According to the hard soft acid-base (HSAB) principle, REE ions are hard acids and have strong affinity for ligands with a hard base, such as hydroxyl (-OH), carboxyl (-COOH), phosphate (PO_4^{3-}), ammonia (NH_3), sulfate (SO_4^{2-}), sulfonate ($-SO_3^{2-}$), and fluoride (F^-) [9]. In fact, REE is known to react with oxygen to form a stable complex. This is also the reason why REE is found in their oxidized form within the environment rather than individual elements. The ionic radius and charge also influence REE adsorption on IAC. Light rare earth elements such as La, Ce, and Pr are less adsorbed than HREE (i.e., Y, Dy, and Er). Larger LREE radii are loosely attracted and adsorbed onto the surfaces of the clay minerals in IAC. This makes the physically adsorbed REE^{3+} ions easily removed from the clay surface by monovalent cations (e.g., Na^+ and NH_4^+) [10].

Table 1. Ionic and atomic radii, electronegativity, and electron configurations of REE.

Elements	Electronic configuration	Ionic Radius (Å)	Atomic Radius (Å)	Electronegativity (Pauling units)
La	$[Xe]5d^16s^2$	1.045	187	1.10
Ce	$[Xe]4f^15d^16s^2$	1.01	182	1.12
Pr	$[Xe]4f^36s^2$	0.997	182	1.13
Nd	$[Xe]4f^46s^2$	0.983	181	1.14
Pm	$[Xe]4f^56s^2$	0.97	181	1.13
Sm	$[Xe]4f^66s^2$	0.958	180	1.17
Eu	$[Xe]4f^76s^2$	0.947	204	1.20
Gd	$[Xe]4f^75d^16s^2$	0.938	179	1.20
Tb	$[Xe]4f^96s^2$	0.923	178	1.10
Dy	$[Xe]4f^{10}6s^2$	0.912	177	1.22
Ho	$[Xe]4f^{11}6s^2$	0.901	176	1.23
Er	$[Xe]4f^{12}6s^2$	0.89	175	1.24
Tm	$[Xe]4f^{13}6s^2$	0.88	174	1.25
Yb	$[Xe]4f^{14}6s^2$	0.868	192	1.10
Lu	$[Xe]4f^{14}5d^16s^2$	0.861	174	1.00
Y	$[Kr]4d^15s^2$	0.9	180	1.22
Sc	$[Ar]4s^23d^1$	0.745	162	1.36

Among the various types of REE found on the Earth, only a few have high economic value, such as monazite (Ce, La, Nd, Th)PO_4, apatite $Ca_5(PO_4)_3(OH, F, Cl)$, xenotime (YPO_4), and bastnaesite (La, Ce, Y)CO_3F. Monazite is the main ore mineral in more than thirty carbonatite-related REE deposits worldwide [11]. The main source of REE in Malaysia comes from monazite and xenotime, which are obtained as by-products of tin mining activities (amang) [12]. These minerals are concentrated through beneficiation processes such as flotation, magnetic separation, or gravity methods to produce REE concentrates [6]. With estimated deposits of around 30,000 tons of rare earth minerals, Malaysian monazite was known to contain 6.5-7.5% ThO_2 and 55.5-75.5% rare earth oxides. The presence of Th is due to rare earth residues from industrial processing, which contain a large amount of Th [13]. Therefore, appropriate processing is necessary to prevent radioactive pollution and contamination of rare earth products.

Ion adsorption clay is also a major source of REE and is composed of various clay minerals, particularly in tropical and subtropical regions. It is generally associated with minerals containing hard bases, such as fluoride, barite, and iron minerals. In Malaysia, weathered granites parallel to the Bentong-Raub Suture zone (i.e., Taiping, Lumut, Bukit Tinggi, Tamping, and Baling) have a high REE content ranging from 0.03 to 0.4 wt% [14]. The IAC minerals are predominantly composed of kaolinite and halloysite, which act as primary minerals for REE through ion exchange and complexation mechanisms. The IAC deposits at Gua Musang, Malaysia contain a kaolinite-rich IAC derived from weathered granite bedrock [15]. Kaolinite, characterized by its non-expanding structure and low cation exchange capacity (CEC), demonstrates notable REE binding affinity due to its high surface charge density and structural stability [16]. Similarly, illite exhibits comparable sorption behavior, often with slightly enhanced REE adsorption efficiency under certain pH conditions [10]. While quartz is commonly present as a secondary mineral in these clays, the small surface area and poor reactivity make it a small contributor to REE adsorption processes [17].

Compared to hard rock ores, IAC offers several advantages, like being low in radioactive elements (e.g., Th and U), requiring mild processing conditions, and enabling cost-effective REE extraction despite their relatively low grade [7]. These characteristics make IAC a promising choice for sustainable REE extraction, especially when combined with selective leaching and a phytoremediation process.

The adsorption-desorption balance of REE is sensitive to environmental factors like pH, temperature, and the presence of competing ions in the leach solution. Rare earth elements with smaller ionic radii, such as Lu^{3+} and Yb^{3+}, have stronger electrostatic interactions with functional groups on clay surfaces or water molecules, resulting in more stable complexes in the soil. This results in larger hydrated radii and lower mineral resorption capacity. In general, the ionic radius of REE decreases with increasing atomic number. HREE, which have higher surface charge density and higher hydration number (n), tend to be more difficult to reabsorb by minerals. Ion adsorption clay is often rich in HREE compared to LREE as they are more strongly adsorbed on mineral surfaces [18]. Furthermore, IAC usually contains kaolinite, halloysite, or other types of clays with low crystallinity. The leaching process for extracting REE generally uses $(NH_4)_2SO_4$ or ammonium chloride (NH_4Cl), allowing the recovery of high-purity REE. The extraction process is generally considered safer for the environment than traditional mining, although it still has ecological impacts.

Extraction of REE from IAC can be achieved using a variety of leaching processes in various setups, including heap, tank/pond, and *in situ*. Barrel leaching technology involves placing REE ores in wooden barrels and gradually leaching the REE with a leaching agent. Due to its high cost, low yields, and limited scale of production, this technology was rapidly replaced by pool-leaching technology in the late 1970s. Pool leaching uses a cement-sloping bottom to facilitate the outflow of REE during the leaching process. However, potential environmental contamination from this process may require the restoration of vegetation in contaminated areas [19]. Heap leaching is an extractive metallurgy process that involves mining clay ore and piling it before spraying or pouring the leaching solution into the pile, allowing the solution to soak into the ore and dissolve the REE [20].

Figure 1. Arial image and map of the REE mine at Kenering, Perak, Malaysia that adopts *in-situ* leaching method.

In-Situ Leaching

In-situ leaching is commonly used to recover REE due to minimal damage to the surface vegetation of the mining area [21]. Malaysia has explored the *in-situ* leaching method at its pilot REE mine located in Kenering, Perak, Malaysia (Figure 1). The step-by-step procedure of *in-situ* leaching used in REE extraction is shown in Figure 2. Liquid injection wells with a diameter of 0.8 m and a depth of 1.5–3.0 m are dug at an intermittent distance of 2–3 m. Aqueous solution containing a leaching agent is directly injected into the liquid injection wells, which diffuses into a network of porous subsoil layers before being diverted at the bottom of the hole. The leaching process occurs over a duration of 150–400 days using 3–5% $(NH_4)_2SO_4$ as the leaching agent [22]. The REE ore is recovered from the liquid injection wells located at the foot of the mine deposit [8]. An inadequate dose of $(NH_4)_2SO_4$ may contribute to a reduction of REE recovery by up to 5%, while its excessive usage may contaminate water resources [23]. During the *in-situ* leaching process, a significant amount of NH_4^+, SO_4^{2-}, Ca^{2+}, and Mg^{2+} can be accidentally released into the environment. These ions easily migrate with rain or runoff into the surrounding soil, rivers, and groundwater, where they interact with other compounds in the environment, causing adverse impacts on aquatic ecosystems [21]. Furthermore, the additional process for eliminating contaminants and concentrating the REE from the leachate requires various chemicals such as HCl, H_2SO_4, and NaOH. In most cases, the liquor from *in-situ* leaching contains a large number of impurities, including $(NH_4)_2SO_4$, Al^{3+}, Fe^{3+}, Ca^{2+}, Fe^{2+}, Pb^{2+}, and Mn^{2+}. The traditional process of extracting REE from such a liqueur is usually conducted by precipitation using toxic chemicals such as oxalic acid or ammonia carbonate as a precipitant. It forms rare earth oxides or carbonates, which are then washed, filtered, and decomposed into rare earth oxides by combustion [12]. Moreover, the large amount of tailings containing natural radionuclides (e.g., ^{232}Th and ^{238}U) and their decay products may be produced during the refining, extraction, and separation processes. The environmental impact from the chemical processing can be reduced by recycling chemicals (e.g., HCl), as is done at Mountain Pass [24]. Thus, a thorough geotechnical survey must be conducted at the proposed mining area and the surrounding area before the *in-situ* leaching process to ensure minimum impact on the environment.

Leaching Agents for *in-situ* Leaching of IAC

Conventional REE extraction methods using $(NH_4)_2SO_4$ concentrate can increase ammonia-N levels in water. Lai et al. [25] found that $(NH_4)_2SO_4$ concentrations in groundwater and surface water can reach 3500 to 4000 mg/L and 80 to 160 mg/L, respectively, and may cause eutrophication to the water bodies. Non-ammonium leaching techniques have been developed as an alternative to $(NH_4)_2SO_4$, offering a more environmentally friendly approach to rare earth ore leaching. Natural organic acids have been explored for REE extraction [26]. A new leaching agent can significantly reduce nitrogen concentration and pollution at the source. Table 2 shows the classification of leaching agents based on their chemical properties and applications.

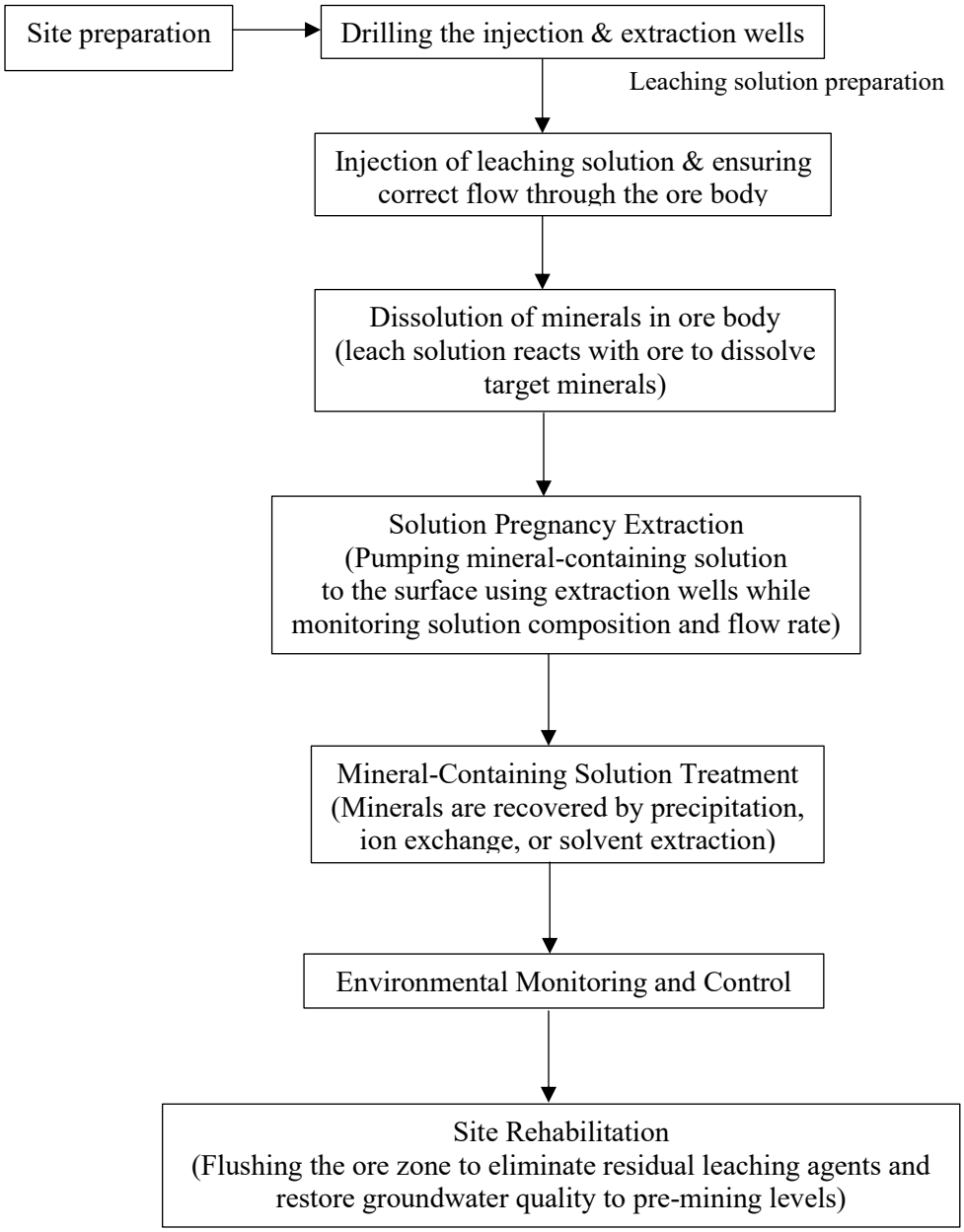

Figure 2. Flowchart of *in-situ* leaching technology of REE extraction from IAC.

The efficiency of REE leaching is strongly influenced by the chemical composition of the leaching agent, including the hydrogen dissociation constant (pK_a), solubility, and complexation ability. The strength of an acid was determined by pK_a, which indicated how easily the acid donated a hydrogen proton [42]. A lower pK_a value indicated greater acid strength, allowing the agent to release protons more easily and facilitate ion exchange or complex formation with REE^{3+} ions. Ammonium-based agents typically exhibit high pK_a values and are known to form relatively stable bonds with REE, resulting in leaching via ion exchange. In contrast, non-ammonium organic acids display variable solubility and coordination behavior, which can impact their leaching performance under different pH conditions. According to the HSAB principle, REE ions, classified as hard acids, tend to interact with chelating ligands that contain hard base O atoms. Organic ligands such as oxalate and citrate are notable examples. While both are capable of complexing with REE, citrate forms stronger and more stable complexes with HREE due to their smaller ionic radii and higher charge density, resulting from lanthanide contraction [43, 44]. This suggests that ligand hardness plays an important role in the selectivity of REE complexation. Furthermore, humic acid, a naturally occurring macromolecule rich in oxygen-containing functional groups, can serve as a hard base ligand. The negatively charged humate ions exhibit stronger electrostatic attraction to REE cations.

Table 2. Physical and chemical properties of leaching agents.

Leaching agent	Molar mass (g/mol)	Solubility (g/L)	pK_a	Leaching efficiency (%)	Reference
Ammonium Based Leaching Agent					
Ammonium sulfate $(NH_4)_2SO_4$	132.1	750	9.25	93.8	[27]
Ammonium hydroxide (NH_4OH)	35.05	Water soluble	9.25	NA	[28]
Ammonium citrate ($C_6H_{11}NO_7$)	209.2	Water soluble	9.25	120	[29, 30]
Non-Ammonium Based Leaching Agent					
Ethylenediaminetetraacetic acid (EDTA)	292.3	1.0	0.26	NA	[31]
Diethylenetriaminepentaacetic acid (DTPA)	393.4	5.0 at 20°C	1.5-10.6	NA	[32]
Calcium chloride ($CaCl_2$)	110.9	Water soluble	NA	70.16	[33]
Sodium chloride (NaCl)	58.44	58.44 at 20°C	NA	17.28	[34, 35]
Citric Acid ($C_6H_8O_7$)	192.1	1330	$pK_{a\,1}$= 3.13 $pK_{a\,2}$ = 5.77 $pK_{a\,3}$ = 6.4	NA	[36, 37]
Oxalic acid ($C_2H_2O_4$)	90.03	220 at 25°C	$pK_{a\,1}$= 1.27 $pK_{a\,2}$ = 4.28		[36, 38]
Fulvic acid ($C_{14}H_{12}O_8$)	308.2	Soluble in strong acid, chloroform, and methanol	2.18	NA	[39]
Sulfuric acid (H_2SO_4)	98.08	Soluble in water and ethyl alcohol	NA	80.12	[19, 40]
Hydrochloric acid (HCl)	36.46	Soluble in water, alcohol, and ether	NA	81.52	[19]
Nitric acid (HNO_3)	63.01	Water soluble	NA	83.21	[19]
Sodium hydroxide (NaOH)	39.99	39.99 at 20°C	NA		[41]
Magnesium sulfate ($MgSO_4$)	120.4	Water soluble	NA	60.01	[28, 35]

Ammonium Sulfate ($(NH_4)_2SO_4$)

Ammonium sulfate (Figure 3) is often reported as an effective leaching agent for extracting REE due to its ability to exchange and release trivalent REE cations on mineral surfaces of IAC.

Ion-adsorbed REE typically exists as simple trivalent cations (REE^{3+}) that are loosely attached to the surface of clay minerals. These cations can be effectively desorbed via ion-exchange reactions, particularly using ammonium-based leaching agents like $(NH_4)_2SO_4$.

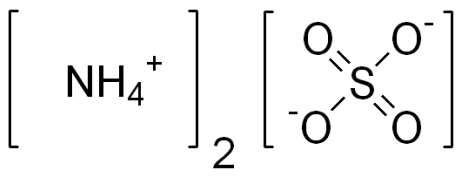

Figure 3. Chemical structure of $(NH_4)_2SO_4$.

A maximum REE leaching efficiency of up to 93.8% has been reported, using 0.5 M of $(NH_4)_2SO_4$ at pH 5, a liquid-to-solid (L/S) ratio of 3:1, and with 30 minutes of contact time [27], according to the following chemical equation:

$$2Clay^{3-}REE^{3+} + 3(NH_4)_2SO_4 \rightarrow 2Clay^{3-}(NH_4)_3{}^{+} + 2REE^{3+} + 3SO_4^{2-}$$

[45] proposed a five-step leaching mechanism:

1. Outward diffusion: In the leaching system, NH_4^+ diffuses from the diffusion layer to the surface of passing particles, forming a solid-liquid interface film with ore particles.
2. Internal diffusion: NH_4^+ on mineral particle surfaces diffuses into clay particles.
3. Ion exchange: Clay particles contain NH_4^+, which substitutes REE^{3+} adsorbed on mineral particles.
4. Internal diffusion. Mineral particles exchange REE^{3+} for NH_4^+ as it diffuses from their inside to their surface.
5. Outward diffusion. REE^{3+} mineral particles diffuse into the solution via the liquid-solid interfacial layer surrounding the ore particles.

This mechanism improves the efficiency of REE especially when using $(NH_4)_2SO_4$. According to [46], the composite leaching agent, which consisted of 2 wt% $(NH_4)_2SO_4$ and 0.02 wt% cationic hydroxyethyl cellulose, significantly improved the leaching efficiency of REE and reduced the leaching equilibrium time from 465 min to 130 min. The result was significantly faster than that of a single leaching agent using $(NH_4)_2SO_4$. The leaching process showed selective leaching behavior, where the peak leaching concentration of REE was significantly higher than aluminium under the same conditions. This selectivity provides a potential pathway to separate REE from impurities such as aluminium during leaching.

The leaching efficiency exceeds 98% when using $(NH_4)_2SO_4$ combined with other materials such as tartaric acid. Ammonium sulfate has a higher leaching efficacy compared to other ammonium salts like NH_4Cl and ammonium nitrate (NH_4NO_3). Ammonium chloride is more widely available and less expensive; however, it produces more impurity ions, which can impair the purity of the extracted REE. While NH_4NO_3 has two nitrogen atoms per unit molecule, it can raise ammonia-N and cause water pollution. Ammonium sulfate has a higher selectivity in leaching than NH_4Cl and NH_4NO_3, resulting in high-purity REE [47]. Overall, ammonium-based leaching systems have shown strong interactions with clay minerals, making them suitable candidates for IAC REE extraction applications.

Aside from its ability as a leaching agent, $(NH_4)_2SO_4$ serves as a source of nitrogen and sulfur, essential elements involved in the synthesis of proteins, enzymes, vitamins, and chlorophyll, which are crucial for plant growth [48]. Ammonium (NH_4^+) is directly absorbed by plants and contributes to the formation of amino acids both in the roots and stems [49]. Thus, the use of $(NH_4)_2SO_4$ not only facilitates the extraction of REE from the soil but also supports plant vitality.

Sodium Chloride (NaCl)

In the 1970s, NaCl was used as a leaching agent to extract REE in China. Up to 1 mol/L of NaCl is used, whereby sodium cation (Na^+) replaces REE^{3+}, and the chloride (Cl^-) becomes the counter ion:

$$Clay^{3-}REE^{3+} + 3NaCl \rightarrow Clay^{3-}(Na^+)_3 + REE^{3+} + 3Cl^-$$

However, *in-situ* leaching with 1 mol/L NaCl resulted in a lower total REE than that of $(NH_4)_2SO_4$. As a result, *in-situ* leaching with NaCl may require a higher NaCl concentration and may incur higher operational costs. Furthermore, long-term use of NaCl may increase the risk of equipment corrosion and operational costs [50]. High concentrations of NaCl also produce wastewater with high salt levels, which will cause soil salinization and environmental pollution [51]. Due to the low leaching efficiency, this inferior leaching agent has been replaced by $(NH_4)_2SO_4$ [45].

Calcium chloride ($CaCl_2$) and Magnesium Sulphate ($MgSO_4$)

REE has been extracted from IAC using electrolyte solutions such as $CaCl_2$, $MgSO_4$, and $Al_2(SO_4)_3$. Contrary to NaCl, both Ca^{2+} and Mg^{2+} which are produced from the ionization of $CaCl_2$ and $MgSO_4$, respectively, possess a greater charge density and electrostatic attraction to the negative surface of minerals in IAC. On the surface of clay minerals, Ca^{2+}/Mg^{2+} ions will exchange with REE^{3+} ions:

$$2Clay^{3-}REE^{3+} + 3CaCl_2 \rightarrow (Clay^{3-})_2(Ca^{2+})_3 + 2REE^{3+} + 6Cl^-$$

$$2Clay^{3-}REE^{3+} + 3MgSO_4 \rightarrow (Clay^{3-})_2(Mg^{2+})_3 + 2REE^{3+} + 3SO_4^{2-}$$

Under the influence of electrostatic contact, Ca^{2+}/Mg^{2+} is adsorbed onto the diffusive electric double layer in this reaction, affecting the double layer equilibrium and altering the pore shape. The $-OH$ groups in the mineral components will dissolve as the leaching solution becomes more acidic, causing small particles to precipitate and delaying the change in porosity. Meanwhile, the leaching solutions increased the hydrogen ion content, thickening the clay mineral bilayer, thus changing its internal pores, and increasing the quantity of big pores [52].

The environmental impact of calcium and magnesium salts is minimal when compared to other, less environmentally friendly electrolytes. For example, NaCl and $(NH_4)_2SO_4$ can be substituted with $MgSO_4$ and $CaCl_2$ as leaching agents [53]. Furthermore, the $MgSO_4$ leaching process is significantly improved when combined with ascorbic acid, whereby the improved leaching efficiency was attributed to the formation of stable complexes between REE and ascorbic acid, and the Mg^{2+} cation promoting the ion exchange rate. The leaching efficiency can reach up to 107.5% under optimal conditions (i.e., pH 2, 0.15 mol/L $MgSO_4$, and 1.0 g/L ascorbic acid). This results in a more effective and environmentally friendly leaching process compared to $MgSO_4$ without ascorbic acid [25]. The application of $MgSO_4$ can also reduce aluminium leaching by 10-15% while maintaining rare earth efficiency. $MgSO_4$ concentrations of 2.0–4.0 wt% contributed to an increase in rare earth concentrations of 5.49–10.21 g/L with a shorter leach solution collection period. Lower $MgSO_4$ concentrations (0.5–1.0 wt%) significantly reduced the amount of aluminium leaching by 116.91–158.52 mg/kg [54]. According to [55], $MgSO_4$-ascorbic acid achieved a leaching efficiency of 86.2%. The addition of ascorbic acid allows the dissolution of $Ce(OH)_4$ and $Fe(OH)_3$ at higher pH levels. The presence of ascorbic acid can reduce the acidity required for effective washing. The washing process is endothermic, driving the reaction at high temperatures. Higher temperatures lead to increased washing efficiency and faster rates.

Contrary to $(NH_4)_2SO_4$, enriching REE from $CaCl_2$ and $MgSO_4$ leaching solutions is more challenging, though. HREE chloride and LREE chloride concentrations in solution reached 240 g/L and 200 g/L, respectively, as a percentage of the total recovery of REE leached using $MgSO_4$ [56]. Hence, the application of $CaCl_2$ and $MgSO_4$ for *in-situ* leaching may not be an attractive option for mining REE. However, if the application is solely for mobilizing REE for agromining, $CaCl_2$ and $MgSO_4$ are suitable because both divalent salts are soil nutrients that also simultaneously improve soil structure.

Synthetic Ligands for Selective Complexation with REE

REE is highly unique in forming coordinate bonds. [57] reported that despite its high number of coordination (8–12), lanthanides form monodentate complexes and bidentate complexes with four or less coordinate sites, but only monodentate complexes with higher coordinate ligands. As elaborated earlier, REE has a strong affinity to oxygen donor ligands (i.e., molecules that contain carboxylate, phenolate, hydroxyl, or ether). Based on the concept of HSAB, REE belonging to the hard acid category can easily form coordination bonds with hard bases (i.e., oxygen donors) or intermediate bases (i.e., nitrogen donors). Hence, many synthetic ligands are designed with multiple oxygen donors to enhance interaction with REE via bidentate complexation. Figure 4 shows the formation of bidentate REE complex by carboxyl group. The deprotonation of the carboxyl forms a negative charge derivative called carboxylate ($-COO^-$) and strongly attracts REE^{3+} to form a coordination bond. The lone pair electrons in the oxygen atom may form a weaker covalent bond known as the dative bond (dotted line) with REE^{3+}:

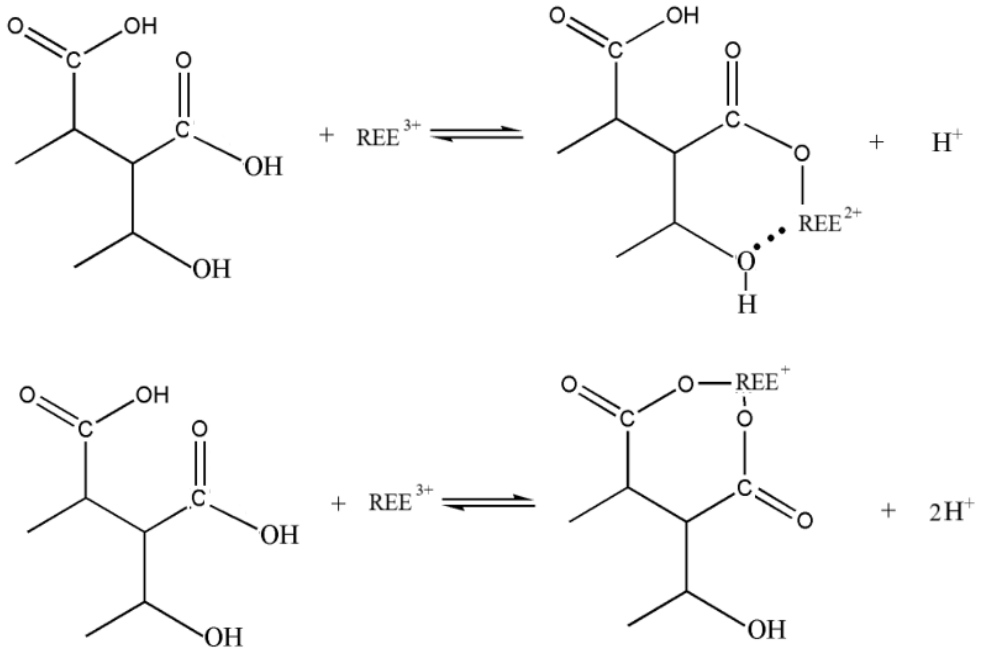

Figure 4. Formation of bidentate REE complex by carboxyl group.

Nitrogen donors are able to accept REE as well and may be included in the ligand design. [58] have reported that the glycolamic ligand that has the methoxy, amine, and carbonyl moiety has high sorption with the heavy REE. Complexes of REE would usually have a 1:1 ligand-to-REE stoichiometric ratio. The angles between the oxygen donor and REE dictate the stability of the complex, thus giving the selectivity to the synthetic ligand. As the amide group was considered to have good selectivity for Th separation from REE [59], oxygen donor ligands can be designed with weak electrostatic attachment to an insoluble polyamide.

The use of chelating chemicals to mobilize and remove harmful metals from metal-contaminated soils is a low-cost, effective, and extensively used soil remediation approach that can be performed *in situ* (soil flushing) or *ex situ* (column leaching). Chelating agents can mobilize metals from the soil's solid phase by creating strong, water-soluble compounds that are stable throughout a wide pH range. These compounds are subsequently removed via phytoextraction techniques or increased soil washing. Synthetic amino-polycarboxylic acids (amino-PCAs), such as ethylenediaminetetraacetic acid (EDTA) and diethylenetrinitrilepentacetic acid (DTPA), are commonly used industrial chelating agents in pulp and paper, cleaning, chemical processing, agriculture, and water treatment [50]. Synthetic complexing agents such as ethylene-diamine-tetraacetic acid disodium salt (Na_2EDTA), diethylenetriamine pentaacetate (DTPA), and propyleneenedinitrotetraacetic acid (PDTA), are excellent in chelating and solubilizing metal ions in soil. Despite the advantages of low cost and high chelation efficiency, these reagents are toxic, resistant to standard biological or physicochemical water treatment procedures, relatively non-biodegradable. Their direct application for leaching IAC may increase the risk of leaching geogenic, toxic elements into water resources. As a result, DTPA is only used for functionalizing sorbents in concentrating REE [60].

Chelating agents are effective for mobilizing toxic metals and enhancing REE recovery. Lanthanides often interact with electronegative atoms, particularly oxygen in ligands. Complexation involves the substitution of metal-oxygen bonds, especially electrostatic interactions. An effective chelating agent must contain numerous oxygen-containing functional clusters. The stability constant (log K) indicates the strength of the ligand-metal complex. Table 3 shows the log K values for the formation of REE complexes with multidentate (EDTA), tridentate (citrate), and bidentate chelating agents (oxalate). In general, a higher log K value indicates a stronger REE complex, possibly contributed by the stronger bonds between the ligands and REE. A gradual increase of log K for EDTA complex with increasing REE atomic number is consistent with the similar trend of electronegativity, caused by the lanthanide contraction. Most notably, all REE-oxalate complexes possess high log K values. The exceptionally high stability makes them very stable and tends to form solid precipitate. The structure of chelating agents may be designed to suit various applications, including the mobilization and extraction of REE from the liquid phase.

Table 3. The log K values of REE complexes with various chelating agents (adapted from [50, 61]).

REE^{3+}	log K		
	EDTA	Citrate	Oxalate
La	15.5	9.5	28.22
Ce	16	9.6	30.18
Pr	16.4	9.7	-
Nd	16.6	9.8	31.11
Sm	17.1	-	31.35
Eu	17.3	9.8	31.38
Gd	17.4	9.9	31.37
Tb	17.9	-	-
Dy	18.3	-	30.70
Ho	18.6	-	-
Er	18.9	-	30.05
Tm	19.3	-	-
Y	-	-	28.17
Yb	19.6	-	-
Lu	19.9	-	

Oxalic Acid ($C_2H_2O_4$)

Oxalic acid (Figure 5) can dissolve large amounts of other major metals, such as aluminium and sodium into the leaching solution. Additionally, REE will remain in the leaching residue due to the low solubility of rare earth oxalates. Oxalic acid can be used to remove iron and aluminium from red mud. The acid's leaching residues will enhance REE, which can subsequently be recovered selectively using mineral acids [62].

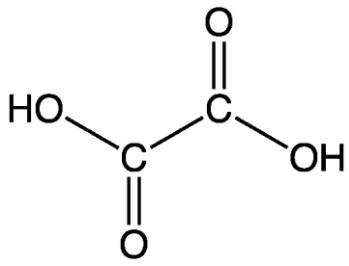

Figure 5. Chemical structure of $C_2H_2O_4$.

Oxalic acid can promote REE migration and dissolution in minerals. [18] found that oxalic acid is more effective than HREE in increasing LREE dissolution. As the concentration of oxalic acid increases from 0.01 to 0.05 mol/L, the rate of ∑REE dissolution increases. Oxalic acid has a strong ability to dissolve minerals because it has more H^+ and ligands. During mineral dissolution in oxalic acid immersion solution, REE^{3+} on the mineral surface can exchange ions with the hydrogen ions produced by oxalic acid electrolysis and dissolve into the oxalic acid solution, forming hydrated cations. The surface charge density and hydration number increase as the radius of REE^{3+} decreases.

Oxalic acid molecules can undergo a two-step ionization process, in aqueous solution, thus forming hydrogem oxalate ($HC_2O_4^-$) and oxalate ($C_2O_4^{2-}$) ions. The process is shown in the following equation:

Primary ionization: $$H_2C_2O_4 \rightleftarrows HC_2O_4^- + H^+$$

Secondary ionization: $$HC_2O_4^- \rightleftarrows C_2O_4^{2-} + H^+$$

These dissociated species are capable of forming stable complexes with REE^{3+} ions, which play a key role in REE leaching and separation using oxalic acid. Oxalic acid in solution consists mainly of $H_2C_2O_4$ and $HC_2O_4^-$, with a trace of $C_2O_4^{2-}$. Higher quantities of oxalic acid contain more $HC_2O_4^-$. REE in minerals exchanges ions with H^+ in an oxalic acid solution, promoting secondary ionization and forming $C_2O_4^{2-}$. Dissolved REE^{3+} can bind $HC_2O_4^-$ and $C_2O_4^{2-}$ to create oxalate, which then coordinates with water molecules to form oxalate complexes. Dissolved REE^{3+} from mineral samples in oxalic acid leaching solution are REE^{3+} that quickly produce aqueous cation ions ($REE(H_2O)_n^{3+}$) and bind with $HC_2O_4^-$ produced by ionizing oxalic acid to dissolve it in solution.

When the rare earth ions in the oxalic acid leach solution have the same valence and concentration, REE with small ionic radius have larger covalent bonds and electrostatic interactions, forming more stable complexes with water molecules, which have larger hydrated radii and weaker mineral resorption ability. The ionic radius of REE generally decreases with increasing atomic number. HREE with higher surface charge density and hydration number (n) is more difficult to re-adsorb by minerals, resulting in increased content in low-concentration oxalic acid leach solution. LREE-oxalate has a lower complexation ability and a higher fraction of hydrated cations, which facilitates LREE re-adsorption in low-concentration oxalic acid solution.

Oxalic acid is commonly used as a precipitation agent for REE due to the strong affinity between oxalate ions ($C_2O_4^{2-}$) and REE^{3+} cations, and the low solubility of the resulting REE-oxalate complexes. This method leads to the formation of hydrated REE salts, as illustrated in the following equation:

$$2REE^{2+} + 3{C_2O_4}^{2-} + nH_2O \rightarrow REE_2(C_2O_4)_3\, nH_2O$$

After leaching, REE can be recovered from the solution using the selective precipitation method, where oxalate precipitation is widely applied due to the low solubility and strong binding affinity of oxalate ions for REE^{3+}. However, oxalate precipitation might cause the emission of carbon dioxide (CO_2) in a sequence of reactions during the calcination of $(REE)_2(C_2O_4)_3$,nH_2O to form rare earth oxides, which can pose environmental issues [63]. The overall reaction is as follows:

$$2REE_2(C_2O_4).8H_2O \xrightarrow{650-800℃} 2REE_2O_3 + CO_2 + 8H_2O$$

Biodegradable Organic Acids for Leaching REE

Organic acids or salts are commonly used as leaching agents to improve the ion-adsorption process of rare earth ores. Organic acids have high complexing activity with REE^{3+} in solution. The dissociation of organic acids affects the pH of the leaching solution, which is used to determine metal desorption.

The stability of Eu and Y complexes with organic acids is influenced by their complexation constants. Higher complexation constants indicate stronger interactions between metal ions and organic acids. For example, the complexation of Eu(III) with citric acid is significant, as it forms stable complexes like Eu-citrate^0, which dominates in solution at pH values up to 4.5. This indicates that citric acid has a strong ability to stabilize Eu compared to other acids.

The pK_a value of organic acids also determines their dissociation in solution, which affects the ability to complex with REE. Acetic acid has a relatively high pK_a, indicating it is a weaker acid compared to citric acid. This results in a lower degree of dissociation and, consequently, a lower ability to form stable complexes with Eu and Y. The addition of $(NH_4)_2SO_4$ can change the ionic strength and affect the stability of the complexes formed. The presence of ammonium ions can increase the solubility of certain organic acid complexes. In addition, the stability of the complexes is influenced by electrostatic interactions. For example, monodentate complexes such as Eu-malonate$^+$ and Eu-citrate^0 are poorly adsorbed on rare earth ion adsorption surfaces due to weak electrostatic attractions [64].

The recovery of REE, especially HREE and Sc, was improved by using selected organic acids. Rather than complexing, the organic anionic species likely played a function of solubilizing REE from the IAC. Citric acid and DL-malic acid perform well in leaching REE, whereas malonic acid, oxalic acid, and DL-tartaric acid are inferior to hydrochloric acid [65]. Recently, a study reported that the descending order of REE leaching efficiency from coal ash is tartaric acid > lactic acid > citric acid > malonic acid > succinic acid [66]. The enhancement of metal leaching in the presence of organic acids is likely due to three mechanisms: (1) protons dissociated from organic acid molecules increase the acidity of leaching systems; (2) organic species affect the saturation state of leach solutions with respect to mineral solids; and (3) organic species change the speciation of metal ions in solution [65]. Organic acids imposed a more positive impact on the leaching recovery of HREE. By complexing with the HREE, organic acids can keep the middle and heavy REE in solution and improve the leaching recovery [67]. Organic acids and siderophores produced by microbes may drastically increase REE mobility. Secretion from phosphate-solubilizing microbes (PSM), including gluconic, citric, acetic, oxalic, succinic, 2-ketogluconic, and malic acids solubilize REE phosphate [68]. The organic acids, such as succinic, fumaric, lactic, malic, citric, oxalic, and acetic acid produced by *Acetobacter sp*. can extract > 50% of Y and Sc from red mud through REE-organic acid complex formation [69]. Gluconic acid forms complexes with REE (i.e., Ce, Nd, Sm, Eu, and Yb) and causes a dissolution effect [70]. Polycarboxylic and amino carboxylic acids are known to form highly stable complexes with the REE. Siderophores such as desferrioxamine B (DFO-B) have been reported to form complexes with REE ions and enhance the dissolution of REE [71]. Although hydroxamic acid has been known as a collector [72] and ion-exchange resin for REE recovery [73], smaller and more polar derivatives may form a soluble complex with REE ions.

Organic acids may have promoted LREE release from soil and then uptake by the roots of the *D. pedata* [74]. Although the phytoaccumulation of REE, in general, is enhanced by complexation, the fractionation of REE in *Dicranopteris sp.* depends on the stability of the REE-humate complex. The fractionation of LREE and HREE in the foliage may be caused by complexation during their upward transfer processes because the binding capacity of organic acid and HREE is greater than that of LREE.

Citric Acid ($C_6H_8O_7$)

Citric acid (Figure 6) is an organic acid that contains three carboxylic groups, with three hydrogen dissociation constants $pK_{a\,1} = 3.13$, $pK_{a\,2} = 4.76$, and $pK_{a\,3} = 6.40$ at 25 °C. It has weak reducing properties that contribute to metal leaching, but also high coordination ability and chelating properties with metal ions [75]. Compared to sodium citrate (65.91% ± 4.96%) and ammonium citrate (65.94% ± 7.85%), citric acid has a good REE leaching efficiency of 77.25% ± 0.83%. This indicates that when compared to Na^+ and NH_4^+ from IAC with the same organic acid anion (citric), H^+ has distinct primary driving forces for REE leaching. According to thermodynamic data, a higher atomic number of REE-citrate indicates greater stability in solution.

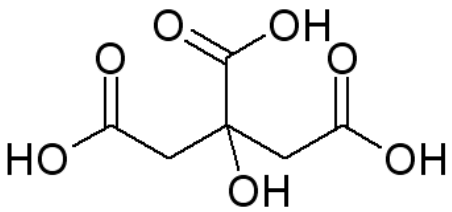

Figure 6. Chemical structure of $C_6H_8O_7$.

When citric acid was compared to sodium and ammonium citrate, it demonstrated a strong leaching ability for HREE, Ce, Gd, Dy, Y, and Th. Citric acid is a hard base because it contains numerous carboxylic acid groups -COOH that undergo deprotonation to create carboxylate ions $-COO^-$ in solution. The carboxylate group's electron density allows for strong ionic or covalent interactions with hard acids. Chelation involves multiple bonding connections between REE ions and carboxylate groups, which improve the complex's stability and solubility. Citric acid is a stronger hard acid than LREE due to its lower ionic radius and higher charge density. The carboxylate groups of citric acid interact more strongly with these smaller and highly charged ions. In sodium and ammonium citrates, the presence of counter ions (Na^+, NH_4^+) can compete with REE^{3+} for citrate. This competition weakens the leaching efficiency compared to citric acid, which does not have such competitors and interacts directly with REE^{3+}.

The increased leaching efficiency of cerium indicates that citric acid might be able to release cerium from the phase of colloidal sediment. Ce^{4+} can be reduced to the more soluble form Ce^{3+} in the presence of reducing citric acid. At pH 2.0, significant HREE fractionation features are observed. It was found that a concentration of 0.02 mol/L (96.52%) produced the maximum leaching efficiency. More than 95% of the La is complexed with citrate in rare earth-citrate complexes such asLa-Citrate and dissolved rare earth ions, with the remaining La existing in ionic form. At low pH levels, the presence of H^+ ions inhibits the hydrolysis of citrate and consequently suppresses the formation of the REE-citrate complexes. In both acidic and neutral solutions, citric acid undergoes stepwise dissociation through three stages, forming citrate species with varying degrees of deprotonation [76]:

$$H_3Cit + H_2O \rightleftarrows H_2Cit^- + H_3O^+ \qquad (pK_{a\,1} = 3.13)$$

$$H_2Cit^- + H_2O \rightleftarrows HCit^{2-} + H_3O^+ \qquad (pK_{a\,2} = 4.76)$$

$$HCit^{2-} + H_2O \rightleftarrows Cit^{3-} + H_3O^+ \qquad (pK_{a\,3} = 6.4)$$

The degree of citric acid dissociation is strongly pH-dependent and influences the availability of citrate anions for REE complexation. At higher pH, more fully deprotonated forms (e.g., Cit^{3-}) dominate, facilitating stronger complexation with REE^{3+} ions. Although their capacity to complex with La is not as strong as that of Citrate^{3-}, H-Citrate^{2-}, and H_2-Citrate$^-$, which are generated as a result of partial dissociation of citrate, they may be complexed with La. La-H-Citrate and La-H_2-Citrate complexes reach their maximum levels at pH values around 4 and 5, respectively, before switching to La-Citrate [77].

Rare earth ores that retain REE through an ion adsorption mechanism can be leached using organic acids via multiple pathways, including: (1) ion exchange processes mediated by protons; (2) increased leaching through organic acid complexation; (3) redox reactions; and (4) protons facilitate dissolution.

Citric acid dissociates stepwise under varying pH conditions and produces multiple anionic species [77]:

$$C_6H_8O_7 \rightleftarrows H^+ + C_6H_7O_7^- \ (pK_{a\,1} = 2.79)$$

$$C_6H_7O_7^- \rightleftarrows H^+ + C_6H_6O_7^{2-} \ (pK_{a\,2} = 4.30)$$

$$C_6H_6O_7^{2-} \rightleftarrows H^+ + C_6H_5O_7^{3-} \ (pK_{a\,3} = 6.39)$$

The dissociated protons (H^+) facilitate REE desorption through ion exchange with surface-bound REE^{3+}, while the citrate anions form soluble REE-citrate complexes. [78] reported the formation of species such as NdCit, NdHCit, $NdHCit_2$, and $NdCit_2$ in the pH range of 2 to 5, confirming the effective complexation of Nd^{3+} by citrate. This interaction can be generally described by the following equilibrium:

$$nNd^{3+} + jH^+ + kCit^{3-} \leftrightarrows Nd_kH_jCit_k^{(3n+j-3k)}$$

Similarly, [79] demonstrated that Nd^{3+} forms sequential mononuclear complexes according to the following equilibrium:

$$Nd^{3+} + jCH_3COO^- \leftrightarrows Nd_k(OOCCH_3)_j^{(3-j)+}, \ j = 1, 2, 3$$

The mechanism of REE leaching by citric acid involves both ion exchange and complexation. When citric acid contacts with REE, protons replace REE^{3+} on mineral surfaces, and the released REE^{3+} forms a soluble REE-citrate complex. The reaction pathways can be summarized as follows:

$$[Al_4(Si_4O_{10})(OH)_8]_a \cdot mREE^{3+}(s) + 3mH^+(aq) + 3mC_6H_7O_7^-(aq) \rightleftarrows [Al_4(Si_4O_{10})(OH)_8]_a \cdot mH^+(s) + mREE(C_6H_7O_7)_3(aq)$$

$$Al_4(Si_4O_{10})(OH)_8]_a \cdot mREE^{3+}(s) + 3mH^+(aq) + \frac{3}{2}mC_6H_6O_7^{2-}(aq) \rightleftarrows [Al_4(Si_4O_{10})(OH)_8]_a \cdot mH^+(s) + \frac{3}{2}mREE_2(C_6H_6O_7)_3(aq)$$

$$[Al_4(Si_4O_{10})(OH)_8]_a \cdot mREE^{3+}(s) + 3mH^+(aq) + mC_6H_5O_7^{3-}(aq) \rightleftarrows [Al_4(Si_4O_{10})(OH)_8]_a \cdot mH^+(s) + mREEC_6H_5O_7(aq)$$

The REE^{3+} adsorbed into rare earth minerals is replaced by the H^+ produced during the dissociation of citric acid. Citric acid-dissociated organic anions also combine with REE^{3+} to create stable complexes that facilitate a balanced ion exchange shift and speed up the leaching process. The next step in dissociating citric acid is the production of H^+, which can dissolve rare earth oxides and carbonates. This can help dissolve some colloid precipitation stages and mineral phases of REE. To facilitate the solubility of rare earth elements that are only slightly soluble, citric acid can also decrease Ce^{4+} to Ce^{3+}. During this process, the citric acid is oxidized to hydroxy acids.

Monodentate, Eu-malonate, and Eu-citrate complexes in citric acid increase when pH rises due to more organic anions dissociating from organic acid molecules. At pH 4.5, Eu-citrate is the major species in citric acid. Greater complexing capacity results in more monodentate complexes. Monodentate compounds are poorly adsorbed due to their weak electrostatic attraction. Citric acid has the maximum coordination ability but the lowest REE extraction at pH levels over 5.25 due to insufficient organic ligands for REE ions [64].

Ammonium Citrate ($C_6H_{11}NO_7$)

Ammonium citrate (Figure 7), which is linked to citric acid radicals, has been reported to achieve excellent rare earth leaching efficiency at low ammonium concentrations. Studies have shown that $C_6H_{11}NO_7$ is more effective than $(NH_4)_2SO_4$. At a similar concentration (15 mmol/L), $C_6H_{11}NO_7$ showed REE extraction reached up to120%, while $(NH_4)_2SO_4$ only achieved 40%. This indicates that organic complexing agents may facilitate REE leaching efficiency more effectively than inorganic salts [29]. Compared to sulfate radicals and other inorganic salt anions, citric acid radicals have a significantly greater coordination. During extraction, citric acid radicals coordinate with rare earth ions in exchange for ammonium ions that promote the release of rare earth metals. Citric acid radicals also facilitate the release of REE by decreasing the hydration power of mineral surfaces and attracting cations from leaching agents. Thus, the extraction capacity of leaching materials for rare earths is increased, thereby reducing the required cation concentration [29].

Fulvic Acid ($C_{14}H_{12}O_8$)

Fulvic acid (Figure 8) is a part of humic substances, known as organic materials, produced by plant decomposition products and soil microbes. It has the potential to improve the washing process by increasing its efficiency. Previous studies have investigated the effectiveness of fulvic acid. For instance, [80] reported that applying 0.1wt% fulvic acid can increase REE leaching by 8.38%. Apart from its role in leaching, fulvic acid has a major impact on reducing the need for fertilizer and maintaining soil pH. This can increase the plant's ability to absorb nutrients from the soil and increase resistance to drought [81].

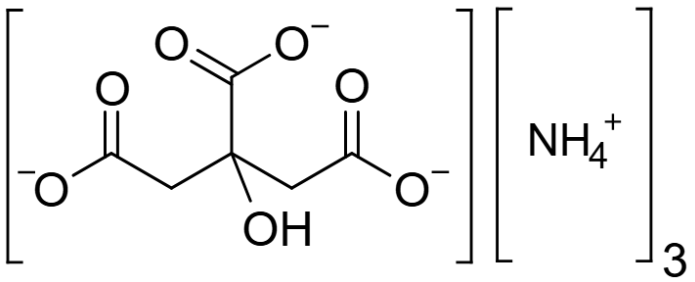

Figure 7. Chemical structure of $C_6H_{11}NO_7$.

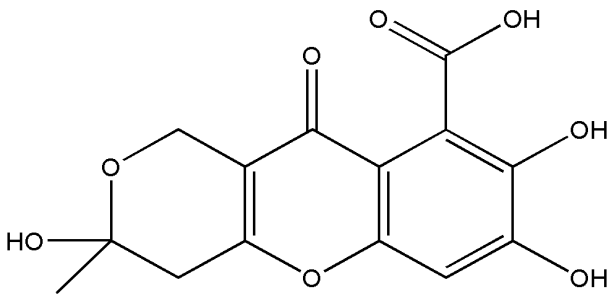

Figure 8. Chemical structure of fulvic acid.

Mineral Acid Leaching Agent

Acid was used as a leaching agent to extract REE from phosphate rock using hydrometallurgical techniques such as H_2SO_4, HNO_3, H_3PO_4, and HCl. H_2SO_4 and HCl provide the highest leaching efficiency. Sulfuric acid and HCl are commonly used for precipitation and solvent extraction, respectively. However, HNO_3 is often avoided due to the development of NO_x and the production of water nitrate waste [82]. A study by [83] found that more than 85% of LREE and 89% of HREE were effectively dissolved using a 1 M H_2SO_4 solution at 20°C within one hour. HREE were extracted using 1.2 M di-(2-ethylhexyl) phosphoric acid (D2EHPA) as a cation exchanger, while LREE was released into aqueous solution and precipitated as RE oxalate with the addition of 0.08 M oxalic acid. Meanwhile, a study conducted by [84] on the recovery of REE from phosphogypsum using H_2SO_4 washing showed a leaching efficiency of 92% produced at a concentration of 2 M H_2SO_4, by utilizing undried and finely ground particles (≤200 µm) at a temperature of 60°C. HCl is a more economical leaching agent than HNO_3 and H_3PO_4. According to [85], the optimal conditions for REE extraction from Moroccan phosphate rock using HCl leaching include a maximum of 23% HCl with a reaction time of 45 minutes at a temperature of 44°C and a stirring speed of 233 rpm, ultimately achieving 75% dissolution for REE. [86] added that using HCl as a leaching agent with an acid concentration of 1.65 mol/L and a reaction temperature of 60 ºC showed a maximum leaching recovery of 65.6% for ∑REE, with Y having the greatest leaching level at 73.8%. According to [82], the chemical reactions of La, Ce, and Nd with H_2SO_4 and HCl are as follow:

$2La(OH)_3 + 3H_2SO_4 \rightarrow 6H_2O + La_2(SO_4)_3$ $\Delta G° = -392.55$ kJ/mol
$2Nd(OH)_3 + 3H_2SO_4 \rightarrow 6H_2O + Nd_2(SO_4)_3$ $\Delta G° = -234.60$ kJ/mol
$2Ce(OH)_3 + 3H_2SO_4 \rightarrow 6H_2O + Ce_2(SO_4)_3$ $\Delta G° = -417.40$ kJ/mol
$La(OH)_3 + 3HCl \rightarrow 3H_2O + LaCl_3$ $\Delta G° = -123.20$ kJ/mol
$Nd(OH)_3 + 3HCl \rightarrow 3H_2O + NdCl_3$ $\Delta G° = -101.02$ kJ/mol
$Ce(OH)_3 + 3HCl \rightarrow 3H_2O + CeCl_3$ $\Delta G° = -116.76$ kJ/mol

Furthermore, HNO_3 has been reported as a highly effective lixiviant for REE recovery from phosphogypsum. According to [87], leaching with 3.0 M HNO_3 with a mixing time of 3 hours at room temperature produces more than 66% lanthanides, outperforming H_2SO_4 under similar conditions. This highlights the importance of acid type and concentration in determining leaching efficiency.

Even though mineral acid is very effective in leaching REE, it is extremely harsh to the environment, particularly when used at a high concentration. Hence, the application of mineral acid for *in-situ* leaching is unlikely. However, it can be used under a controlled environment, such as an *ex-situ*, batch leaching setup, such as the chemical purification of REE from monazite.

Phytoremediation of REE

Phytoremediation is a sustainable and environmentally friendly technique for restoring soils contaminated with toxic elements by utilizing the ability of plants to absorb, accumulate, and stabilize pollutants through physical, chemical, or biological processes [88]. In general, phytoremediation involves five mechanisms: phytoextraction, phytostabilisation, phytovolatilization, phytodegradation, and phytofiltration (Table 4).

Table 4. The different mechanisms of phytoremediation

Mechanism	Description	Reference
Phytoextraction	Using hyperaccumulating plants that can absorb metals from the soil through their roots and accumulate them in the stems and leaves.	[89]
Phytostabilization	Using metal-tolerant plants to immobilize heavy metals underground and reduce their bioavailability, thereby preventing the migration of heavy metals into the ecosystem.	[90]
Phytovolatilization	Pollutants are absorbed from the soil, transported through the xylem, converted into less hazardous volatile chemicals, and released into the atmosphere.	[91]
Phytodegradation	Plants are used to degrade or break down contaminants in soil by metabolizing or transforming pollutants into less hazardous molecules via biochemical processes.	[92]
Phytofiltration	It is used in both terrestrial and aquatic environments to purify groundwater and other bodies of water. This process involves heavy metals being absorbed by roots, collected, and transported to stems or leaves.	[93]

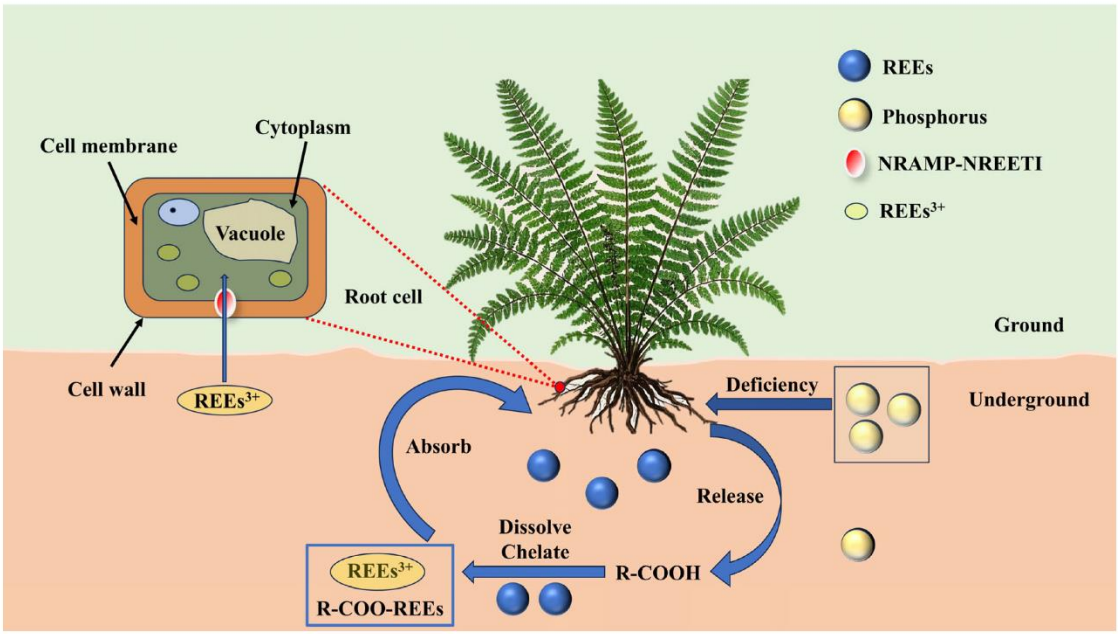

Figure 9. Conceptual model of rhizosphere processes in REE mobility and absorption (adapted from [96]).

Phytoextraction has emerged as a promising strategy for soil remediation because this method is considered cost-effective, simple, and environmentally friendly. Some plant species, particularly hyperaccumulators, have developed physiological mechanisms such as metal tolerance and efficient translocation systems that enable them to tolerate and accumulate the concentrations of REE. This provides a practical strategy not only for remediating contaminated soils, but also for sustainable resource recovery through phytomining [93].

Rare earth hyperaccumulators are typically defined by their ability to accumulate from 100 to 1000 mg/kg of REE in their tissue [94]. The success of REE phytoextraction depends on several factors, including plant-microbe interaction, the ability to take up contaminants from the substrate, translocation and tolerance mechanisms, and plant chelating ability [95]. Figure 9 presents a conceptual model illustrating rhizospheric interactions, emphasizing the roles of biotic and abiotic factors in modulating REE speciation, desorption, and transport of REE to the root zone. The uptake of REE by plants is a complex process influenced by a range of interactions occurring in the rhizosphere. Factors like the presence of organic acids from root exudates, microbial communities, redox potential, and soil mineralogy determine the mobility and availability of REE in the soil. Plants gather REE from the soil and move them to the roots and other plant components during the phytoextraction process. The majority of plants, including food crops, often have relatively low REE concentrations in the topsoil, ranging from 5 mg/kg (in dry matter) to 150 mg/kg on average. Because the majority of REE is absorbed by root cell walls and deposited by phosphate in the root apoplast, only a small amount may travel from roots to shoots.

Table 5 shows various plant species that can accumulate REE. Ferns represent the dominant group of REE hyperaccumulator plants. Among them, *D. linearis* has been identified as an efficient hyperaccumulator plant that is capable of accumulating significant amounts of REE, and thrives under acidic conditions (pH 4-5) and in soils with limited phosphorus availability [97]. These physiological traits, combined with its high biomass and extensive root system, make *D. linearis* a suitable plant for application in chemically assisted phytoremediation strategies. Table 5 shows previous studies on the effectiveness of *D. linearis* as an REE hyperaccumulator.

According to earlier studies, *D. linearis* can accumulate REE in the lower roots of mining soil in South China including La (118.8-141.5 mg/kg), Ce (108.4-157.7 mg/kg), Pr (36.9-201.5 mg/kg), and Nd (146.3-1247.9 mg/kg) [98]. *D. linearis* is a species that can absorb radionuclides, including thorium (447 µg/kg) and radium (4.53×10^{-3} µg/kg) [99]. *Dicranopteris* is a great plant for lowering soil contamination and toxicity because of its high biomass accumulation, quick development, flexibility, and strong bioconcentration ability [100]. Phytoaccumulation of REE has been reported in *Dicranopteris* species, such as *D. linearis* and *D. pedata*, reaching levels of 3,500 mg/kg and 7,000 mg/kg, respectively [101].

Table 5. REE accumulated by various plant species.

Plant species	Element	**Σ**REEs (mg/kg)	Reference
Mockernut hickory	All REE except Pm, Sc	2300 (dry leaf)	[106]
Phytolacca americana	REE	1040 (leaf), 70.6-386 (root), 27.5-154 (stem)	[107]
Dryopteris erythrosora	La, Ce, Eu, Gd	22.11 (leaf) and 151.68 (root)	[108]
Asplenium ruprechtii	La, Ce	40 and 14 (leaf)	[109]
Pronephrium simplex	All REE	1200	[110]
Alsophila sternbergii	Ce, Eu, La, Sc, Sm	57	[111]
Onoclea sensibilis	La, Ce, Sm, Gd, Yb, Y	More than 200	[110]
Dicranopteris dichotoma	REE	238.93 to 2364.51	[112]
Dicranopteris linearis	All REE except Pm, Sc	2700 (leaf)	[113]
Dicranopteris linearis	All REE	> 1000	[37]
Dicranopteris linearis	All REE except Pm	3,730	[114]
Dicranopteris linearis	REE	848.7 (leaves), 264.7 (roots), and 186.5 (stems)	[115]
Dicranopteris linearis	All REE	3,500	[101]

Furthermore, *Pronephrium simplex* has been found as an REE hyperaccumulator with an uptake of up to 3,000 mg/kg [102]. According to [103], *D. pedata* can accumulate LREE such as La, Ce, Pr, and Nd. On the other hand, its roots have a larger concentration of HREE like Tb, Yb, and Lu than leaves [104]. Most of the literature indicates that under natural settings, REE distribution in the soil-plant system is fractionated, going from soil > roots > leaves > stem > seeds. REE accumulation is observed in fern roots and leaves [105]. Therefore, high REE uptake by hyperaccumulators may also result in increased REE accumulation in fern stems.

Hyperaccumulators may actively deposit metals in the roots, and the distribution of REE in the roots and shoots differs according to plant species. Studies have shown two dominant accumulation trends: (1) roots > leaves > stems [116, 117], and (2) leaves > roots > stems [118], indicating the mobility of various elements in different plants results in varied concentration of REE in plants. The two main parameters that are used for describing the accumulation and distribution of REE in hyperaccumulator are the bioconcentration factor (BCF) and the translocation factor (TF). BCF is the ability of plants to accumulate metals from the soil which can be estimated using the ratio of metal content in the roots or shoots of the plant to the metal content in the soil, while TF is the ability of plants to translocate metals from roots to shoots, measured using the ratio of metal concentration in shoots to roots [119]. Plants with more than one TF and BCF (TF > 1 and BCF > 1) are expected to be used in phytoextraction [88]. *D. linearis* has been widely reported as a promising accumulator of REE, exhibiting high TF and BCF value across various studies. These findings, summarized in Table 6 and Table 7 suggest that *D. linearis* may serve as a suitable candidate for phytoremediation or agromining applications in REE-contaminated soils.

Table 6. The BCF value of *D. linearis* in REE soil.

No	REEs	BCF value	Reference
1.	La, Sc, Y, Ho, Tb, Eu, and Yb	151.11	[103]
2.	All REE	0.7-9.7	[120]
3.	All REE except Pm, Sc	6.2	[37]
4.	All REE	1.24	[115]
5.	REE	1.11-14.8	[95]

Table 7. The TF value of *D. linearis* in REE soil.

No	REE	TF value	Reference
1.	Tm, Ho, Lu, Pr, Tb and Tm	3.2	[103]
2.	REE	0.39	[37]
3.	Ce, La, and Y	1.00	[121]
	Pr	1.58	
	Sc	1.19	
4.	REE	1.31-19.6	[95]

Leaching Agent-assisted Phytoaccumulation

As discussed in the earlier section, all leaching agents mobilize REE from IAC with various reaction mechanisms. The enhanced concentration of REE in soil moisture allows greater mobility to the root zone and potentially increases uptake by hyperaccumulators. Leaching agents assist the uptake of REE in hyperaccumulators primarily by increasing their mobility and bioavailability in the soil.

As discussed earlier, $(NH_4)_2SO_4$ is a strong ionic leaching agent that enhances the mobilization of REE in the soil. For example, Pr uptake by *D. linearis* was improved with treatment of $(NH_4)_2SO_4$ [121]. This increased mobility allows more REE to be available for root absorption and subsequent translocation to shoots in hyperaccumulator species such as *D. linearis* [101]. Compared to organic acids (e.g., citric acid, hydrolyzed fulvic acid, etc.), $(NH_4)_2SO_4$ causes greater mobilization of some REE and uranium, resulting in higher uptake and shoot translocation. Moreover, $(NH_4)_2SO_4$ is also a fertilizer, supplying macronutrients such as N and S for plant growth. This would contribute to a greater accumulation of biomass and possibly a greater bioaccumulation of REE of the hyperaccumulator. However, $(NH_4)_2SO_4$ may increase ammonia levels in the environment, potentially causing ecological concerns such as eutrophication, degradation of water resources, and release of greenhouse gas (i.e., nitrous oxide) that exacerbate climate change. The application of $(NH_4)_2SO_4$ must be conducted at low concentration (~0.1%wt) to avoid adverse impact on the environment.

Organic acids are still a great interest due to the selective recovery of specific REE and are considered safer alternatives environmentally. The application of organic acid maintains a reasonable level of soil organic matter, improving retention of soil moisture for plant growth. Naturally occurring organic acids, such as humic/fulvic acids, are particularly suitable for fern hyperaccumulator species such as *D. linearis* that thrive in poor nutrient soil. However, due to the strong interaction with geogenic aluminium and iron, they may compete with REE in forming complexes with organic acids, resulting in a lower uptake of REE. Mild acidic leaching (pH ~4.8) with organic acids is feasible in recovering REE from soil and enhancing plant uptake and translocation to the shoot [121]. Fulvic acid has also been reported to enhance defence mechanisms and the activity of antioxidant enzymes, thereby increasing growth and development [122]. This benefit makes fulvic acid valuable in the phytoremediation process by supporting the absorption of REE and simultaneously strengthening the hyperaccumulator. In addition, humic substances such as fulvic acid have been shown to stimulate the exudation of organic acids by roots, which can dissolve REE and provide nutrients to the rhizosphere, thereby enhancing nutrient cycling and root-soil interaction [123]. This interaction highlights the potential of fulvic acid not only as a leaching agent but also as a facilitator of REE phytoextraction.

CONCLUSION AND RESEARCH PROSPECTS

The abundance of NH_4^+ and SO_4^{2-} that $(NH_4)_2SO_4$ releases into the environment during its application as a leaching agent has been established in existing literature as a cause of water resource pollution. Organic acids are effective leaching agents for REE recovery. Citric acid exhibits a total REE effectiveness of 96.52%, whereas fulvic acid can boost REE leaching by 8.38% at a weight percentage of 0.1%.

A biological-based mining technique called "bioleaching" allows elements to be extracted using microbes or their byproducts. Energy costs and gas emissions can be decreased via biomining, which operates at very low temperatures and atmospheric pressure without requiring chemicals [124]. [125] reported the effectiveness of bioleaching utilizing *Aspergillus niger, Aspergillus terreus*, and *Paecilomyces* during an abiotic leaching process to recover REE from sand monazite with minimal environmental impact. Meanwhile, [126] said that REE bioleaching from fluidized catalytic cracking (FCC) catalysts by *Gluconobacter oxydans* is economically more profitable than chemical leaching.

Compared with conventional chemical leaching materials, bioleaching is more efficient, less environmentally damaging, and environmentally friendly. One or a combination of the following mechanisms: (a) increased dissolution complexation (complexolysis), (b) protons driving dissolution (acidolysis), and (c) redox reactions (redoxolysis) can lead to the dissolution of minerals. Dissociated organic acid anions can chelate rare earth ions and increase the process of ion exchange reactions, resulting in microorganisms leaching REE through various organic acid secretions [77].

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