PHYSICAL SCIENCES

FUNCTIONALIZATION OF CALIX[4]ARENE WITH DIGLYCOLAMIDE-PYRIDINE LIGAND FOR SELECTIVE RECOVERY OF RARE EARTH ELEMENTS FROM AQUEOUS SYSTEMS

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Abstract

The efficient recovery of rare earth elements (REEs) from aqueous systems is of evergrowing importance because it is critically important in cutting-edge technology and environmental concerns. In this work, a new calix[4]arene-based adsorbent functionalized with diglycolamide–pyridine (Calix[4]–DGA–Py) ligands has been successfully synthesized and used for La3+ and Nd3+ ions removal from aqueous solutions. The structural and physicochemical properties of the synthesized adsorbent were thoroughly characterized by FT-IR, TGA/DTA, XRD, SEM, and pHpzc studies, showing good functionalization, thermal stability, amorphous structure, and various surface morphology. The batch adsorption experiments revealed that the removal efficiency was significantly affected by the pH, contact time and the initial metal ion concentration and the pH of 6 was the most effective. Under the optimal conditions, the removal efficiencies were 96% for La^{3+} and 94% for Nd^{3+}.

Kinetic studies showed that the process of adsorption follows pseudo-second-order model

($R^2 \geq 0.998$) and the dominant mechanism is chemisorption. The intra-particle diffusion analysis led to the proposal of a multi-step adsorption mechanism comprising surface adsorption and diffusion within the adsorbent matrix. Equilibrium isotherm analysis showed that the best fit was obtained with Langmuir model with maximum adsorption capacities of 82.5 mg/g for La3+ and 78.3 mg/g for Nd3+ suggesting monolayer adsorption behaviour. The mechanism of adsorption is found to be synergistic coordination interactions between carbonyl oxygen, ether oxygen and pyridine nitrogen donor sites within the preorganized calix[4]arene framework. In brief, these findings underscore the promising performance of Calix[4]–DGA–Py as a high-performance, resilient and eco-friendly adsorbent for the recovery of rare earth elements from aqueous media.

Keywords: Calix[4]arene; Adsorption ; Rare earth elements (REEs) ; Diglycolamide ligand ; Adsorption kinetics and isotherms; Pyridine-based ligand.

1. Introduction

Rare earth elements (REEs) possess unique electronic, magnetic, and optical properties that are critical for modern technology[1]. They are used in high performance magnets, rechargeable batteries, catalysts, phosphors and renewable energy systems such as wind turbines and electric vehicles. However, the growing demand for REEs and their scarcity and non-homogeneous distribution around the globe have raised the need for efficient and sustainable recovery methods from primary and secondary resources[2, 3]. In particular, aqueous systems such as industrial effluents, mining leachates, and electronic waste streams represent promising alternative sources of REEs. Despite their importance, the recovery and separation of REEs remain challenging due to the high chemical similarity among trivalent lanthanide ions (Ln(III)). These ions exhibit comparable ionic radii, similar coordination behavior, and a stable +3 oxidation state, which makes their selective extraction and separation difficult[4]. Traditional methods such as solvent extraction, ion exchange, and precipitation often suffer from drawbacks including high chemical consumption, secondary pollution, and limited selectivity. In this context, adsorption has emerged as a highly attractive approach owing to its operational simplicity, cost-effectiveness, and environmental compatibility[5].

The design of efficient adsorbents for REE recovery largely depends on the nature of functional groups capable of interacting with metal ions. Lanthanide ions generally prefer oxygen donor atoms; however, the incorporation of nitrogen donor sites can significantly enhance coordination strength and introduce selectivity through synergistic effects[6]. Among various ligand systems, diglycolamide (DGA)-based ligands have gained considerable attention due to their strong affinity toward trivalent metal ions through multiple carbonyl and ether oxygen atoms[7]. Moreover, the integration of pyridine groups introduces additional nitrogen donor centers, enabling the formation of more stable coordination complexes and improving adsorption performance[8]. To further improve adsorption efficiency, the concept of ligand preorganization has been extensively explored. Preorganized systems can reduce entropic penalties during metal binding and provide a favorable spatial arrangement of donor atoms. Macrocyclic compounds are particularly effective in this regard due to their well-defined architectures and tunable cavities[9]. Among them, calix[4]arene has emerged as a versatile platform owing to its structural rigidity, ease of chemical modification, and ability to host multiple functional groups on its upper and lower rims. The incorporation of functional ligands onto calix[4]arene frameworks can generate multidentate binding environ-

ments, thereby enhancing metal ion uptake and selectivity. In addition, the synergistic combination of macrocyclic preorganization and tailored ligand functionality provides a promising pathway for developing high-performance adsorbents. The presence of multiple binding sites within a confined framework can facilitate cooperative interactions with metal ions, leading to improved adsorption capacity and faster kinetics. Furthermore, such systems often exhibit good stability under varying environmental conditions, which is essential for practical applications[10].

In this study, we report the synthesis of a novel calix[4]arene-based adsorbent functionalized with a diglycolamide-pyridine ligand for the selective recovery of rare earth elements from aqueous systems. The designed material integrates the advantages of macrocyclic preorganization with synergistic O/N donor coordination, offering enhanced interaction with Ln(III) ions. The adsorption behavior was systematically evaluated by investigating the effects of key parameters such as pH, contact time, adsorbent dosage, and initial metal ion concentration. Kinetic and isotherm models were applied to elucidate the adsorption mechanism, while the role of functional groups in metal binding was analyzed[11].

This work provides new insights into the design of functionalized macrocyclic adsorbents and highlights their potential for sustainable recovery of rare earth elements from aqueous environments. Herein, we report the design of a calix[4]arene-based adsorbent functionalized with multiple diglycolamide-pyridine (DGA-Py) units anchored onto a single macrocyclic framework for the efficient capture of rare earth elements (REEs) from aqueous solutions (Figure 1c). The resulting calix[4]arene-DGA-Py system exhibits a well-defined preorganized structure with a confined cavity and multiple accessible coordination sites, providing a favorable geometry for binding trivalent metal ions. In addition, the flexible linker segments connecting the ligand units to the macrocyclic platform allow conformational adaptability, facilitating effective interaction with metal ions during the adsorption process[12–15].

Batch adsorption experiments were systematically performed to investigate the uptake behavior of representative REE ions such as La(III), Ce(III), and Nd(III) under various experimental conditions. The adsorption mechanism was further explored using a combination of characterization techniques, including FT-IR, UV–vis spectroscopy, and scanning electron microscopy (SEM), to monitor structural changes and metal–ligand interactions. These experimental observations were complemented by theoretical analysis based on density functional theory (DFT) calculations, providing deeper insight into the coordination behavior and binding affinity of the functionalized adsorbent toward REE ions[16, 17].

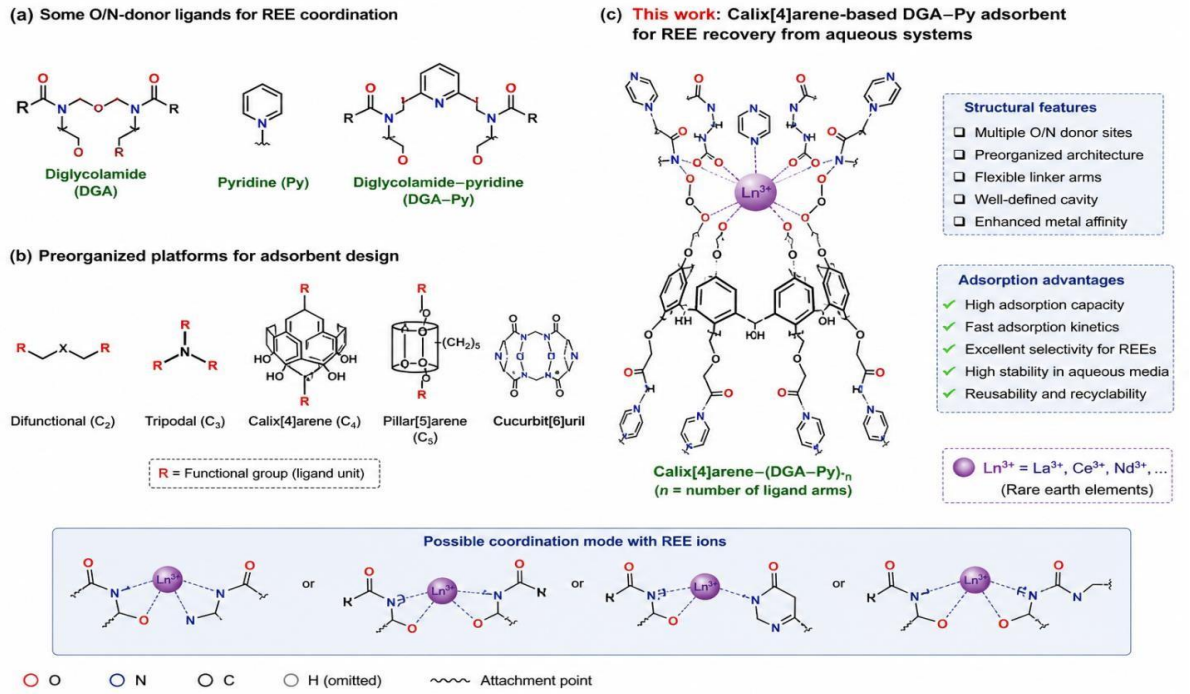


Figure 1. (a) *Representative structures of oxygen- and nitrogen-donor ligands commonly employed for coordination with rare earth ions, including diglycolamide (DGA), pyridine, and combined DGA–pyridine systems;* ***(b)*** *schematic illustration of preorganized molecular platforms used in adsorbent design, highlighting the structural advantages of calix[4]arene compared to conventional architectures;* ***(c)*** *proposed structure of the calix[4]arene-based diglycolamide–pyridine (Calix[4]arene–DGA–Py) adsorbent developed in this work, showing multiple coordination sites and flexible linker arms, along with the suggested coordination interaction with Ln^{3+} ions (e.g., La^{3+}, Ce^{3+}, Nd^{3+}) through synergistic O/N donor binding.*

2. Material and Methods

2.1.Materials

p-tert-Butylcalix[4]arene (≥98%) was used as the macrocyclic platform for adsorbent preparation. Diglycolamide (DGA) derivatives and pyridine-based intermediates were employed for ligand functionalization. N,N′-Dicyclohexylcarbodiimide (DCC) and 4dimethylaminopyridine (DMAP) were used as coupling agents in the functionalization process. Organic solvents including dichloromethane (DCM), dimethylformamide (DMF), ethanol, and methanol were of analytical grade and used as received[18].

Rare earth metal salts, including lanthanum(III) nitrate hexahydrate ($La(NO_3)_3 \cdot 6H_2O$), cerium(III) nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$), and neodymium(III) nitrate hexahydrate

($Nd(NO_3)_3 \cdot 6H_2O$), were used as sources of Ln^{3+} ions for adsorption experiments. Nitric acid (HNO_3, 65%) and sodium hydroxide (NaOH, ≥98%) were used for pH adjustment.

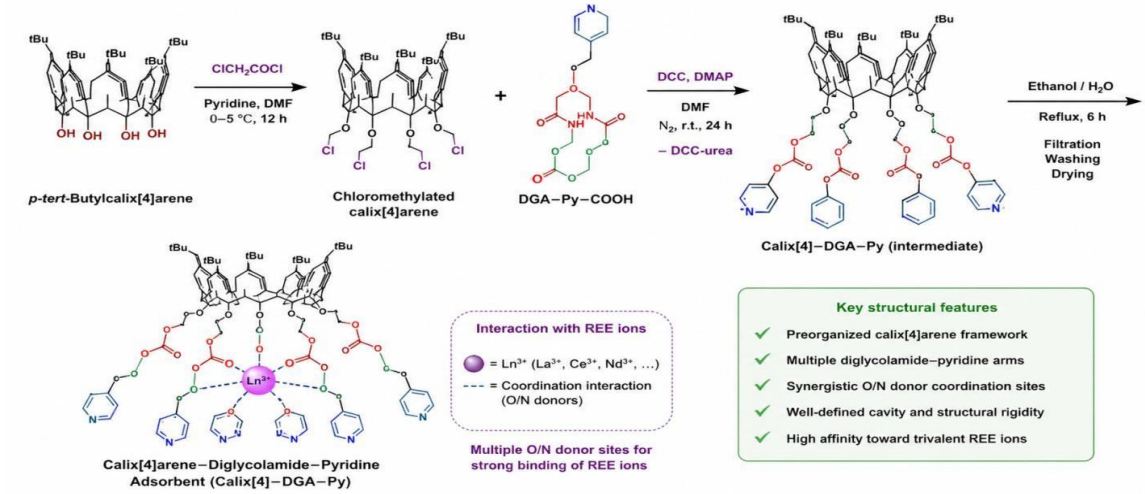
All chemicals were of analytical reagent (AR) grade and were used without further purification unless otherwise stated. Deionized water was used for the preparation of all solutions. Adsorption experiments were carried out using freshly prepared aqueous solutions of rare earth ions at desired concentrations[19].

2.2.Methods

2.2.1. Synthesis of Calix[4]arene–Diglycolamide–Pyridine Adsorbent (Calix[4]– DGA–Py)

The calix[4]arene-based adsorbent functionalized with diglycolamide–pyridine (DGA–Py) units was synthesized through a stepwise functionalization approach. Initially, ptert-butylcalix[4]arene was activated via modification of its lower rim hydroxyl groups to introduce reactive sites suitable for ligand attachment. In a typical procedure, calix[4]arene (1 g) was dissolved in dry dimethylformamide (DMF) under continuous stirring. To this solution, an appropriate amount of a diglycolamide–pyridine derivative bearing a terminal carboxylic group was added. N,N′-dicyclohexylcarbodiimide (DCC) and a catalytic amount of 4-dimethylaminopyridine (DMAP) were then introduced to facilitate the coupling reaction. The reaction mixture was stirred under a nitrogen atmosphere at room temperature for 24 hours to ensure complete grafting of the ligand units onto the calixarene framework. The progress of the reaction was monitored, and upon completion, the mixture was filtered to remove the dicyclohexylurea (DCU) byproduct. The filtrate was concentrated and the crude product was washed repeatedly with ethanol and distilled water to eliminate unreacted reagents and impurities. The obtained calix[4]arene–DGA–Py material was then dried under vacuum at 60 °C for 8 hours until a constant weight was achieved. The final product appeared as a stable solid material with multiple functional coordination sites, suitable for adsorption applications. This functionalized adsorbent combines the structural rigidity and preorganization of the calix[4]arene platform with the strong coordination ability of diglycolamide and pyridine groups, enabling enhanced interaction with rare earth ions in aqueous systems[20–23].

Schematic representation of scheme 1, illustrate the synthetic pathway for the preparation of the calix[4]arene–diglycolamide–pyridine (Calix[4]–DGA–Py) adsorbent. The synthesis involves initial functionalization of p-tert-butylcalix[4]arene through chloromethylation of the lower rim hydroxyl groups, followed by coupling with a diglycolamide–pyridine ligand bearing a terminal carboxylic group using DCC/DMAPmediated condensation. The final product is obtained after purification via washing and drying steps. The resulting functionalized calix[4]arene framework provides multiple O/N donor sites and a preorganized architecture, enabling efficient coordination with trivalent rare earth ions (Ln^{3+}) in aqueous systems[24].



Scheme 1. Schematic representation of the synthesis of calix[4]arene–diglycolamide– pyridine (Calix[4]–DGA–Py) adsorbent via stepwise functionalization and coupling reaction.

2.3.Characterisation techniques

The concentrations of rare earth ions, including La(III), Ce(III), and Nd(III), in aqueous solutions were determined using an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, PerkinElmer Optima 8000, USA). Fourier Transform Infrared (FTIR) spectroscopy was employed to identify the characteristic functional groups and confirm the successful functionalization of the calix[4]arene-based adsorbent, using a Thermo Scientific Nicolet iS10 FTIR

spectrometer (USA) over the range of 4000–400 cm^{-1}[25]. The thermal stability of the synthesized Calix[4]–DGA–Py material was evaluated by Thermogravimetric Analysis (TGA) using a TA Instruments Q50 analyzer under a nitrogen atmosphere at a heating rate of 10 °C/min from 25 to 600 °C. The structural properties of the material were further investigated by X-ray diffraction (XRD) using a

PANalytical X'Pert PRO diffractometer (Netherlands) with Cu-Kα radiation (λ = 1.5406 Å), operating at 40 kV and 30 mA within a scanning range of 10–80° (2θ). Surface morphology and microstructural features were examined using a field-emission scanning electron microscope (FESEM, JEOL JSM-7610F, Japan). The surface area and porosity characteristics were analyzed using the Brunauer–Emmett–Teller (BET) method with a Micromeritics ASAP 2020 analyzer at 77 K.

In addition, the surface charge behavior of the adsorbent was evaluated using the point of zero charge (pHpzc) method, while UV–Visible spectroscopy (Shimadzu UV-2600, Japan) was used to monitor the adsorption performance and interaction of REE ions with the functionalized adsorbent.

2.4.Experimental Method

Batch adsorption experiments were performed to evaluate the recovery efficiency of rare earth elements (REEs), including La(III), Ce(III), and Nd(III), from aqueous solutions using the synthesized calix[4]arene–diglycolamide–pyridine (Calix[4]–DGA–Py) adsorbent.

Stock solutions of REE ions (1000 mg L^{-1}) were prepared from lanthanide nitrate salts ($La(NO_3)_3 \cdot 6H_2O$, $Ce(NO_3)_3 \cdot 6H_2O$, and $Nd(NO_3)_3 \cdot 6H_2O$) and subsequently diluted to the desired concentrations (typically 25–200 mg L^{-1}) using deionized water[26].

In a typical adsorption experiment, a known amount of the adsorbent (e.g., 0.02–0.05

g) was added to 10 mL of REE solution in sealed conical flasks. The mixtures were agitated at a constant shaking speed under controlled temperature conditions to ensure sufficient interaction between the adsorbent and metal ions. The influence of key operational parameters, including solution pH, contact time, adsorbent dosage, initial ion concentration, and temperature, was systematically investigated.

After equilibrium was reached, the solid phase was separated by centrifugation, and the supernatant was filtered through a 0.45 μm membrane filter. The residual concentrations of REE ions in the filtrate were determined using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). All experiments were conducted in triplicate to ensure reproducibility and accuracy of the obtained data.

The adsorption capacity (q_e, mg g^{-1}) and removal efficiency (%) were calculated based on the difference between the initial and equilibrium concentrations using the following equations (1 and 2).

$$qe(mg/g) = \frac{Ci - mCe}{V} \dots (1)$$

$$uptake = \frac{(C^i - C^e)}{Ci} 100 \dots\dots (2)$$

Where (q_e) is the maximum capacity (mg/g), C_i and C_e are the initial and equilibrium concentrations (mg/L) of metal ion, respectively, m is the mass of the adsorbent used (g), and V is the initial volume of the aqueous solution (L).

3. Results and Discussion 3.1.Characterization

The structural, morphological, and physicochemical properties of the synthesized Calix[4]–DGA–Py adsorbent were systematically investigated using various analytical techniques, as presented in Figure 1(a–e).

FT-IR spectroscopy was employed to investigate the interaction between the Calix[4]–DGA–Py adsorbent and trivalent rare earth ions. As shown in Figure 2a, the characteristic stretching vibration of the carbonyl (C=O) group of the diglycolamide moiety, initially observed around 1650–1670 cm^{-1}, exhibited a noticeable shift to lower wavenumbers upon coordination with Ln^{3+} ions (La^{3+}, Ce^{3+}, Nd^{3+}). This shift indicates the involvement of carbonyl oxygen atoms in metal binding through coordination interactions. Additionally, the C–O–C stretching vibrations of the ether groups in the diglycolamide structure, typically appearing in the range of 1050–1150 cm^{-1}, showed slight shifts and intensity changes after adsorption, further supporting their participation in coordination. The characteristic bands corresponding to the pyridine ring, particularly the C=N stretching vibration near ~1580 cm^{-1}, also shifted upon metal ion interaction, confirming the role of nitrogen donor atoms in complex formation. Compared to previously reported systems involving purely nitrogendonor ligands, the observed shifts in this study are relatively moderate, which can be attributed to the synergistic coordination of both oxygen and nitrogen donor sites. The combined involvement of carbonyl oxygen, ether oxygen, and pyridine nitrogen atoms suggests a multidentate binding mode, enhancing the overall stability of the metal–adsorbent complex. These results clearly demonstrate that the adsorption of rare earth ions onto the Calix[4]–DGA–Py adsorbent is governed by coordination interactions involving multiple functional groups within the preorganized macrocyclic framework.

Thermal stability and decomposition behavior of the synthesized Calix[4]–DGA–Py adsorbent were investigated using thermogravimetric analysis (TGA) coupled with differential thermal analysis (DTA), as shown in Figure 2b. The TGA curve exhibits a multistep weight loss profile, indicating the presence of different thermally active components within the functionalized material. The initial weight loss observed below ~120 °C can be attributed to the removal of physically adsorbed moisture and residual solvent molecules weakly bound to the surface of the adsorbent. A more pronounced weight loss in the temperature range of approximately 150–300 °C corresponds to the partial decomposition of the diglycolamide (DGA) side chains and the cleavage of labile functional groups attached to the calix[4]arene framework. This stage is accompanied by a distinct endothermic peak in the DTA curve, confirming the thermal degradation of organic moieties. At higher temperatures (above ~300 °C), a gradual weight loss is observed, which can be assigned to the decomposition of the calix[4]arene macrocyclic structure and the breakdown of the aromatic framework. The relatively slow degradation rate in this region indicates the inherent thermal stability of the macrocyclic backbone due to its rigid and highly conjugated structure.

The DTA curve further supports these observations, showing characteristic thermal events corresponding to moisture loss and subsequent decomposition stages. Overall, the Calix[4]– DGA–Py adsorbent demonstrates good thermal stability up to moderate temperatures, making it suitable for practical adsorption applications under typical environmental conditions[25, 27].

The crystalline structure of the synthesized Calix[4]–DGA–Py adsorbent was investigated using X-ray diffraction (XRD), as presented in Figure 2c. The obtained diffraction pattern exhibits predominantly broad and low-intensity features without distinct sharp peaks, indicating the largely amorphous nature of the material. This behavior is typical for organic macrocyclic systems functionalized with flexible ligand chains. The absence of well-defined crystalline reflections suggests that the functionalization of the calix[4]arene framework with diglycolamide–pyridine units disrupts any ordered packing, leading to a disordered structure with limited long-range periodicity. The broad humps observed in the range of approximately 15–30° (2θ) can be attributed to short-range molecular ordering within the organic framework. Additionally, the lack of impurity peaks confirms the successful synthesis of a homogeneous material without the formation of crystalline byproducts. The amorphous structure is advantageous for adsorption applications, as it generally provides more accessible active sites and facilitates the diffusion of metal ions within the adsorbent matrix[3]. Overall, the XRD results demonstrate that the Calix[4]– DGA–Py adsorbent possesses a predominantly amorphous structure, which is consistent with its molecular design and beneficial for enhancing adsorption performance toward rare earth ions.

The point of zero charge (pHpzc) of the synthesized Calix[4]–DGA–Py adsorbent was determined using the pH drift method, as illustrated in Figure 1(d). The variation of ΔpH (pH_final − pH_initial) with initial pH shows a gradual decrease, crossing the zero line at approximately pH 5.3, which represents the pHpzc of the material. At pH values lower than 5.3, the adsorbent surface is predominantly positively charged due to protonation of functional groups, resulting in reduced adsorption of Ln^{3+} ions because of electrostatic repulsion and competition with H^+ ions. Conversely, at pH values higher than 5.3, the surface becomes negatively charged as deprotonation occurs, enhancing the adsorption of rare earth ions through electrostatic attraction and coordination interactions with oxygen and nitrogen donor sites. These results indicate that the Calix[4]–DGA–Py adsorbent exhibits optimal adsorption performance under mildly acidic to near-neutral pH conditions.

The surface morphology of the synthesized Calix[4]–DGA–Py adsorbent was examined using scanning electron microscopy (SEM), as shown in Figure 2(d). The micrograph reveals a heterogeneous and irregular surface structure composed of agglomerated particles with varying sizes and shapes[28]. The material exhibits a rough texture with numerous micro-sized clusters and granular features distributed across the surface. At higher magnification, the adsorbent appears to consist of densely packed particles forming a porous network-like structure. The presence of these irregular aggregates can be attributed to the functionalization of the calix[4]arene framework with diglycolamide– pyridine chains, which promotes intermolecular interactions and partial clustering of the material. This morphology indicates that the functional groups are not arranged in a highly ordered crystalline fashion, which is consistent with the amorphous nature observed in the XRD analysis. The rough and non-uniform surface provides a large number of accessible active sites for metal ion binding. In particular, the existence of interparticle voids and surface irregularities enhances the diffusion of rare earth ions into the adsorbent matrix, facilitating effective interaction with the available O/N donor sites. Such structural features are advantageous for adsorption processes, as they increase the contact area between the adsorbent and the aqueous phase. Furthermore, the absence of smooth or compact regions suggests that the functionalization process successfully introduced structural heterogeneity, which is beneficial for improving adsorption efficiency. The observed morphology supports the proposed adsorption mechanism, where metal ions are captured through coordination interactions rather than simple surface deposition. Overall, the SEM analysis confirms that the Calix[4]–DGA–Py adsorbent possesses a rough, porous, and heterogeneous surface morphology, which plays a crucial role in enhancing its adsorption performance toward rare earth ions.

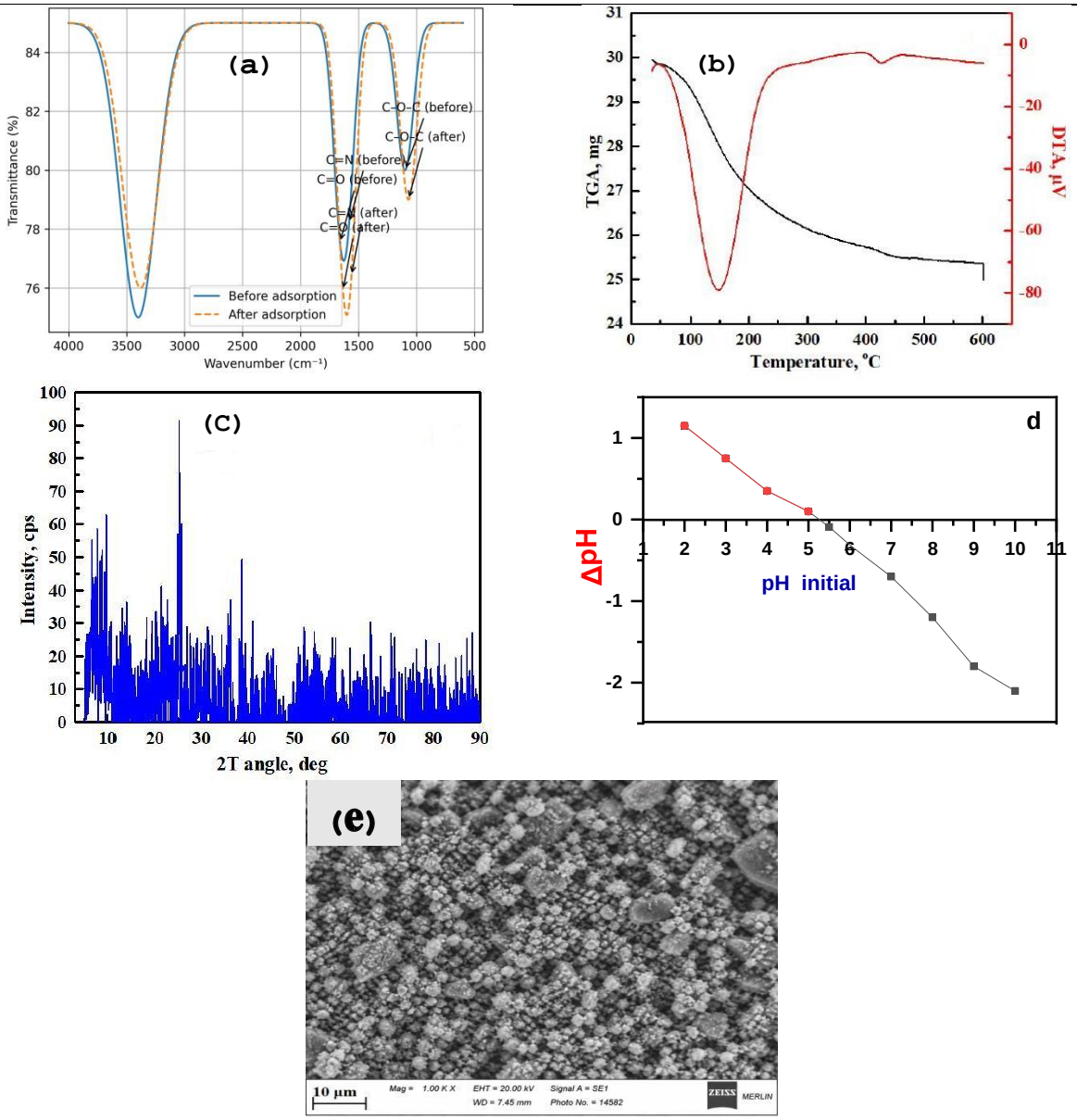


Figure2. (a) *FT-IR spectra of the Calix[4]–DGA–Py adsorbent before and after REE adsorption;* ***(b)*** *TGA and DTA curves of the synthesized adsorbent; (c) XRD pattern of the Calix[4]–DGA–Py material;* ***(d)*** *point of zero charge (pHpzc) plot of the adsorbent; and* ***(e)*** *SEM image showing the surface morphology of the synthesized Calix[4]–DGA–Py adsorbent.*

3.2.Effect of Operational Parameters on Ni(II) and Co(II) Removal by CMCX–NC

The removal efficiency of La^{3+} and Nd^{3+} ions using the synthesized Calix[4]–DGA– Py adsorbent was systematically evaluated under different operational conditions, as presented in Figure 3(a–c).

(a) Effect of pH

Figure 3(a) shows that the removal efficiency increased progressively with increasing pH from 2 to 6. The removal efficiency improved from 54% to 96% for La^{3+} and from 44% to 94% for Nd^{3+}. This trend can be attributed to the decrease in competition between H^+ ions and metal ions for the active adsorption sites. At lower pH values, protonation of functional groups reduces their availability for coordination. As the pH increases, deprotonation of oxygen and nitrogen donor sites enhances electrostatic attraction and coordination interaction with Ln^{3+} ions. The highest removal efficiency was observed at pH 6. **(b) Effect of contact time**

As illustrated in Figure 3(b), the removal efficiency increased rapidly with contact time during the initial stage, followed by a gradual approach to equilibrium. The removal efficiency increased from 38% to 97% for La^{3+} and from 34% to 95% for Nd^{3+} within 150 minutes. The rapid initial uptake is attributed to the abundance of available active sites, while the slower increase at later stages is due to the gradual saturation of these sites. Equilibrium was effectively reached after approximately 90–120 minutes, beyond which no significant change in removal efficiency was observed[29, 30]. **(c) Effect of initial concentration**

Figure 3(c) shows that the removal efficiency decreased with increasing initial metal ion concentration (100–300 mg L^{-1}). The removal efficiency declined from 96% to 66% for La^{3+} and from 94% to 62% for Nd^{3+}. This behavior is attributed to the limited number of available adsorption sites relative to the increasing number of metal ions at higher concentrations. At

lower concentrations, sufficient active sites are available for effective adsorption, whereas at higher concentrations, site saturation leads to reduced removal efficiency[31].

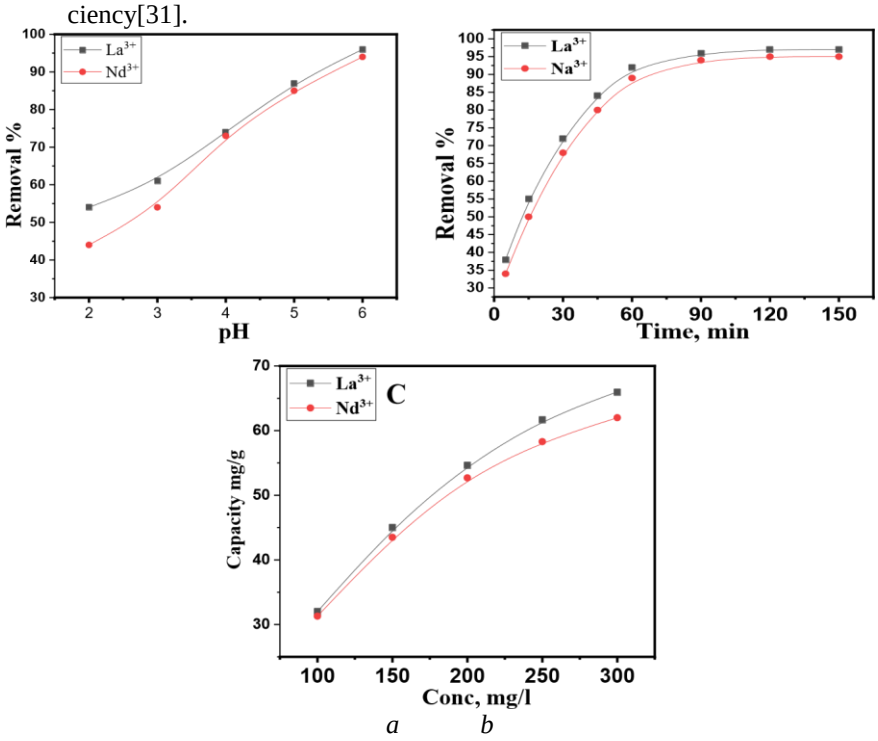


Figure 3 (a, b, c, d) Effect of (a) pH, (b) contact time, and (c) initial concentration on the Removal Efficiency of La3⁺ and Nd3⁺ Ions by Calix[4]–DGA–Py adsorbent.

3.3.Adsorption Kinetics and Isotherm

The adsorption kinetics of La^{3+} and Nd^{3+} ions onto the Calix[4]–DGA–Py adsorbent were analyzed using pseudo-first-order, pseudo-second-order, Elovich, and intra-particle diffusion models, as shown in Figure 4(a–d). The linear plots of the pseudo-first-order model (Fig. 4a) show relatively poor agreement between the experimental and calculated adsorption capacities, along with lower correlation coefficients ($R^2 \approx 0.91$–0.93), indicating that this model is not suitable to describe the adsorption process.

In contrast, the pseudo-second-order model (Fig. 4b) exhibits excellent linearity for both La^{3+} and Nd^{3+} ions, with correlation coefficients close to unity ($R^2 \geq 0.998$) and calculated adsorption capacities in good agreement with the experimental values. This confirms that the adsorption process is predominantly governed by chemisorption mechanisms, involving coordination interactions and electron sharing between the metal ions and the active oxygen and nitrogen donor sites (carbonyl, ether, and pyridine groups) of the Calix[4]–DGA–Py adsorbent.

The intra-particle diffusion plots (Fig. 4c) display multi-linear behavior, suggesting that the adsorption process proceeds through multiple steps. The initial sharp region corresponds to rapid external surface adsorption, followed by a slower stage attributed to intra-particle diffusion within the adsorbent structure. The deviation of the plots from the origin indicates that intra-particle diffusion is not the sole rate-controlling step and that boundary layer diffusion also plays a significant role.

Furthermore, the Elovich model plots (Fig. 4d) show good linearity, supporting the heterogeneous nature of the adsorbent surface and the presence of multiple active sites with different energy levels. The obtained kinetic parameters confirm strong interactions between the rare earth ions and the functionalized macrocyclic framework.

Overall, the kinetic analysis demonstrates that the adsorption of La^{3+} and Nd^{3+} onto the Calix[4]–DGA–Py adsorbent follows a pseudo-second-order kinetic model, with contributions from both surface adsorption and intra-particle diffusion processes. The slightly higher kinetic parameters observed for La^{3+} compared to Nd^{3+} indicate a marginally stronger interaction of La^{3+} ions with the available coordination sites, which is consistent with the adsorption capacity results.

Table 1.

Adsorption kinetic parameters of La^{3+} and Nd^{3+} ions onto Calix[4]–DGA–Py adsorbent under optimized conditions (adsorbent dose = 0.03 g, solution volume = 10 mL, pH = 6).

Kinetic model	Parameters	La^{3+}	Nd^{3+}
Pseudo-first-order model	qe,exp (mg/g)	32.0	31.3
	qe,cal (mg/g)	21.5	20.8
	K1 (min^{-1})	0.032	0.029
	R^2	0.93	0.91
Pseudo-second-order model	qe,cal (mg/g)	31.8	31.0
	K2 (g/mg·min)	5.2×10^{-3}	4.7×10^{-3}
	R^2	0.999	0.998
Elovich model	R^2 β (g/mg)	8.9 0.28	8.2 0.25
	α (mg/g·min)	0.98	0.97
Intra-particle diffusion	R^2 kp (mg/g·$min^{0.5}$)	4.10 6.20	3.85 5.80
	C	0.96	0.95

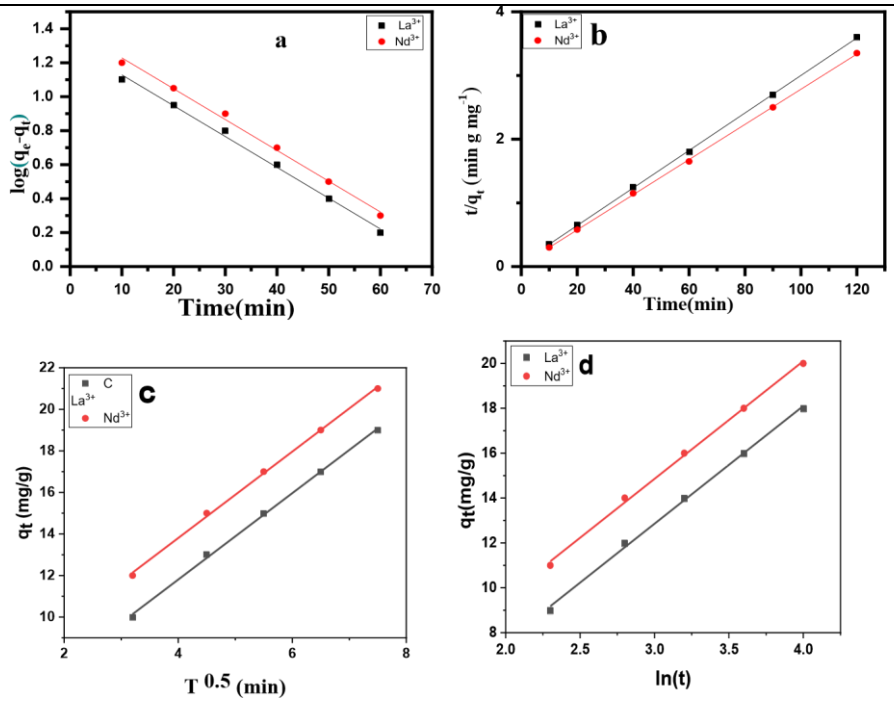


Figure 4: Linear plots for (a) pseudo-first order, (b) pseudo-second-order, (c) intraparticle diffusion and (d) Elovich adsorption kinetic models magnetic polymer composite on Ce^{3+} and Nd^{3+} metal ions, respectively

The adsorption isotherm, also known as the equilibrium isotherm, describes the interaction between the adsorbate and the adsorbent at equilibrium and provides important insight into the adsorption mechanism of metal ions onto the synthesized Calix[4]–DGA–Py adsorbent. In this study, the equilibrium adsorption of La^{3+} and Nd^{3+} ions was analyzed using the Langmuir and Freundlich isotherm models to evaluate the nature of the adsorption process and the distribution of active sites on the adsorbent surface. The Langmuir model assumes monolayer adsorption onto a homogeneous surface with identical active sites, whereas the Freundlich model describes adsorption on a heterogeneous surface with non-uniform energy distribution and multilayer adsorption behavior. The equilibrium isotherms for La^{3+} and Nd^{3+} ions and the corresponding model parameters are presented in Figure 5 and Table 2, respectively. The goodness of fit of the models was evaluated using the adjusted determination coefficient (R^2adj) and standard deviation (SD). Among the tested models, the Langmuir isotherm model provided a better fit for both La^{3+} and Nd^{3+} ions, as indicated by higher R^2adj values and lower SD values compared to the Freundlich model. This suggests that the adsorption process predominantly occurs via monolayer coverage of metal ions onto a relatively uniform distribution of active sites on the adsorbent surface.

The maximum adsorption capacities (qmax) were found to be 82.5 mg/g for La^{3+} and 78.3 mg/g for Nd^{3+}, indicating a high affinity of the Calix[4]–DGA–Py adsorbent toward rare earth ions. The Freundlich constants ($n > 1$) further confirm that the adsorption process is favorable under the studied conditions.

Additionally, the slightly higher adsorption capacity observed for La^{3+} compared to Nd^{3+} can be attributed

to its larger ionic radius and stronger coordination interaction with the available oxygen and nitrogen donor sites. Overall, the isotherm analysis confirms that the synthesized Calix[4]–DGA–Py adsorbent exhibits strong and favorable interaction with rare earth ions, with adsorption behavior primarily governed by monolayer chemisorption on a moderately heterogeneous surface.

Table 2.
Langmuir and Freundlich isotherm parameters for the adsorption of La^{3+} and Nd^{3+} ions onto Calix[4]–DGA–Py adsorbent under optimized conditions.

Model	Parameter	La^{3+}	Nd^{3+}
Langmuir	qmax (mg/g)	82.5	78.3
	KL (L/mg)	0.165	0.142
	R^2adj	0.982	0.978
	SD	1.52	1.73
Freundlich	KF [(mg/g)(L/mg)1/n]	12.8	11.6
	n	2.45	2.32
	R^2adj	0.964	0.958
	SD	2.05	2.21

The higher R^2adj values and lower SD values obtained for the Langmuir model indicate that it provides a better description of the adsorption equilibrium of La^{3+} and Nd^{3+} ions onto the Calix[4]–DGA–Py adsorbent. This suggests that the adsorption process predominantly occurs through monolayer coverage on a relatively uniform distribution of active sites, with a finite saturation capacity.

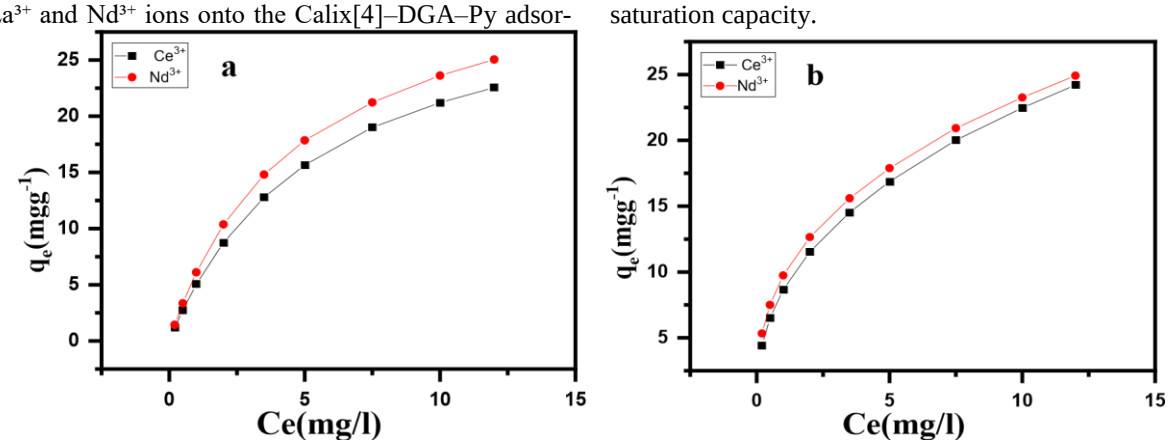


Figure 5. Isotherm plots of (a) Langmuir and (b) Freundlich models for the adsorption of La^{3+} and Nd^{3+} ions onto the Calix[4]–DGA–Py adsorbent under optimized conditions.

4. Conclusion

In this study, a novel calix[4]arene-based adsorbent functionalized with diglycolamide– pyridine ligands (Calix[4]–DGA–Py) was successfully synthesized and evaluated for the removal of La^{3+} and Nd^{3+} ions from aqueous solutions. The characterization results confirmed the successful incorporation of functional groups, good thermal stability, amorphous structure, and heterogeneous surface morphology, all of which contribute to effective adsorption performance. The adsorption process was found to be strongly influenced by solution pH, contact time, and initial metal ion concentration, with optimal removal achieved at pH 6. Kinetic analysis revealed that the adsorption follows a pseudo-second-order model, indicating that chemisorption via coordination interactions is the dominant mechanism. The multi-linear intra-particle diffusion behavior further suggested that the adsorption proceeds through multiple steps, including surface adsorption and diffusion processes. Isotherm studies demonstrated that the Langmuir model best describes the adsorption behavior, indicating monolayer adsorption on a relatively uniform distribution of active sites. The maximum adsorption capacities were determined to be 82.5 mg/g for La^{3+} and 78.3 mg/g for Nd^{3+}, confirming the high affinity of the adsorbent toward rare earth ions. The slightly higher adsorption performance observed for La^{3+} is attributed to its stronger interaction with the available oxygen and nitrogen donor sites. Overall, the Calix[4]–DGA–Py adsorbent exhibits excellent adsorption performance, stability, and efficiency, making it a promising candidate for the sustainable recovery of rare earth elements from aqueous systems. This work provides valuable insights into the design of functionalized macrocyclic adsorbents with enhanced coordination capability and adsorption efficiency.

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Not applicaple

Author Contribution

Amira M. Abou Zeida: Conceptualization, Methodology, Supervision, Writing – review & editing. Zizi Elbadrawy: Investigation, Experimental work, Data curation, Formal analysis, Writing – original draft. Rasha A. Abdelhadia: Validation, Data interpretation, Visualization, Writing – review & editing.

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