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Preliminary Flowsheet Development for Mixed Rare Earth Elements Production from Apatite Leaching Aqueous Solution Using Biosorption and Precipitation

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Abstract: A flowsheet was developed to extract mixed Rare Earth Elements (REEs) from an aqueous solution generated by nitric acid leaching of apatite concentrate. In this study, *Platanus orientalis* (*P. orientalis*) leaf powder was employed in the biosorption process to purify the pregnant leach solution. The sorption and desorption processes were investigated and optimized. The results demonstrated the successful extraction of REEs from the pregnant leach solution using the biosorbent. Hydrochloric acid effectively desorbed REEs from the loaded *P. orientalis* leaf powder. Thermodynamic studies indicated that REEs' sorption on *P. orientalis* leaf powder was an endothermic and spontaneous process. Precipitation and calcination steps yielded mixed rare earth oxides (REOs) with an assay of approximately 87%. The final product, mixed REOs, can be further refined through releaching and a secondary impurity removal stage prior to entering the individual REE separation process. Alternatively, it can be fed directly into the solvent extraction process or alternative technologies to obtain individual heavy and light REEs.

Keywords: rare earth elements; apatite; leaching; biosorption; precipitation

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1. Introduction

Rare earth elements (REEs) encompass a group of 17 chemically similar metals consisting of 15 lanthanides and also Sc and Y [1]. These elements are typically categorized into light REEs (LREEs: La to Gd) and heavy REEs (HREEs: Tb to Lu). Y, although not an HREE, is often considered alongside the HREEs due to its similar chemical and physical properties related to its trivalent radius. Sc, also trivalent, possesses dissimilar features that prevent its classification as either an LREE or HREE. In order to align with market dynamics and anticipate future supply and demand trends, Seredin and Dai [2] introduced a revised classification system for REEs. This updated classification categorizes REEs into three distinct groups: critical elements (Nd, Eu, Tb, Dy, Y, and Er) that are of paramount importance, uncritical elements (La, Pr, Sm, and Gd) that hold moderate significance, and excessive elements (Ce, Ho, Tm, Yb, and Lu) that are abundant in supply. This classification comprehensively explains different REEs' relative importance and potential implications in various industries [2–4]. REEs are known for their malleability, ease of shaping, and reactivity. They find a wide range of applications in modern technology, from everyday uses such as glass polishing and lighter flints to high-tech applications such as lasers, magnetic refrigeration, magnets, phosphors, batteries, and advanced applications such as safe hydrogen storage and transport in the post-hydrocarbon economy, as well as high-temperature superconductivity [5]. Specifically, standard and high-operating-temperature rare earth NdFeB magnets hold indispensable significance as vital components in various industries, including the production of cell phones, advanced robotics, electric vehicles (EVs), hybrid

vehicles (HVs), large and offshore wind turbines, and military defense systems. These magnets are widely recognized for their unique properties and find irreplaceable applications in these advanced technologies [6].

Among the most common minerals containing REEs are apatite, monazite, bastnäsite, and xenotime. Apatite, with a standard formula of $Ca_{10}(PO_4)_6X_2$ (where X can be a fluorine ion, chlorine ion, or hydroxyl group) [7], is important as a source of phosphate fertilizers and phosphoric acid, with an average content of 0.1% to 0.8% rare earth oxides [8]. To extract REEs from apatite, leaching lixiviants such as hydrochloric, nitric, and sulfuric acids have been employed. Solvent extraction is the conventional method used to recover REEs from the leach liquor, and the REEs are ultimately precipitated as rare earth oxalates from the strip solution. Calcination of the oxalates yields a mixture of rare earth oxides, while various methods such as selective oxidation or reduction, fractional precipitation, ion exchange, solvent extraction, and fractional crystallization are utilized to separate individual REEs [9–11]. Each method has its advantages and disadvantages, including the issue of environmentally hazardous waste disposal. Biosorption represents a biotechnological innovation and cost-effective method for recovering metals from industrial effluents and aqueous solutions, utilizing certain inactive or dead biomass types that bind and concentrate metal ions in their cell walls [12–14]. Dead vegetative biomasses such as tree leaves, sawdust, bark, algae, and cone biomass are used in biosorption processes [15–17]. These materials, which are relatively inexpensive and abundantly available, require no additional nutrients and can withstand high-toxicity environments [18,19]. Brown et al. [20] recently reviewed nature-based biological methods, specifically bioleaching, and biosorption, for extracting REEs from electronic wastes (e-wastes) and ore deposits. They argued that these biological methods offer a more environmentally friendly approach compared to conventional methods currently employed in the REE mining industry, such as acid leaching and solvent extraction. According to their findings, targeted extraction of mixed REEs for specific products holds potential as a sustainable pathway for extracting REEs from both ore and e-wastes. This approach could reduce separation costs and minimize emissions associated with the use of harsh chemicals. In conclusion, the authors highlighted that nature-based biological solutions for REE extraction present an opportunity to yield significant socio-economic and environmental benefits [20].

In biosorption, REEs are extracted from the leach liquor through various mechanisms, including electrostatic interactions, ion exchange, surface complexation, and precipitation [21]. Electrostatic interactions arise from the weak attraction between regions of opposite charge found on the surface of the biosorbent and the metal ions present in the solution. In the ion-exchange approach, metal ions in the solution displace ions bound to functional groups on the biomaterial's surface. Surface complexes form when metal ions interact with organic molecules on the biosorbent's surface. Precipitation occurs when insoluble metal species are formed on the biosorbent, which can result from the metabolic activity of living biomass or occur independently in the case of inert biomass [20]. Upon completion of the biosorption process, the recovered REEs must undergo a desorption process for separation from the biosorbent. The desorption typically involves using various eluents, including acids, bases, and chelating agents [22]. Acidic eluents, such as hydrochloric acid, nitric acid, and sulfuric acid, play a crucial role in desorption by protonating the biosorbent's surface and facilitating the release of REEs [23]. Ideally, desorption should efficiently remove most recovered REEs, regenerate the biosorbent for future use, and maintain its chemical and physical properties.

Palmieri et al. [24] employed *Sargassum fluitans* to recover La from a synthetic aqueous solution and studied the dynamics of the biosorption process, pH influence, and desorption process. The study concluded that biosorption by non-living *Sargassum fluitans* is a viable alternative method for La recovery from solutions. Diniz and Volesky [25] utilized the Ca-loaded biomass of *Sargassum polycystum* for the biosorption of La, Eu, and Yb from single-component and multi-component batch systems. For the multi-component mixtures, the metal affinity sequence established was Eu > La > Yb, and the maximum metal uptakes

obtained were 0.29, 0.41, and 0.28 mmol g^{-1} for La, Eu, and Yb, respectively. Diniz et al. [26] investigated the biosorption of La and Eu using protonated *Sargassum polycystum* biomass in batch and column systems. They found that *Sargassum polycystum* biomass could be used for at least three consecutive uptake/desorption cycles without any loss of metal uptake capacity, and it could be regenerated using 0.1 N HCl. The application of biosorption for the preconcentration of REEs from waste solutions was reviewed by Gupta et al. [27]. The review covered the adsorption of REEs by biosorbents of diverse origins, detailed studies on thermodynamics and kinetics, and adsorption–desorption mechanisms.

Tree leaves have been extensively used for the recovery of heavy metals such as chromium [15,28,29], cadmium [30], and lead [31,32] from aqueous solutions. Sert et al. [33] utilized leaf powder derived from *Platanus orientalis* (*P. orientalis*) for the biosorption of La and Ce from a synthetic aqueous solution. The effects of initial pH, contact time, initial metal ion concentration, and temperature were investigated and optimized, resulting in reported Langmuir monolayer capacities of 28.65 mg g^{-1} and 32.05 mg g^{-1} for La and Ce, respectively.

Apatite concentrate, which is rich in REEs, is one of the byproducts of the Chadormalu iron ore concentrator plant in the central Iranian province of Yazd [34–36]. The objectives of this study are as follows: (a) to employ powdered leaves of *P. orientalis* as a biosorbent for recovering Y, La, Ce, and Nd ions from the aqueous solution produced by nitric acid leaching of apatite concentrate; (b) to optimize the effects of pH, contact time, temperature, and biosorbent quantity in the sorption stage, as well as the hydrochloric acid concentration in the desorption stage; (c) to determine thermodynamic parameters and conduct isotherm investigations; and (d) to produce mixed REEs oxides through precipitation and calcination. To the best of the authors' knowledge, this is the first investigation and report on the direct extraction of the aforementioned REEs from apatite leach solution using *P. orientalis*.

2. Materials and Methods

2.1. Sample Collection and Preparation of Pregnant Liquor

The apatite concentrate used in this study was obtained from the Chadormalu iron-ore concentrator plant, which is produced as a byproduct of iron-ore concentration. A representative sample of the apatite concentrate was taken, and its particle size distribution was analyzed. The majority (80 wt.%) of the sample comprised particles smaller than 50 µm. The apatite concentrate's REEs were analyzed using ICP-MS technique. The assay results for light and heavy REEs are presented in Tables 1 and 2, respectively. Figure 1 illustrates the comparative distribution of REEs in the apatite concentrate. Analyzing Figure 1, it was observed that La, Ce, Nd, and Y were the dominant forms of REEs in the apatite concentrate. The distribution of the remaining REEs in the concentrate was found to be negligible (as indicated in Figure 1). Therefore, due to their quantitative presence, our primary focus was on monitoring the extraction behavior of the main REEs, namely, La, Ce, Nd, and Y. This explains why we only reported the analyses of these REEs in the subsequent optimization stages. The leaching process was conducted by treating the apatite sample with a 60% nitric acid solution. The leaching conditions involved a temperature of 60 °C, a solid-to-liquid ratio of 30% (*w*/*w*), and agitation at 200 rpm for 30 min [36].

The slurry underwent filtration to separate the insoluble constituents. Following the filtration process, the residue on the filter paper was washed with hot deionized water. This washing step effectively eliminated any dissolved elements present within the residue and facilitated their transfer into the pregnant leach solution (PLS). Consequently, the collected PLS contained the dissolved REEs in phosphoric acid, as well as any previously trapped elements from the washed residue. The chemical analysis of the pregnant liquor is presented in Table 3.

Table 1. Assay of light REEs in the apatite concentrate.

Light REEs	La	Ce	Pr	Nd	Sm	Eu	Total
Assay (ppm)	1514	4204	455	1738	293	24.5	8228.5
Assay (%)	18.39	51.1	5.52	21.12	3.58	0.29	100

Table 2. Assay of heavy REEs in the apatite concentrate.

Heavy REEs	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y	Total
Assay (ppm)	233	28.9	145	24.2	63.2	7.76	40.9	4.94	855	1402.9
Assay (%)	16.61	2.07	10.34	1.73	4.51	0.55	2.9	0.35	60.94	100

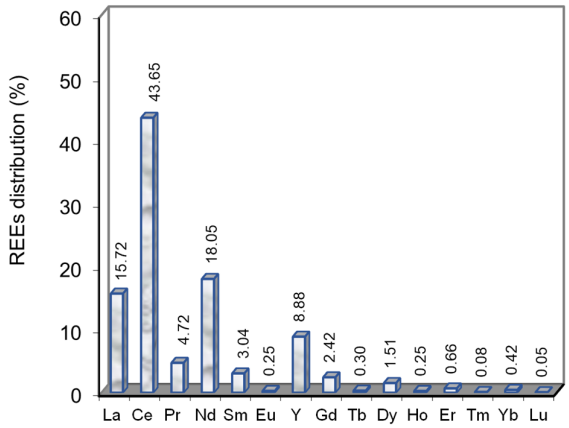


Figure 1. Comparative distribution of different REEs in apatite concentrate.

Table 3. Chemical analysis of pregnant liquor.

Element	Ca	Fe	Mg	P	S	F	La	Ce	Nd	Y
Content (ppm)	100,000	1280	2450	56,400	1015	6880	362	1221	394	290

It is evident from Table 3 that the pregnant liquor contains undesired ions, such as Ca^{2+}, Mg^{2+}, and Fe^{3+}, which can impact the biosorption process of REEs. Hence, the precipitation of impurities, primarily in the form of hydroxides, oxides, and hydrated nitrates, was assessed at different hydrogen ion concentrations ($[H^+]$) of the pregnant liquor, specifically 10, 1, 0.1, 0.01, 0.001, and 0.0001. The resulting precipitate was then subjected to centrifugation. The criteria for evaluation were maximum impurity precipitation and minimum REEs precipitation. Ultimately, a $[H^+]$ value of 0.001 (pH = 3) was determined as the optimum pH for impurity precipitation. Table 4 illustrates the quantities of impurities, and REEs removed through precipitation at pH = 3. In comparison, at pH = 4, the removal of REEs increased to 58%, 52%, 45%, and 34% for La, Ce, Nd, and Y, respectively, while removing unwanted elements did not show significant improvement. The residue remaining after impurity removal could potentially be combined with the apatite concentrate and subjected to the leaching process to recover the contained REEs.

Table 4. Removal of impurities from pregnant liquor using precipitation at pH = 3.

Element	Ca	Mg	Fe	P	La	Ce	Nd	Y
Removal (%)	97	83	99	99	19	22	20	14

2.2. Preparation of P. orientalis Leaf Powder

The leaves of *P. orientalis* utilized in this study were gathered from trees located in Ekbatan town, Tehran, Iran. They were subjected to a washing process with deionized water to eliminate dust and impurities. Subsequently, they were dried at 80 °C for 24 h and ground to a particle size of −125 µm [33]. Considering that calcium ions have a tendency to compete with REEs in solution for absorption onto the biosorbent, the biomass was loaded with calcium by immersing it in a solution containing 50 mmol L^{-1} $CaNO_3$ at a biomass concentration of 10 g L^{-1}. This process was carried out for 24 h under gentle agitation.

Afterward, the biomass was rinsed with deionized water to remove excess calcium ions. Finally, the biomass was dried overnight at 55 °C and stored in a desiccator prior to its use [25].

By immersing the biomass in a solution containing calcium ions, the biomass becomes pre-loaded or saturated with calcium ions. This pre-loading step ensures that the binding sites on the biomass material, which could potentially be occupied by calcium ions, are already occupied before the biosorption of REEs takes place. In addition, it shows that the Ca-loaded biosorbent acts as an ion exchanger in the aqueous environment. Calcium ions on the biomass surface facilitate the exchange of ions between the biomass material and the solution. During the biosorption process, the trivalent REEs ions and protons in the solution are exchanged with the calcium ions present on the biomass. This ion exchange mechanism ensures that the total number of ions removed from the solution, including the trivalent lanthanide ions and protons, matches the total number of calcium ions released from the biomass into the solution. By maintaining electroneutrality, this ion exchange process helps to minimize the competition between REEs and calcium ions during biosorption and allows for efficient capture and retention of REEs on the biomass material [25]. To summarize, the loading of the biomass with calcium ions not only preoccupies the binding sites but also facilitates ion exchange, where the calcium ions on the biomass surface are replaced by trivalent lanthanide ions and protons from the solution. This ion exchange mechanism ensures balanced ion removal and release, minimizing competition and enhancing the effectiveness of the biosorption process for REEs.

2.3. Metal Biosorption Capacity and Distribution Coefficient

The potential of *P. orientalis* leaves for metal biosorption can be assessed by calculating the biosorption capacity (Q) and distribution coefficient (K_d) using the following equations [33]:

$$Q = (C_i - C_e) \times \frac{V}{M} \quad (1)$$

$$K_d = \frac{(C_i - C_e)}{C_i} \times \frac{V}{M} \quad (2)$$

In these equations, Q represents the metal sorption capacity (mg/g), and C_i and C_e denote the initial and equilibrium metal concentrations in the solution (mg/L), respectively. V represents the solution volume (L), and M corresponds to the mass of the biosorbent (g).

2.4. Analytical Methods

The elements in the aqueous phase, excluding fluorine, were analyzed using inductively coupled plasma atomic emission spectrometry (ICP-AES) on a Perkin Elmer Optima 7300 DV model. Fluorine was analyzed separately using ion chromatography with a Metrohm 733 model.

3. Results and Discussion

3.1. Effect of Initial pH

The pH of the solution plays a critical role in determining the ionization degree of metal ions in the solution, the availability and accessibility of active sites on the biosorbent material, and the surface charge of the biosorbent [37]. Therefore, by adjusting the initial pH of the solution, it is possible to optimize the surface charge of the biosorbent and the speciation of metal ions, leading to enhanced biosorption performance and efficiency for REEs using *P. orientalis*. The influence of pH on metal biosorption has been extensively investigated by previous researchers [25,38,39]. Their findings consistently demonstrate an increase in cation uptake with higher pH values. It is also claimed that metal binding increases with pH due to decreased proton concentration in the system, as protons also compete for the binding sites [25]. In this study, the pH of the aqueous solution was adjusted to 0, 1, 2, and 3 using nitric acid and ammonia solution. Biosorption experiments

were conducted using 10 mL of pregnant liquor and 0.2 g of biosorbent at a temperature of 30 °C, a contact time of 2 h, and a mixing rate of 150 rpm. Figure 2 illustrates the impact of pH on the biosorption capacity of *P. orientalis*. The results clearly indicate that pH is a crucial parameter affecting the sorption process. The biosorption capacities for REEs were highest at pH = 3. Notably, at pH = 4 or higher, significant precipitation of REEs occurred.

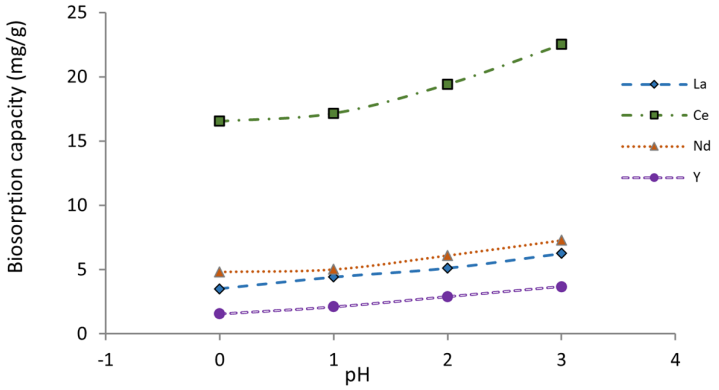


Figure 2. Effect of initial pH on biosorption capacity of REEs by *P. orientalis* leaf powder; 10 mL of pregnant liquor and 0.2 g of biosorbent at a temperature of 30 °C, a contact time of 120 min, and a mixing rate of 150 rpm.

3.2. Impact of Temperature

The influence of temperature on biosorption processes has been investigated in previous studies. Aksu [40] examined the biosorption of cadmium (II) ions by *C. vulgaris* and found that the algal biomass exhibited the highest uptake capacity at 20 °C. Kutahyali et al. [41] studied the biosorption of La and Ce on *Pinus brutia* leaf powder and observed a slight increase in uptake with rising temperature. Takahashi et al. [42] investigated the adsorption of REEs onto bacterial cell walls and reported an increase in the distribution coefficient between the bacterial and aqueous phases with higher temperatures.

In the present study, the effects of different temperatures (20, 30, 40, and 50 °C) on the biosorption capacity of *P. orientalis* were examined while keeping other variables constant and adjusting the pH to pH = 3. Figure 3 illustrates the results, indicating that the biosorption capacity of Ce increased with temperature while the capacities of La, Nd, and Y remained relatively unchanged.

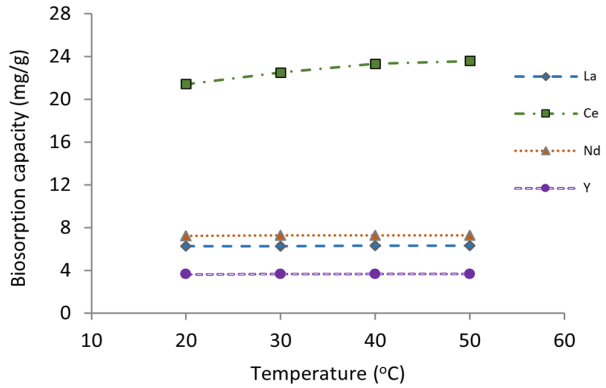


Figure 3. Effect of temperature on biosorption of REEs on *P. orientalis* leaf powder; 10 mL of pregnant liquor, 0.2 g of biosorbent, pH = 3, the contact time of 120 min, and a mixing rate of 150 rpm.

The Van't Hoff equation was used to measure the enthalpy of adsorption. It relates the change in temperature (ΔT) to the change in the equilibrium constant (ΔK) given the

standard enthalpy change (ΔH°) for the process. Since: $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, $\Delta G^\circ = -RT \ln K$, it follows that:

$$\ln K = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (3)$$

where ΔS° is the standard entropy change; therefore, a plot of the natural logarithm of the equilibrium constant versus reciprocal temperature gives a straight line.

The slope of the line is equal to the negative standard enthalpy change divided by the gas constant, $-\Delta H^\circ/R$, and the intercept is equal to the standard entropy change divided by the gas constant, $\Delta S^\circ/R$. The values of ΔH°, ΔS°, and ΔG°, which were calculated from the information presented in Figure 4, are presented in Table 5 for the biosorption of La, Ce, Nd, and Y. As shown, the values of ΔH° = 0.54, 4.76, 0.22, and 0.23 kJ/mol and ΔG° = −9.12, −9.48, −9.44, and −7.64 kJ/mol for La, Ce, Nd, and Y, respectively, at 30 °C suggest that the biosorption of La, Ce, Nd, and Y on *P. orientalis* leaf powder is an endothermic, spontaneous process. Moreover, during the adsorption process, the positive sign of ΔS° causes an increase in entropy [43].

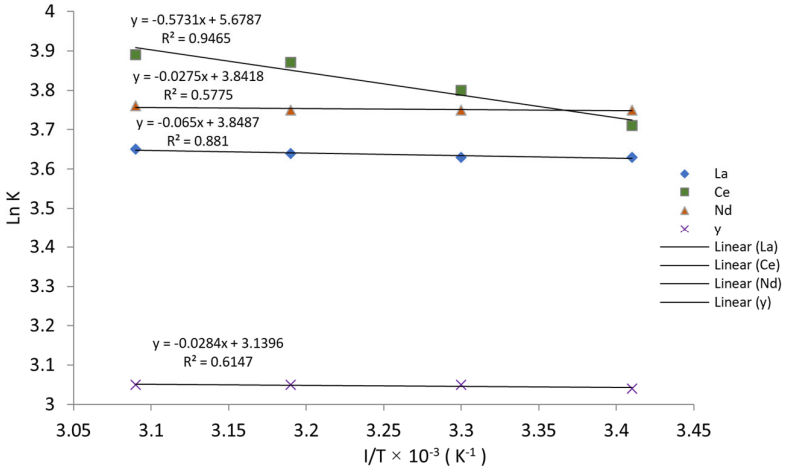


Figure 4. Ln K vs. 1/T for calculating thermodynamic parameters for the biosorption of La, Ce, Nd, and Y on *P. orientalis* leaf powder.

Table 5. Thermodynamic parameters of La, Ce, Nd, and Y biosorption on *P. orientalis*.

	ΔH°	**ΔS°**	**ΔG°(KJ/mol)**			
	(kJ/mol)	**(kJ/mol K)**	**293 °K**	**303 °K**	**313 °K**	**323 °K**
La	0.54	0.0319	−8.80	−9.125	−9.44	−9.763
Ce	4.76	0.047	−9.011	−9.481	−9.951	−10.42
Nd	0.22	0.0319	−9.126	−9.445	−9.764	−10.083
Y	0.23	0.026	−7.388	−7.648	−7.908	−8.168

3.3. Effect of Contact Time

The effect of contact time on the biosorption process has been investigated by various researchers. Sert et al. [33] studied the biosorption of La and Ce from synthetic aqueous solutions using *P. orientalis* leaf powder and found that the highest biosorption occurred at a contact time of 60 min. Kutahyali et al. [41] suggested contact times of 30 and 15 min for La and Ce (III) biosorption, respectively, using *Pinus brutia* leaf powder. In this study, experiments were conducted with 10 mL of the aqueous solution at pH 3 and a temperature of 50 °C. A total of 0.2 g of *P. orientalis* leaf powder was shaken with the solution for various time intervals ranging from 10 to 120 min. The biosorption capacity of *P. orientalis* leaf powder for different REEs, including La, Ce, Nd, and Y, was evaluated. The results are presented in Figure 5. The figure demonstrates that equilibrium was reached at a contact

time of 45 min. Further increases in contact time did not enhance the biosorption capacity of the REEs since the active sites on the biosorbent had already been saturated.

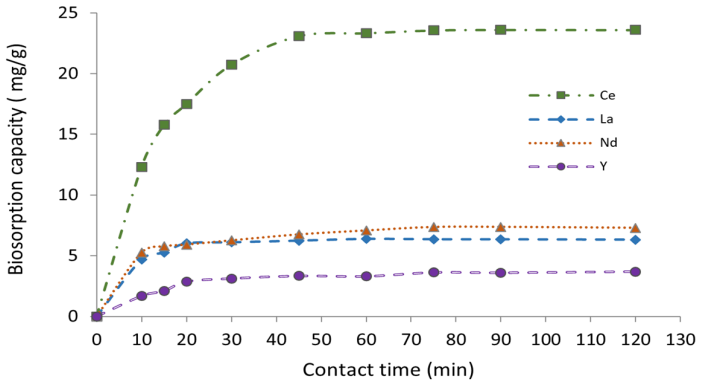


Figure 5. Effect of contact time of biosorbent and aqueous solution on biosorption of La, Ce, Nd, and Y on *P. orientalis* leaf powder.

3.4. Effect of the Mass of Biosorbent

The influence of different masses of *P. orientalis* leaf powder (0.2 g, 0.3 g, and 0.4 g) on the extraction of La, Ce, Nd, and Y from a 10 mL aqueous solution was examined at a contact time of 45 min, a temperature of 50 °C, and a mixing rate of 150 rpm. The results are depicted in Figure 6. As illustrated in Figure 6, an increase in the mass of *P. orientalis* leaf powder resulted in a higher percentage of REEs absorbed from the aqueous phase. This can be attributed to the larger surface area and greater availability of binding sites provided by the increased biosorbent mass. Consequently, more REEs were effectively absorbed onto the biosorbent. However, it is important to note that despite the enhanced metal removal efficiency, the capacity of the biosorbent decreased slightly with the increase in its mass, as indicated in Table 6. Therefore, selecting the appropriate biosorbent mass is crucial to balance achieving high metal removal efficiency and maintaining sufficient adsorption capacity. Optimal biosorbent mass should be determined based on the desired level of metal extraction and the practical considerations of using an efficient and economically feasible biosorption process.

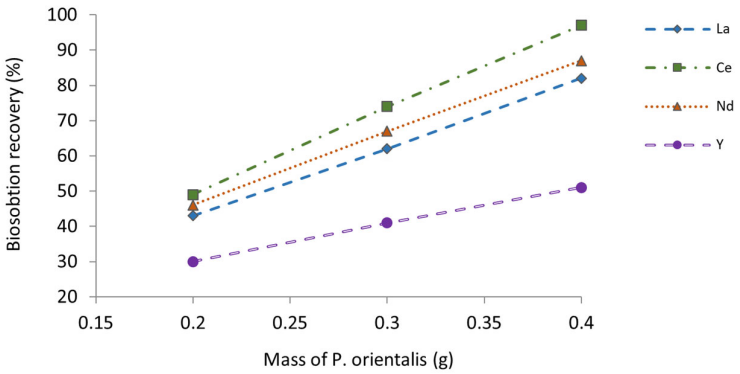


Figure 6. Effect of the mass of *P. orientalis* leaf powder in 10 mL of aqueous solution on biosorption recovery of La, Ce, Nd, and Y.

Table 6. Biosorption capacity (mg/g) of La, Ce, Nd, and Y with the different masses of *P. orientalis*.

Mass of Biosorbent (g)	La	Ce	Nd	Y
0.2	6.31	23.59	7.28	3.68
0.3	6.07	23.38	7.10	3.42
0.4	6.00	23.20	6.89	3.21

3.5. Desorption Study

To maximize the recovery of valuable elements (Y, La, Nd, and Ce) from the biosorbent, a desorption study was conducted using HCl as the desorbing agent. The *P. orientalis* leaf powder, loaded with the extracted rare earth element (REE) ions, was subjected to desorption using HCl solutions of varying concentrations: 7.29 g/L, 10.94 g/L, and 18.23 g/L. The desorption process was carried out for a duration of 15 min.

The results of the desorption study are presented in Figure 7. It is evident from the figure that the 18.23 g/L HCl solution exhibited the highest recovery of REE ions from the *P. orientalis* leaf powder. This indicates that a higher concentration of HCl facilitated the efficient release of the adsorbed REEs from the biosorbent, resulting in a more effective desorption process.

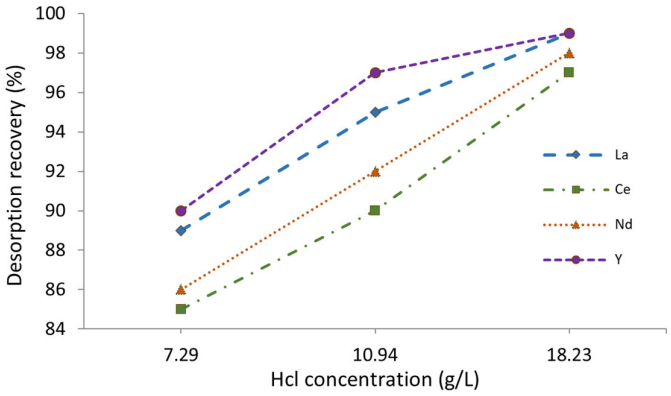


Figure 7. Effect of HCl concentration on desorption of loaded *P. orientalis*.

Desorption is a crucial step in the biosorption process as it allows for the regeneration and reuse of the biosorbent. Selecting an appropriate desorbing agent and its concentration is essential to achieve a high recovery rate of the target elements while minimizing any potential negative effects on the biosorbent or the environment.

Based on the findings of this study, an 18.23 g/L HCl solution is recommended for the desorption of REE ions from the *P. orientalis* leaf powder due to its superior desorption efficiency. However, further optimization and evaluation of the desorption conditions may be necessary to achieve the desired recovery rates and to ensure the feasibility and sustainability of the overall biosorption process.

3.6. Precipitation of REEs

Following the desorption step, the HCl stripping solution containing the recovered rare earth element (REE) ions was subjected to precipitation. The precipitation was achieved by adding a 10% $H_2C_2O_4$ (oxalic acid) solution to the stripping solution and slowly agitating it for 1 h at a pH of 1. The purpose of this precipitation step was to selectively separate and concentrate the REEs from the solution. After the precipitation process, the resulting precipitate was filtered and further processed. It was then subjected to a heating treatment at a temperature of 800 °C. This high-temperature treatment aimed to convert the precipitate into a mixed concentrate of rare earth oxides (REOs). The obtained mixed REOs concentrate (Figure 8) was dissolved in nitric acid and subjected to chemical analysis to determine the composition of the REEs and the presence of any impurities. Table 7 presents the analysis results for the REEs, indicating that their purity exceeded 86%. This signifies the successful concentration and purification of the REEs through precipitation. The precipitated REEs in the form of mixed REOs concentrate hold significant value and can be further utilized in various industrial applications. The high purity of the obtained REEs highlights the efficiency and effectiveness of the precipitation method employed in this study. Further downstream processing and refining steps may be necessary to obtain pure individual REEs of high commercial value.

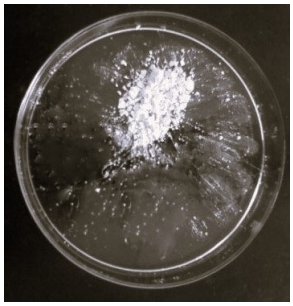


Figure 8. Final mixed REO concentrate.

Table 7. Analysis results of REO.

Elements (%)	Contents (%)
REEs	86.79
Ca	10.27
Mg	2.56
P	0.10
Fe	0.01
S	0.00

4. The Flowsheet for Recovery of REEs from Apatite Concentrate

The recovery process for the mixed REEs precipitate from apatite concentrate using *P. orientalis* leaf powder is outlined in Figure 9. This flowsheet illustrates the main steps involved in extracting and purifying REEs utilizing the biosorption properties of *P. orientalis* leaf powder. The first step in the process involves the preparation of the *P. orientalis* leaf powder, which includes collecting the leaves from *P. orientalis* trees, washing them to remove impurities, drying them, and grinding them to a fine powder. The prepared *P. orientalis* leaf powder is then loaded with calcium ions to minimize competition between calcium and REEs during biosorption and to facilitate the ion exchange process. The biomass is then washed to remove excess calcium ions and dried for subsequent use. This prepared biomass serves as the biosorbent for REEs extraction. The apatite concentrate, containing a range of REEs, is then subjected to a leaching process to dissolve the REEs into the pregnant liquor, which is primarily phosphoric acid. The insoluble constituents are removed through filtration, and the pregnant liquor is recovered. Table 3 presents the chemical analysis of pregnant liquor, highlighting the presence of unwanted ions such as Ca^{2+}, Mg^{2+}, and Fe^{3+} that can interfere with the REEs biosorption process. To address this, a precipitation step is implemented at pH = 3 to remove impurities while minimizing REE precipitation. Table 4 demonstrates the effectiveness of this precipitation process in removing impurities and quantifying the REEs removed. The precipitated impurities contain a certain amount of co-precipitated REEs, leading to a loss of approximately 14% for Y, 20% for Nd, 22% for Ce, and 19% for La. Therefore, it is worth further investigating the potential for recovering REEs from these precipitated impurities. Alternatively, these precipitated impurities could be combined with the apatite concentrate and subjected to the leaching process to recover the contained REEs, as illustrated in Figure 9. In the biosorption step, the effect of initial pH, temperature, contact time, and mass of biosorbent on the biosorption capacity of *P. orientalis* for REEs is investigated and optimized as described in Sections 3.1–3.4. Desorption of the REEs from the loaded biomass is achieved using HCl, and the recovered REE ions are subjected to a precipitation process with oxalic acid. The resulting precipitate is then filtered and heated at a high temperature to obtain a mixed REOs concentrate, as described in Section 3.6. The final product obtained from the process is the mixed REOs concentrate, which contains mainly La, Ce, Nd, and Y (Figure 9). This concentrate can undergo further refining steps, such as releaching and secondary impurity removal, to enhance its purity before feeding it into the individual REEs separation process.

An additional cycle of biosorption may be applied to purify the mixed REEs precipitate in the secondary impurity removal process. Alternatively, various techniques such as solvent extraction using Cyanex 272 and Cyanex 572 [44,45], D2EHPA and TBP [46], or HEHEHP and HDEHP [44,47]; ion exchange using different cationic or anionic resins such as Dowex 50X8 [44,48,49]; or precipitation using $CaCO_3$ and $Ca(OH)_2$ [50,51] or MgO and NaOH [51] can be explored for further purification of the mixed REE precipitate obtained in this study (Figure 9). These techniques have been utilized for impurity removal from REE-containing solutions, and their applicability in refining the mixed REE precipitate can be investigated.

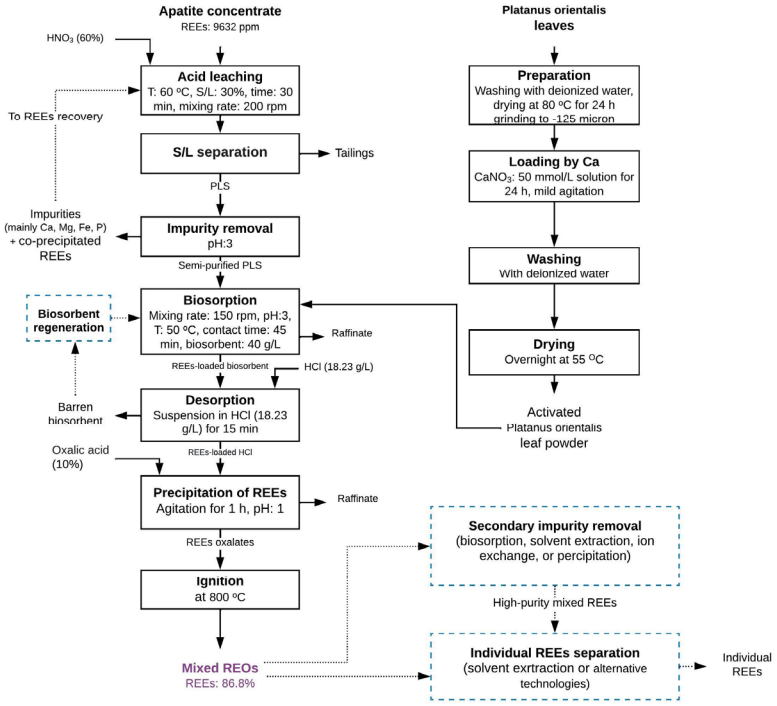


Figure 9. Preliminary flowsheet for recovering mixed REEs from apatite concentrate using nitric acid leaching, *P. orientalis* biosorption, and oxalic acid precipitation.

Alternatively, the mixed REE precipitate can be fed directly into an individual REE separation process to separate and produce individual heavy and light REEs (Figure 9). Separating mixed REEs into individual elements is critical in enabling downstream value-added options for commercial applications. Currently, solvent extraction is the most widely used method for REE separation, specifically using the P507 (HEHEHP) extractant–HCl system or the TBP–nitrate system [52]. These systems have been extensively studied and are commercially employed for REE separation, particularly in China, the leading producer of separated REEs worldwide. The P507 extractant has proven to be effective in achieving the required separation targets and product purity. However, it typically requires an extensive solvent extraction plant with multiple separation stages, resulting in high capital costs [52]. Ongoing research efforts are focused on improving current solvent extraction practices by reducing equipment requirements and the number of stages (e.g., through technologies such as RapidSX) and enhancing separation factors (e.g., by exploring new extractants such as Cyanex 572) [52]. Additionally, alternative technologies are being explored as potential replacements for solvent extraction. These include Solid-Phase Extraction (SPE), ion exchange, chromatography, electrowinning, magnetically assisted precipitation separation, and free-flow electrophoresis [52]. However, new alternatives would need to compete with the standard solvent extraction method while demonstrating economic viability.

P. orientalis is a commonly planted species in urban environments in Iran, particularly in Tehran. Previous studies have reported higher concentrations of heavy metals such as Cd, Pb, Ni, and Cr in the leaves of *P. orientalis* from urban areas compared to forest

parks [53]. Furthermore, there are differences in leaf surface characteristics, including stomatal density, stomatal pore area, epidermis, and spongy thickness between *P. orientalis* leaves from urban and forest park areas. It is worth mentioning that urban leaves exhibit thicker cuticles and palisade layers compared to forest park leaves [53]. Conducting a comprehensive investigation to determine the specific composition and characteristics of the *P. orientalis* leaf powder used in this study and comparing it with leaves from forest parks would be beneficial for future research.

By comparing this work with our previous study on REE extraction from the same apatite sample using solvent extraction with tributyl phosphate [35], we can conclude that the proposed biosorption process has achieved a final mixed REO product with comparable purity (86% in this work vs. 89% via solvent extraction) while offering a simpler process. Additionally, *P. orientalis* leaf powder, which is readily available and inexpensive, serves as an effective biosorbent. Moreover, the biosorption process is environmentally friendly. These factors contribute to the overall effectiveness and potential of this biosorption process.

The credibility of this flowsheet can be supported, and valuable insights into its economic feasibility can be gained through a cost analysis. However, it is crucial to develop further and validate this preliminary flowsheet, which includes investigating the regeneration and reusability of the biosorbent and chemical reagents and conducting material and energy balance calculations before undertaking such an analysis.

5. Conclusions

This research demonstrated the potential of biosorption as an environmentally friendly and cost-effective method for recovering REEs from aqueous solutions. The key findings and conclusions of the study are as follows:

- Optimized acid leaching conditions were determined for apatite concentrate, resulting in the efficient dissolution of REEs using a 60% nitric acid solution at 60 °C with a solid-to-liquid ratio of 30% and agitation for 30 min at 200 rpm.
- The impurity removal step using pH adjustment of the pregnant liquor solution (PLS) to pH 3 was successful in removing unwanted ions, enhancing the purity of the REEs.
- *P. orientalis* leaf powder was effectively activated through a series of treatment steps, including washing, drying, grinding, and treatment with a calcium nitrate solution. This activated biomass showed high biosorption capacity for Ce, La, Nd, and Y.
- Under optimized biosorption conditions (mixing rate of 150 rpm, pH 3, temperature of 50 °C, and contact time of 45 min), the *P. orientalis* leaf powder exhibited significant uptake of REEs from the aqueous solution, with extraction efficiencies of 97% for Ce, 82% for La, 87% for Nd, and 51% for Y. The biosorption capacity of the biomass was 23.0 mg/g for Ce, 6.0 mg/g for La, 6.9 mg/g for Nd, and 3.2 mg/g for Y.
- Desorption experiments using 18.23 g/L hydrochloric acid resulted in high desorption efficiency, with approximately 99% of La and Y, 98% of Nd, and 97% of Ce being desorbed from the loaded biosorbent.
- Thermodynamic studies indicated that the biosorption process was endothermic and spontaneous, as evidenced by positive values of ΔH° and negative values of ΔG° for the REEs. This further supported the feasibility of using *P. orientalis* leaf powder for REE recovery.
- The precipitation of REEs as oxalates using a 10% $H_2C_2O_4$ solution at pH 1, followed by heating at 800 °C, yielded mixed rare earth oxides (REOs) concentrate with an assay of 86.8%. Before proceeding to the individual separation of REEs, the mixed REOs concentrate can be further refined using releaching and secondary impurity removal processes. Alternatively, it can be fed directly into a solvent extraction process or alternative technologies to obtain individual heavy and light REEs.
- Overall, the findings of this research highlight the potential of utilizing *P. orientalis* leaf powder as a biosorbent for the recovery of mixed REEs. The proposed flowsheet provides a comprehensive and sustainable approach for extracting and purifying REEs from apatite concentrate, contributing to efficiently utilizing these valuable elements.

- A comprehensive cost analysis would further enhance the credibility of this study and provide valuable insights into the economic viability of the proposed biosorption process on an industrial scale. However, it is important to note that further extension and verification of our results are necessary before undertaking such an analysis. Conducting a thorough cost analysis in future studies would significantly contribute to a more comprehensive evaluation of the scalability and practical implementation of the proposed process.

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