

Article

Study on the Performance and Mechanism of Separating La from Light Rare Earth Elements Using Single-Column Method with a New Type of Silica-Based Phosphate-Functionalized Resin

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Abstract

This work develops a novel phosphate-functionalized extraction resin (HEHEHP + Cyanex272)/SiO₂-P via the vacuum impregnation method for efficient separation of light rare earth element impurities from lanthanum (La³⁺) in nitric medium through synergistic extraction. Batch experiments have demonstrated superior adsorption selectivity toward impurity ions over La³⁺ in a pH 4 nitric acid solution. Column studies confirmed exceptional performance under ambient conditions, achieving a lanthanum treatment capacity of 120.6 mg/g and over 98% impurity removal, which surpasses most reported values. Notably, this purification process enables direct production of purified La³⁺ solutions through a single-column system without desorption, significantly enhancing efficiency and reducing costs. Mechanistic insights revealed combined ion exchange and coordination interactions between metal ions and P-OH/P=O groups, corroborated by advanced characterization and density functional theory calculations. These findings indicate a higher binding affinity of light rare earth compared with La³⁺. This strategy provides a scalable approach for ultra-high-purity lanthanum compound production in advanced optical and electronic applications.

Keywords: rare earth; La; purification; separation; ultra-high purity



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1. Introduction

Rare earth elements (RE) are referred to as the 17 elements, including all lanthanides as well as scandium and yttrium. Due to their unique electronic layer structure, they play an irreplaceable role in functional materials such as magnetism, optics, and electronics, and are known as the “vitamin of modern industry” and the “treasure house of new materials in the 21st century” [1–3]. RE are extensively utilized in permanent magnets, catalysis, electronic information, and environmental protection fields [4]. With the development of high technology, products using ordinary-grade RE (relative purity = 99% to 99.99%) have been unable to meet the demands of high-end technology fields. To meet the development requirements of society, the demand for single ultra-high-purity rare earth oxides (REO) has increased significantly [5,6].

La is one of the RE with the richest reserves, and ultra-high-purity lanthanum (La) is widely used in fields such as hydrogen storage materials, high-transparency optical glass,

laser crystals, and ultra-large-scale integrated circuit films [7,8]. However, the presence of trace impurities in La may lead to a reduction in product performance or complete failure. For instance, when using La in a laser crystal, the presence of praseodymium (Pr) and neodymium (Nd) impurities may interfere with the output wavelength of the laser [9,10]. RE can be divided into three groups according to their special properties, including the light (La-Sm), medium (Eu-Dy), and heavy RE (Ho-Lu) [11]. Among them, La, Ce, Pr, and Nd belong to the light rare earth elements [12]. Due to the lanthanide contraction effect, the separation of RE within the same group is extremely difficult due to the highly similar chemical properties [13]. The deep removal of associated impurity ions such as Ce, Pr, and Nd has become a key issue restricting La high-end applications [14].

Solvent extraction is the most widely used method in industrial production of $\leq 5N$ RE_2O_3 , including La_2O_3 , although it is less efficient in the preparation of RE_2O_3 ($\geq 5N5$) by further deeply removing the trace impurities, especially RE in the same group [15]. Sahar et al. extracted RE from the NdFeB magnet using the solvent extraction method, although they could only obtain relatively small amounts of RE through multiple stages of extraction and reverse extraction [16]. The ion exchange method is effective for the purification of a single RE. Alexandra et al. separated the RE in acidic mine water by using chelating ion exchange resins, although the resins may experience swelling and cracking, which seriously affects their real application [17]. In addition, the multi-stage separation method of traditional processes leads to a decrease in the lanthanum recovery rate (usually $<85\%$) and a large consumption of acids and bases, which further exacerbates the cost and environmental pressure of preparing high-purity lanthanum [18]. Therefore, in the rare earth industry, developing an environmentally friendly resin with good selectivity, high separation efficiency, and high mechanical strength to produce ultra-pure rare earth elements remains a key challenge.

Recently, solid-phase extraction technology has gained wide attention due to its ability to combine the advantages of solvent extraction and ion exchange while avoiding the use of large amounts of toxic organic solvents [19,20]. For instance, research on phosphate-silica-based resins has shown that they can selectively extract lanthanum while minimizing the contamination of other impure rare earth elements [21,22]. To solve the aforementioned problems, this study explored a new method for obtaining an ultra-high-purity La solution using phosphate-functionalized silica-polymer-based resins. Specifically, (HEHEHP + Cyanex272)/ SiO_2 -P resins were developed through in situ polymerization and vacuum impregnation methods. Due to the presence of abundant hydroxyl and phosphate groups in HEHEHP and Cyanex272, these structures endow them with strong coordination ability and chelating properties towards rare earth ions [23–25]. This resin can be produced on a large scale in a simple manner and can prioritize the removal of rare earth impurities from lanthanum. In addition, the adsorption mechanism of the resins was studied using various methods, including density functional theory (DFT) calculations, revealing the ion exchange and coordination interactions that drive the selective extraction of metal ions. This research provides an innovative solution for the purification of RE and is of great significance for the production of ultra-pure La required by high-end industries.

2. Results and Discussion

2.1. Characterization

The TG-DSC results of the carrier SiO_2 -P, resin, and extractants are shown in Figure 1a–c. As shown in Figure 1a, SiO_2 -P exhibited two exothermic peaks at 573 K and 785 K with a total mass loss of 16.2 wt.% in the two stages, indicating its good thermal stability. These two peaks were, respectively, caused by the thermal decomposition products of styrene and divinylbenzene and their polymers in SiO_2 -P [26]. Figure 1b shows

that (HEHEHP + Cyanex272)/SiO₂-P has three weight-loss stages, namely the thermal decomposition of styrene divinylbenzene, HEHEHP + Cyanex272, and the copolymer of polystyrene. Considering the relative weight ratio of “P” and “SiO₂” in both SiO₂-P and the resin should be the same, it can be calculated that the contents of HEHEHP + Cyanex272 and “P” in (HEHEHP + Cyanex272)/SiO₂-P should be 27.0 wt.% and 12.5 wt.%, respectively. Unexpectedly, this proportion was inconsistent with the theoretical value of 33.3 wt.% as designed during the synthesis. Therefore, the TG-DSC analysis on the mixed extractant HEHEHP + Cyanex272 was performed, and the results are shown in Figure 1c; these results display that, even when heated to a high temperature of 1000 K, the above substances did not completely decompose, with a residual of about 11.4 wt.%. After calculation, it can be determined that the actual proportion of the extractant was approximately 32.3 wt.%, which is very close to the theoretical value of 33.3 wt.%.

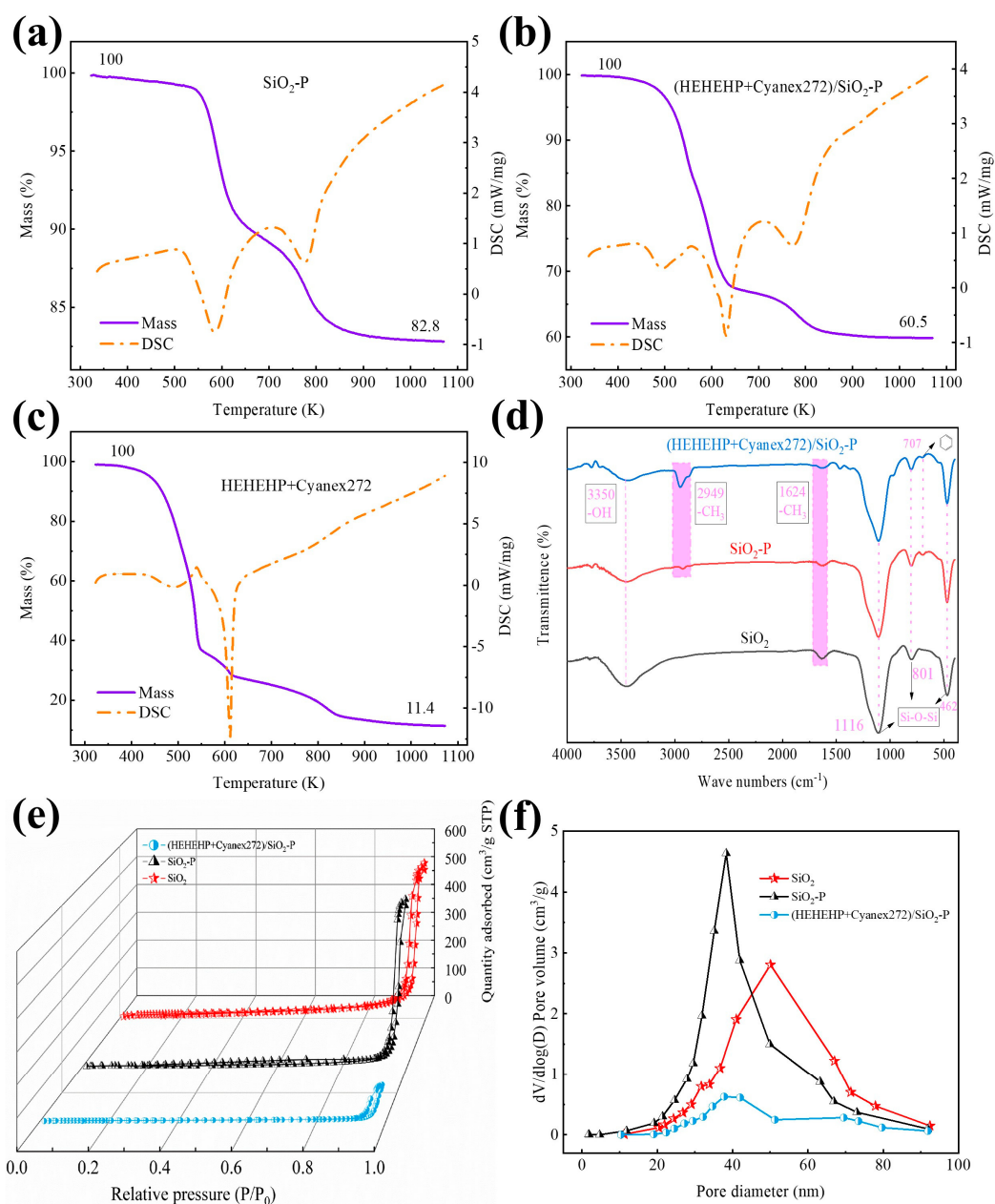


Figure 1. Characterization of the materials: (a–c) TG–DSC analysis; (d) FT–IR spectra; (e) N₂ adsorption–desorption isotherms; and (f) pore diameter distribution.

Figure 1d shows the results of the FT-IR analysis. Peaks at 462, 801, and 1116 cm^{-1} are consistent with the Si-O-Si characteristic peaks of silica-based materials [27]. A peak at 707 cm^{-1} is observed due to the bending vibration of the C-H bond in the benzene ring, indicating the successful polymerization of styrene-divinylbenzene in $\text{SiO}_2\text{-P}$. In the FT-IR spectra of (HEHEHP + Cyanex272)/ $\text{SiO}_2\text{-P}$, new peaks at 2949 and 1624 cm^{-1} appear, which are caused by the stretching and bending vibrations of $-\text{CH}_3$ and $-\text{CH}_2-$ [28]. A weak characteristic peak of P-OH is observed at 970 cm^{-1} , although no characteristic peaks of P=O and P-O-C are observed at 1185 and 1035 cm^{-1} , which might be masked by the strong characteristic peaks of silica [29]. The above results indicate that the extractant HEHEHP + Cyanex272 has been well-loaded into the carrier of $\text{SiO}_2\text{-P}$.

Figure 1e,f and Table S1 present the results of the BET analysis. As shown in Figure 1e, when the relative pressure (P/P_0) is <0.9 , SiO_2 , $\text{SiO}_2\text{-P}$, and (HEHEHP + Cyanex272)/ $\text{SiO}_2\text{-P}$ hardly adsorb N_2 , while when the relative pressure approaches 1.0, the adsorption capacity of N_2 sharply increases. All three materials exhibit an IV-type hysteresis loop, indicating that they all have mesoporous structures and uniform shapes [30]. It is worth noting that the N_2 adsorption capacity in the (HEHEHP + Cyanex272)/ $\text{SiO}_2\text{-P}$ resin is significantly lower than that of the carrier, which is due to HEHEHP and Cyanex272 occupying the internal space of $\text{SiO}_2\text{-P}$. The results in Figure 1f show that $\text{SiO}_2\text{-P}$ is a porous material with a pore diameter of 40–60 nanometers. From $\text{SiO}_2\text{-P}$ to (HEHEHP + Cyanex272)/ $\text{SiO}_2\text{-P}$, the pore volume decreases, indicating that the organic substances have been successfully loaded into the carrier $\text{SiO}_2\text{-P}$.

2.2. Batch Experiments

2.2.1. Effect of Acidity

Firstly, the effect of nitric acidity on the adsorption efficiency and separation performance of the three resins towards main impurity ions in the high-lanthanum solution was studied. The results are shown in Figure 2a–c. With the pH changing from 5 to 3, the three resins, HEHEHP/ $\text{SiO}_2\text{-P}$, Cyanex272/ $\text{SiO}_2\text{-P}$, and (HEHEHP + Cyanex272)/ $\text{SiO}_2\text{-P}$, exhibited significantly higher adsorption efficiencies for Ce^{3+} , Pr^{3+} , and Nd^{3+} compared with La^{3+} . This phenomenon can be explained by the lanthanide contraction effect, which states that as the atomic number increases, the effective hydration radius of rare earth ions shows a decreasing trend. Compared with La^{3+} , Ce^{3+} , Pr^{3+} , and Nd^{3+} have smaller hydration ion radii, thereby enhancing the electrostatic attraction [31]. Taking the comparison between La^{3+} and Ce^{3+} as an example, the hydration radius of hydrated La^{3+} ions (1.25 Å) is significantly larger than that of hydrated Ce^{3+} (1.18 Å). Under the conditions of constant total charge, La^{3+} has a larger ion radius than Ce^{3+} and other light rare earth ions, resulting in a lower charge density for La^{3+} [32]. This difference in charge density leads to a significant weakening of the electrostatic interaction between the resin active groups and La^{3+} . When the acidity increases to pH 1, the hydrogen ion concentration in the system significantly increases, resulting in a general decline in the adsorption performance of the functional resin for light rare earth elements. This phenomenon is mainly caused by the inhibitory effect of high concentrations of hydrogen ions. When the concentration of H^+ in the solution is too high, it can inhibit the process by which R-POH dissociates into H^+ , thereby significantly weakening the ion exchange capacity of the resin and resulting in a decrease in its adsorption capacity.

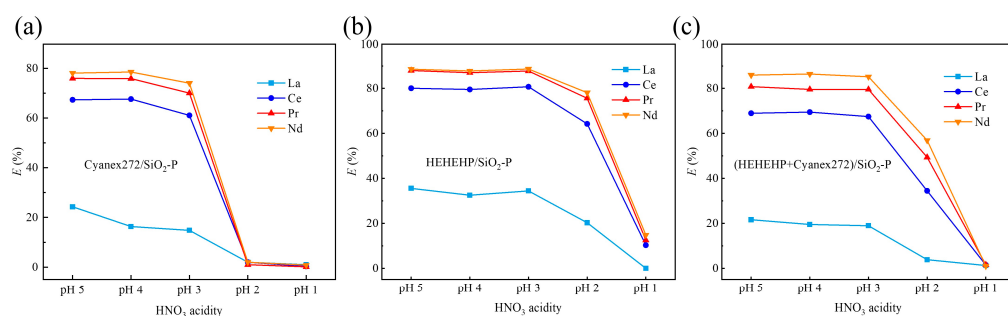


Figure 2. Effect of nitric acidity on the adsorption and separation of the three resins towards main impurity ions in the high-lanthanum solution: (a) Cyanex272/SiO₂-P, (b) HEHEHP/SiO₂-P, (c) (HEHEHP + Cyanex272)/SiO₂-P (S/L ratio = 20 g/L, temperature = 298 K, time = 24 h, C_{La} = 1000 mg/L, C_{Other} = 10 mg/L, pH = 4).

As shown in Tables S2–S4, by comparing the separation factors ($SF_{\text{RE/La}}$, RE = Ce, Pr, Nd) of the three functional resin Cyanex272/SiO₂-P, HEHEHP/SiO₂-P, and (HEHEHP + Cyanex272)/SiO₂-P at different acidity conditions, the (HEHEHP + Cyanex272)/SiO₂-P resin exhibited the highest separation factors at pH 4. This is due to the synergistic effect of HEHEHP and Cyanex272. To verify the sensitivity of the resin, we also added non-rare-earth-metal ion impurities and increased the concentration of all the impurity ions. The results in Figure S1 show that the resin can effectively adsorb the Fe/Al/Ca elements within a wide pH range, and the adsorption behavior of Ce/Pr/Nd is almost the same as that at low concentrations. Therefore, it can be concluded that the functional resin has strong adaptability.

2.2.2. Effect of Mole Ratios of HEHEHP and Cyanex272

The separation performance of (HEHEHP + Cyanex272)/SiO₂-P resins prepared with different molar ratios of HEHEHP and Cyanex272 (0:1, 1:1, 2:1, 4:1, and 1:0) was investigated, with the results shown in Figure 3a. As the proportion of HEHEHP increases, the separation factors ($SF_{\text{RE/La}}$, RE = Ce, Pr, Nd) exhibited a pattern of first increasing and then decreasing. At the 1:1 molar ratio, the separation factors ($SF_{\text{RE/La}}$, RE = Ce, Pr, Nd) reached their optimal level, being 13.24, 26.66, and 33.79, respectively (Table S5).

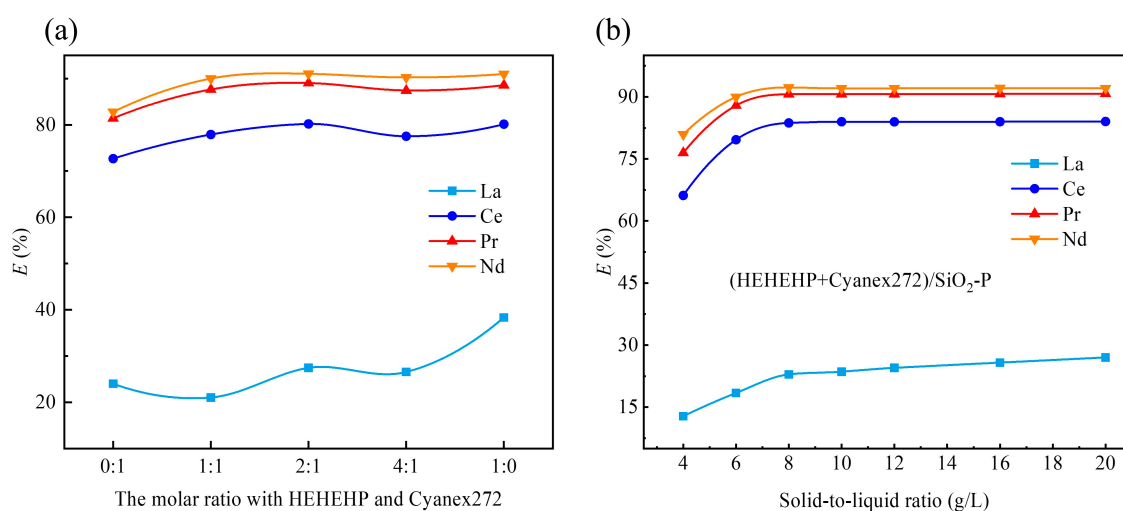


Figure 3. Effect of molar ratio of HEHEHP and Cyanex272 (a), solid-to-liquid ratio (b) on the adsorption and separation performance of (HEHEHP + Cyanex272)/SiO₂-P (temperature = 298 K, time = 24 h, C_{La} = 1000 mg/L, C_{Other} = 10 mg/L, pH = 4).

This phenomenon is closely related to the Lewis acid–base mechanism: compared with La^{3+} , Ce^{3+} , Pr^{3+} , and Nd^{3+} have smaller ionic radii, exhibit harder Lewis acidity, and tend to combine more readily with alkaline extraction agents [33]. According to the sequence of alkalinity of the extraction agents $\text{R}_3\text{C}=\text{O} < (\text{RO})_3\text{P}=\text{O} < \text{R}_3\text{P}=\text{O}$, extraction agents (containing C–P bonds) have stronger alkalinity than those containing C–O–P bonds [34]. It is worth noting that HEHEHP and Cyanex272 can form a stable dimer structure through intermolecular hydrogen bonding (Figure S2), and this molecular structure may optimize the interface properties and metal coordination ability of the extraction system through a synergistic effect [35]. This molecular-scale interaction provides a theoretical basis for regulating the functionalization ratio of the extraction agent; that is, a moderate HEHEHP/Cyanex272 compound ratio can achieve the maximum selection of RE through balancing the alkalinity of the extraction agent and the steric hindrance effect.

2.2.3. Effect of Solid–Liquid Ratio

The effect of the solid–liquid ratio on the separation performance of (HEHEHP + Cyanex272)/ SiO_2 -P resin was further studied, as shown in Figure 3b, Table S6. When the solid–liquid ratio was gradually increased from 4 g/L to 8 g/L, the adsorption efficiency of metal ions showed a significant upward trend. When the solid–liquid ratio exceeded 8 g/L, the adsorption efficiency tended to stabilize. It is noteworthy that as the solid–liquid ratio increased, the separation factors of Ce^{3+} , Pr^{3+} , Nd^{3+} , over La^{3+} first significantly increased and then gradually decreased (Table S6), reaching the maximum value at a solid–liquid ratio of 10 g/L. This phenomenon indicates that an appropriate solid–liquid ratio can achieve the optimal separation effect by balancing the adsorption capacity and the selectivity.

2.2.4. Kinetics

The effect of temperature on the adsorption kinetics of (HEHEHP + Cyanex272)/ SiO_2 -P resin was further studied. As shown in Figure 4a–c, at the three experimental temperatures, the adsorption equilibrium time of the resin towards four rare earth elements was achieved at 4 h, 2 h, and 30 min at 298 K, 318 K, and 348 K, respectively. This phenomenon indicates that the increase in temperature can effectively accelerate the adsorption kinetics, which is consistent with the mechanism that increasing temperature enhances molecular thermal motion and reduces system viscosity, thereby improving interfacial mass transfer. It is worth noting that the resin still maintains excellent adsorption and separation performance at 348 K under high-temperature conditions, confirming its excellent thermal stability characteristics.

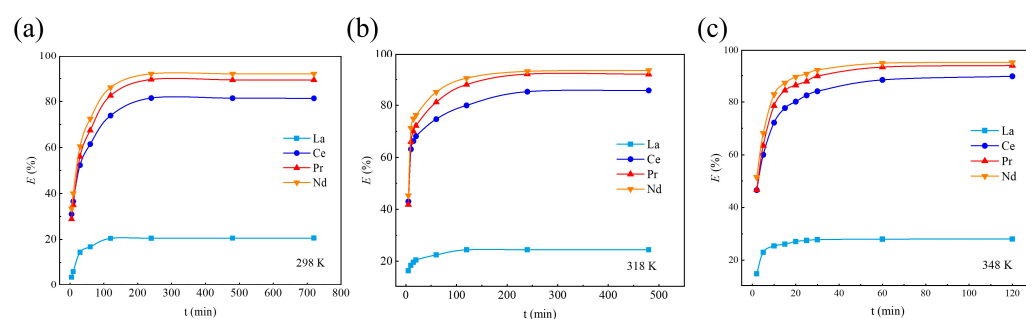


Figure 4. Adsorption kinetics of (HEHEHP + Cyanex272)/ SiO_2 -P at different temperatures: (a) 298 K, (b) 318 K, (c) 348 K (S/L ratio = 10 g/L, time = 24 h, $C_{\text{La}} = 1000$ mg/L, $C_{\text{Other}} = 10$ mg/L, pH = 4).

To clarify the adsorption mechanism, the pseudo-first-order kinetics model, pseudo-second-order kinetics model, and intraparticle diffusion model were used to analyze the adsorption kinetics data, with the results shown in Figure S3 and Tables S7 and S8. The results showed that the pseudo-second-order kinetics model exhibited the better fitting

correlation with an $R^2 > 0.99$, and the calculated equilibrium adsorption amount was highly consistent with the experimental data, with the difference less than 1%. This result reveals that this adsorption process is dominated by chemical adsorption [36]. The straight line passes through the origin of the coordinate system and exhibits distinct multi-segment linear characteristics. This suggests that particle internal diffusion is not the sole rate-limiting step, and the adsorption process may be influenced by both membrane diffusion and surface chemical reactions [37]. Detailed descriptions can be found in the Supplementary Materials.

Batch experiments demonstrated that at pH = 4, this resin achieved the maximum separation factor of (Ce^{3+} , Pr^{3+} , and Nd^{3+}) over La^{3+} through synergistic effects. When HEHEHP and Cyanex272 were mixed in a 1:1 ratio, selectivity was significantly improved. The separation efficiency reaches its optimum at a solid–liquid ratio of 10 g/liter. Heating can accelerate the adsorption kinetics so that the adsorption equilibrium can be obtained within 30 min at 348 K, and is dominated by a pseudo-second-order kinetic model, indicating that chemical adsorption and membrane diffusion jointly control the rate.

2.3. Column Experiments

The separation performance of (HEHEHP + Cyanex272)/ SiO_2 -P resin for the removal of impurities in RE using pH 4, high-lanthanum-containing solutions was studied through dynamic column experiments. Experiments were conducted using a double-layer column (inner diameter: 5.5 mm, height: 300 mm, bed volume (BV): 7.12 cm^3) with a resin-filled inner layer and a thermostatic water jacket. The breakthrough curves at room temperature are shown in Figure 5a. The adsorption process was characterized by four distinct stages.

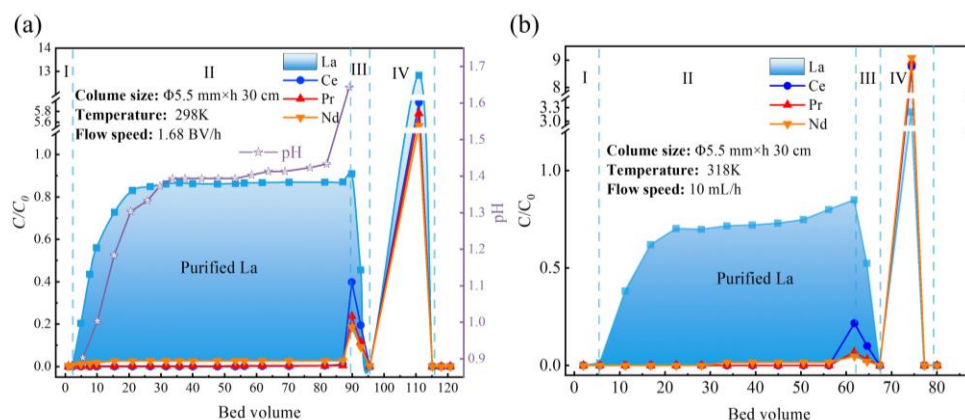


Figure 5. Column experiment results of (HEHEHP + Cyanex272)/ SiO_2 -P resin for the removal of impurities in RE using pH 4, high-lanthanum-containing solutions: (a) $T = 298 \text{ K}$, (b) $T = 318 \text{ K}$ (column size: $\Phi 5.5 \text{ mm} \times h 30 \text{ cm}$, flow rate: 1.68 BV/h , I: pH = 4 HNO_3 , II: pH = 4, $C_{\text{La}} = 1000 \text{ mg/L}$, $C_{\text{other}} = 10 \text{ mg/L}$, III: pH = 4 HNO_3 , IV: 1 M HNO_3).

In the first stage, a pump was used to flow 10 mL of pH = 4 HNO_3 solution at a rate of 1.68 BV/h upwards through the column for pre-equilibration. In the second stage, the feed was stopped when the concentration of Ce^{3+} in the effluent reached 10% of the initial value. At this point, approximately 85 BV of high-purity lanthanum solution could be collected, with an impurity removal rate exceeding 98%, achieving the separation of LRE from lanthanum. In the third stage, ultra-pure water was used to replace the residual liquid in the column to clean the unadsorbed ions. In the fourth stage, 1 M HNO_3 was used to completely desorb the metal ions, with an element recovery rate approaching 100% (Table S9). It should be noted that the purpose of using 1 M HNO_3 here is merely for the resin's recycling and regeneration. There is no need for a separate desorption step for collecting the La products as the La is already present in the effluent. When desorption is

complete, replace the remaining eluent in the column with pH 4 HNO_3 , clean the adsorbent at the same time, and then start a new cycle. After calculation, the treatment capacity of (HEHEHP + Cyanex272)/ SiO_2 -P resin for lanthanum ions is approximately 120.6 mg/g.

Column separation performance at 318 K was further studied to evaluate the effect of temperature. A thermostatic circulating water bath system was used to maintain the temperature through the outer glass jacket, and the breakthrough curve is shown in Figure 5b. Experimental data revealed that approximately 55 BV of purified lanthanum solution could be obtained under these conditions, indicating a significant reduction in resin treatment capacity and lanthanum purification efficiency compared with separation at room temperature. Figure S4 shows the cycle performance. The results indicate that after three column experiments, the processing capacity decreased by approximately 82% compared to the initial level, demonstrating good reusability. More details are provided in the Supplementary Materials.

2.4. Study on the Adsorption Mechanism

The adsorption and selectivity mechanism of the resin was further systematically elucidated. The FT-IR spectra of the samples after adsorption of Ce^{3+} , Pr^{3+} , and Nd^{3+} are shown in Figure S5. The peak at 970 cm^{-1} , corresponding to the P-OH functional group, exhibited no significant shift in position but showed a marked reduction in intensity after adsorption of RE^{3+} , confirming its direct involvement in the reaction [38]. Moreover, the absence of a distinct peak at 1380 cm^{-1} indicates that NO_3^- ions do not participate in the adsorption process; therefore, to keep charge balance during the adsorption, it is supposed that the adsorption mechanism is dominated by ion exchange. To validate the ion exchange mechanism, the pH of the eluent during column separation was monitored using a pH meter, as shown in Figure 6a. The initial pH of the eluent sharply decreased from the input pH 4 to 0.92 and, subsequently, increased and remained at 1.41 for a long time; then, when it was near breakthrough, it further increased to 1.62, caused by the decrease in ion exchange ability. This phenomenon aligns closely with the H^+ - RE^{3+} ion exchange mechanism that, after H^+ from the P-OH functional groups in the resin surface exchanges with RE^{3+} , H^+ is released into the liquid phase, causing a transient increase in acidity. The corroborative evidence from pH analysis demonstrates that H^+ exchange with rare earth ions at the P-OH functional groups serves as a primary driving force for adsorption. Moreover, the change in pH in the eluent can be an index to judge the breakthrough conveniently. This approach not only eliminates the complex procedures required for synchronous multi-element concentration detection but also significantly enhances the controllability and repeatability of the separation process. This methodological innovation provides a theoretical basis for the intelligent control of continuous rare earth separation processes, with significant meaning in practical application.

SEM-EDS was also employed to characterize the micromorphology and elemental distribution of (HEHEHP + Cyanex272)/ SiO_2 -P resin before and after adsorption of Ce^{3+} , Pr^{3+} , and Nd^{3+} , as shown in Figure 6b–d. For the fresh (HEHEHP+Cyanex272)/ SiO_2 -P resin (Figure 6a), uniform distributions of carbon (C) and phosphorus (P) elements were observed, confirming the successful immobilization of HEHEHP and Cyanex272 into the internal pores of the SiO_2 -P carrier. After the adsorption of RE, the EDS of (HEHEHP + Cyanex272)/ SiO_2 -P loaded with RE was analyzed and shown in Figure 6c,d, where Ce, Pr, and Nd were clearly and evenly observed, indicating the successful and efficient adsorption. Notably, no nitrogen (N) signal was detected in the (HEHEHP + Cyanex272)/ SiO_2 -P after adsorption of RE, implying that NO_3^- does not participate in the coordination process. As can be seen from Figure S6, the mass proportions of all three elements are greater than 0.5, and the atomic ratio is above 0.05.

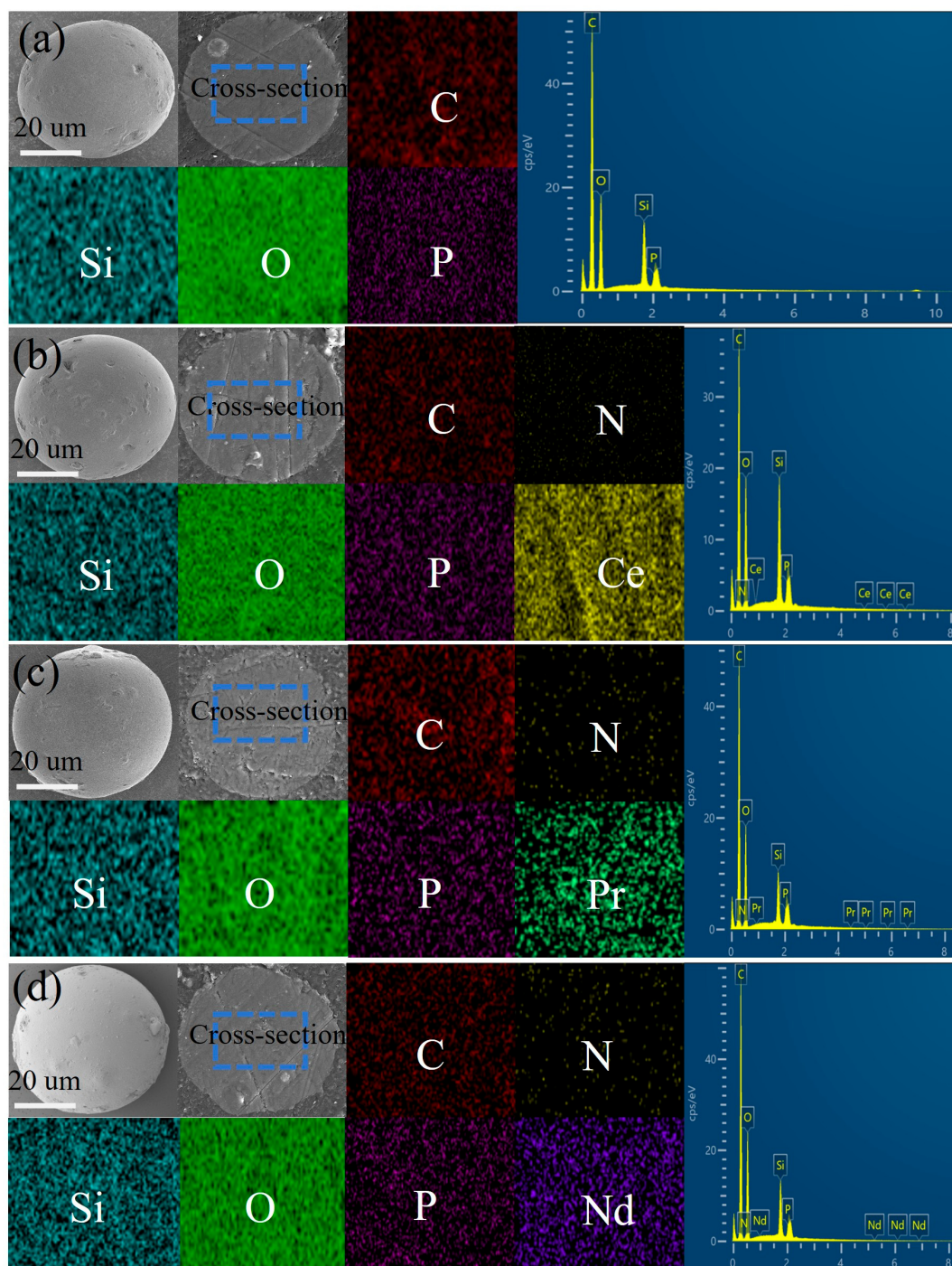


Figure 6. The results of SEM-EDS analysis: (a) (HEHEHP + Cyanex272)/SiO₂-P; (b–d) (HEHEHP + Cyanex272)/SiO₂-P after adsorption of Ce, Pr, and Nd.

Figure 7a presents the XPS full spectra of fresh (HEHEHP + Cyanex272)/SiO₂-P resin and that after adsorption of Ce³⁺, Pr³⁺, and Nd³⁺. The spectra exhibited distinct C 1s and P 2p characteristic peaks, confirming the successful synthesis of the resin. After adsorption of RE, the characteristic peaks of Ce 3d, Pr 3d, and Nd 3d appeared, indicating the effective adsorption of the elements. Further, analysis of the high-resolution spectra for Ce, Pr, and Nd (Figure 7b–d) revealed that the binding energies of Ce³⁺/Ce⁴⁺ were located at 884.1 eV and 902.5 eV, respectively [39]. The Pr 3d peaks were observed at 933.9 eV and 955.3 eV, while the Nd 3d peaks were observed at 979.3 eV and 1001.9 eV [40,41]. The fine spectra of the P 2p spectra of the resin before and after adsorption of RE were compared and shown

in Figure 7e–f. In the fresh resin, the binding energies of P=O, P–O, and P–C are 132.62 eV, 133.59 eV, and 134.02 eV, respectively. After Ce^{3+} adsorption, the peak corresponding to P–C (133.98 eV) remains almost unchanged, whereas the binding energies of P–O and P=O decreased to 133.02 eV and 132.38 eV, respectively, with P–O exhibiting a more pronounced shift. Analogous trends in peak position changes for P=O, P–O, and P–C were observed in the cases of Pr^{3+} and Nd^{3+} adsorption. These observations suggest that both P–OH and P=O groups in the resin participate in coordination, with P–OH serving as the dominant active adsorption site [22]. To investigate if NO_3^- participated in the adsorption, the fine spectra of N 1s were tested (Figure S7); the absence of characteristic signals within the 395–410 eV binding energy range confirms that NO_3^- does not contribute to the rare earth ion adsorption process.

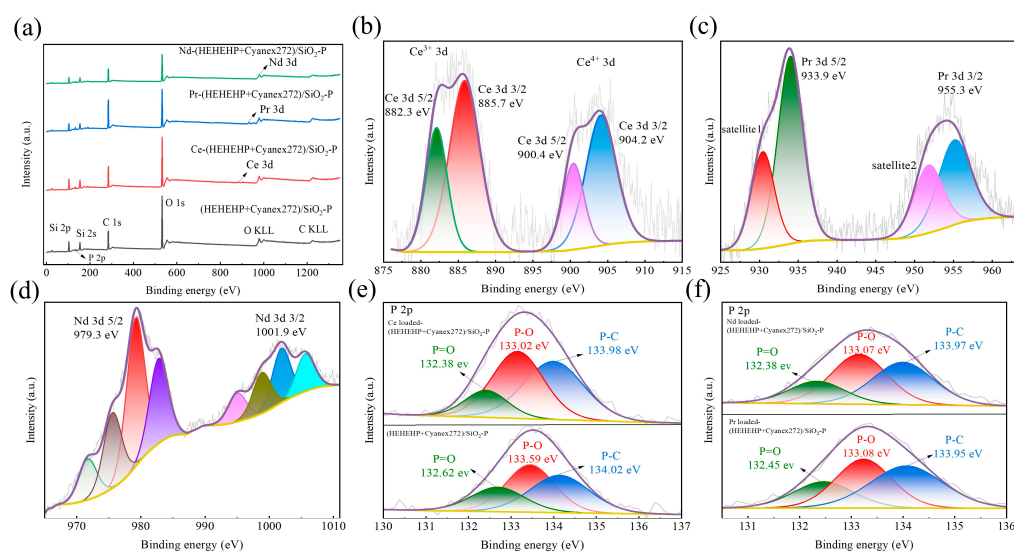


Figure 7. Study on the adsorption mechanism: (a) XPS full spectra; (b–d) XPS fine spectra of Ce 3d, Pr 3d, and Nd 3d; (e,f) XPS fine spectra of P 2p before and after adsorption by (HEHEHP + Cyanex272)/SiO₂-P.

2.5. Study on Polymer Conformation and Selectivity Mechanism

DFT calculations were employed to further elucidate the selective mechanism. Based on previous experimental results, the dimer formed by HEHEHP and Cyanex272 played a dominant role in the adsorption process; therefore, the adsorption mechanism of this dimer was systematically investigated, and La^{3+} and Nd^{3+} were selected as the representative elements for analysis. ESP images of the dimer and its simplified configuration were analyzed (Figure S8). The simplified configuration exhibited electronegative distribution characteristics nearly identical to those of the original structure. To facilitate calculations, the simplified dimer configuration was used for subsequent computations. The hydration shell of La^{3+} and Nd^{3+} comprises six water molecules [42], as illustrated by the electrostatic potential energy of the hydrated metal ions in Figure S8. The dimer demonstrated relatively higher electron density in the region surrounding the phosphoric acid groups, indicating that the adsorption sites are concentrated on the phosphorus and oxygen moieties. Upon adsorption of La^{3+} and Nd^{3+} , the Mulliken charge of the central oxygen atom increased significantly from -0.738 e to -0.708 e and -0.710 e (Figure 8a,c), indicating that oxygen atoms act as electron donors in the coordination process, while rare earth ions function as electron acceptors, thereby forming stable coordinate bonds between the ligand and metal [43]. Notably, each of the three dimeric ligands dissociated one proton (H^+) from its hydrogen bonding network, undergoing ion exchange with RE^{3+} , ultimately leading to the formation of a stable octahedral coordination complex. To quantitatively characterize the

adsorption equilibrium, a series of adsorption experiments was conducted by adjusting the solution pH, yielding distribution coefficients (K_d) for La^{3+} and Nd^{3+} . Linear fitting of $\lg K_d$ versus pH (Figure S9) revealed that the slopes of both fitted lines were close to the theoretical value of 3.0 ($R^2 > 0.99$). This feature explicitly demonstrates that the adsorption of one RE^{3+} ion is coupled with the release of three protons, which is fully consistent with the stoichiometric relationship involving the dissociation of one H^+ from each of the three dimeric ligands. The experimental observations and DFT calculation results mutually validate the scientific design of the polymer configuration, with detailed mechanisms provided in the Supplementary Materials.

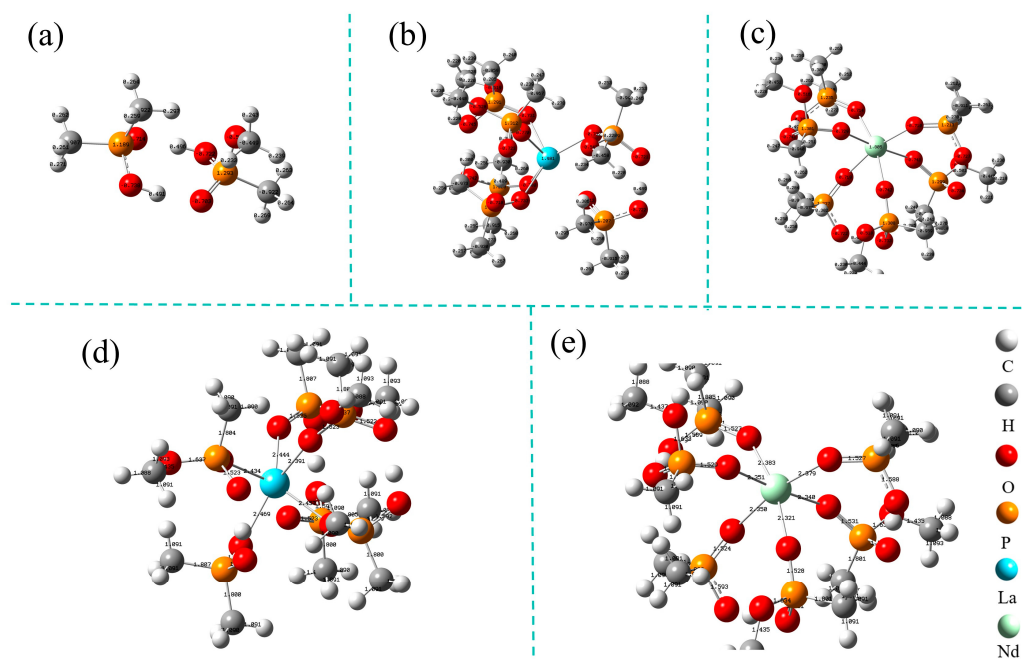


Figure 8. Central oxygen atom charge and coordination bond length: (a) the charge of the oxygen atom at the center of the dimer; (b,c) the charge of the central oxygen atom after being loaded with La and Nd; (d,e) atomic bond lengths after loading La and Nd.

Figure 9a–c illustrate the electrostatic potential energy of the dimeric ligand and its complexes with La^{3+} and Ce^{3+} , while Table S10 summarizes the calculated reaction equations and Gibbs free energy changes (ΔG) for both coordination processes [44]. The negative $\Delta G < 0$ confirmed the spontaneous nature of these reactions. All optimized geometries and energies involved in the equations are provided in Figure S10. The binding energies calculated using Equation (5) are listed in Table 1, revealing exothermic values of -67.8 kcal/mol for La^{3+} and -108.9 kcal/mol for Nd^{3+} . More negative binding energies correspond to higher reaction feasibility and stronger ion selectivity. Notably, the Nd^{3+} complex exhibited a more negative binding energy, indicating a thermodynamically favored coordination process compared to La^{3+} . Furthermore, as shown in Figure 8d,e, the bond length analysis showed that the P–O bond average distances in the complexes were 2.439 Å (La^{3+}) and 2.354 Å (Nd^{3+}), respectively. The shorter bond length for Nd^{3+} suggests stronger P–O–metal interactions, consistent with the binding energy trends [45]. Collectively, these findings demonstrated a clear adsorption preference of the ligand for Nd^{3+} over La^{3+} , as corroborated by both thermodynamic and structural analyses.

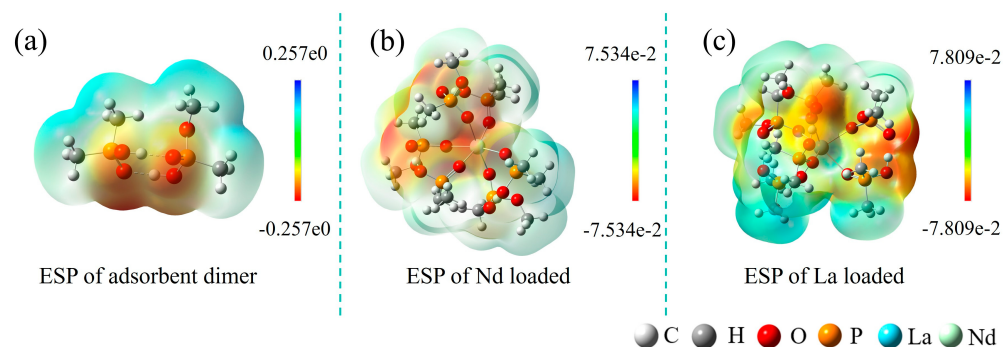


Figure 9. ESP images before (a) and after loading (b) Nd^{3+} and (c) La^{3+} with dimer, respectively; blue area: positive charge, red area: negative charge.

Table 1. Binding energy of metal ion and ligand complex.

Reaction	$\Delta E_{\text{binding-energy}}$ (kcal/mol)
$\text{Nd}^{3+} \cdot (\text{H}_2\text{O})_6 + 3(\text{HL}_2)^- \rightarrow \text{Nd}(\text{HL}_2)_3 + 6\text{H}_2\text{O}$	−108.9
$\text{La}^{3+} \cdot (\text{H}_2\text{O})_6 + 3(\text{HL}_2)^- \rightarrow \text{La}(\text{HL}_2)_3 + 6\text{H}_2\text{O}$	−67.8

Molecular orbital (MO) theory analysis further elucidated the adsorption selectivity difference in the resin toward La^{3+} and Nd^{3+} . Based on DFT calculations, the frontier molecular orbital characteristics (HOMO and LUMO) of metal ions and ligands were systematically analyzed [46]. According to hard–soft acid–base (HSAB) theory, hard acids tend to interact with hard base ligands, and the strength of coordination interactions depends on orbital energy matching. Computational results indicate that the HOMO–LUMO energy gap of metal ions correlates positively with their hardness index, while the intensity of coordination interactions is determined by the energy proximity between the ligand HOMO and metal LUMO [47]. As shown in Figure 10a–c, the energy difference between the HOMO of the dimeric ligand and the LUMO of Nd^{3+} (−0.13 au) was smaller than that with La^{3+} (−0.24 au), demonstrating superior energy matching between Nd^{3+} LUMO and the ligand HOMO, which facilitates stronger coordinate bond formation.

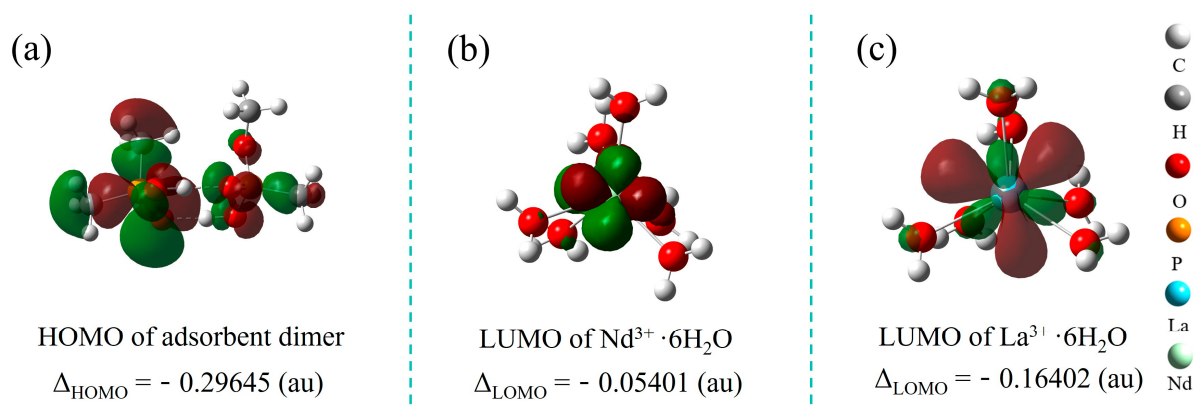


Figure 10. The HOMO (a) of the dimeric ligand and the LUMO of the (b) Nd^{3+} and (c) La^{3+} metal ions.

Combining ESP analyses, Gibbs free energy changes (ΔG), binding energy calculations, and molecular orbital theory, the adsorption selectivity of the resin toward rare earth ions was systematically revealed: light rare earth element (LREE) trivalent cations exhibit higher adsorption priority than La^{3+} , with interaction strengths following the order $\text{Nd}^{3+} > \text{La}^{3+}$. This conclusion is highly consistent with experimental observations and is corroborated by

theoretical calculations at the electronic-structure level, forming a complete “experiment–theory” evidence chain.

2.6. Comparison

To evaluate the production efficiency of (HEHEHP + Cyanex272)/SiO₂-P resin for high-purity lanthanum, it was compared with other functional materials. From the data in Table 2, it can be seen that the maximum purification capacity of lanthanum in many scholars’ studies is lower than our work (120.6) mg/g, which demonstrates the superiority of our resin.

Table 2. Purification of La by (HEHEHP + Cyanex272)/SiO₂-P resin compared with other materials.

Materials	Acidity	Purity	E%	Q (mg/g)	Ref.
La-IIP-Schiff-base	pH = 6 HNO ₃	298	80	25.0	[48]
GMZ Bentonite	pH = 6 HCl	298	95	42.0	[49]
D2EHPA/DIAION SA 10 A	pH = 3 HCl	298	90	67.2	[49]
DEPTS/SBA-15	pH = 7 HCl	298	95	114.8	[50]
(HEHEHP + Cyanex272)/SiO ₂ -P	pH = 4 HNO ₃	298	98	120.6	This work

3. Experimental Section

3.1. Chemicals

RE(NO₃)₃·nH₂O (RE = La, Ce, Pr, Nd, n = 5 or 6), mono-2-ethylhexyl (2-ethylhexyl) phosphonate (HEHEHP, 95%), and bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex272, 90%) were purchased from McLean Biochemical Co., Ltd., Shanghai, China. Styrene (C₈H₈, 99.5%), acetophenone (CH₃COC₆H₅, 98%), diethyl phthalate (C₁₂H₁₄O₄, 99.5%), α, α′-azodiisobutyronitrile (AIBN, 98%), dichloromethane (CH₂Cl₂, 98%), acetone (C₃H₆O, 99.5%), methanol (CH₃OH, 99.5%), divinylbenzene (DVB, 55%), sodium hydroxide (NaOH, 97%), nitric acid (HNO₃, 65–68%), ethanol (C₂H₆O₂, 99.8%), and anhydrous oxalic acid (H₂C₂O₄, 99.999%) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd., Shanghai, China. All solutions were prepared with ultra-pure water with a resistance of 18.2 MΩ (High-tech Master S, Shanghai, China). All the chemical reagents mentioned in the manuscript were purchased from China.

3.2. Synthesis and Characterization of the Resin

The synthesis process of the resin, (HEHEHP + Cyanex272)/SiO₂-P, was divided into two steps. Firstly, styrene and divinylbenzene were loaded into the interior of the porous silica through an in situ polymerization method to obtain a stable functionalized silica-polymer carrier SiO₂-P [26]. A mixture comprising 3.18 mL of divinylbenzene and 9.11 mL of styrene was completely dissolved in a solution containing 22.3 mL of acetophenone and 14.9 mL of diethyl phthalate. Subsequently, 0.2653 g of AIBN was added as a radical initiator, and the resulting mixture was homogenized using a magnetic stirrer. Meanwhile, 50 g of silica carrier was placed in a round-bottom flask mounted on a rotary evaporator (EYELA-1300vh WB, Tokyo, Japan). The system was subjected to three consecutive cycles of evacuation followed by nitrogen backfilling to establish an inert nitrogen atmosphere. Then, the mixture of HEHEHP and Cyanex272 was vacuum-impregnated into the interior of the SiO₂-P carrier in a certain proportion to obtain (HEHEHP + Cyanex272)/SiO₂-P functional resin [51]. Figure 11 shows the flowchart of the synthesis process, and the detailed steps can be found in the Supplementary Materials.

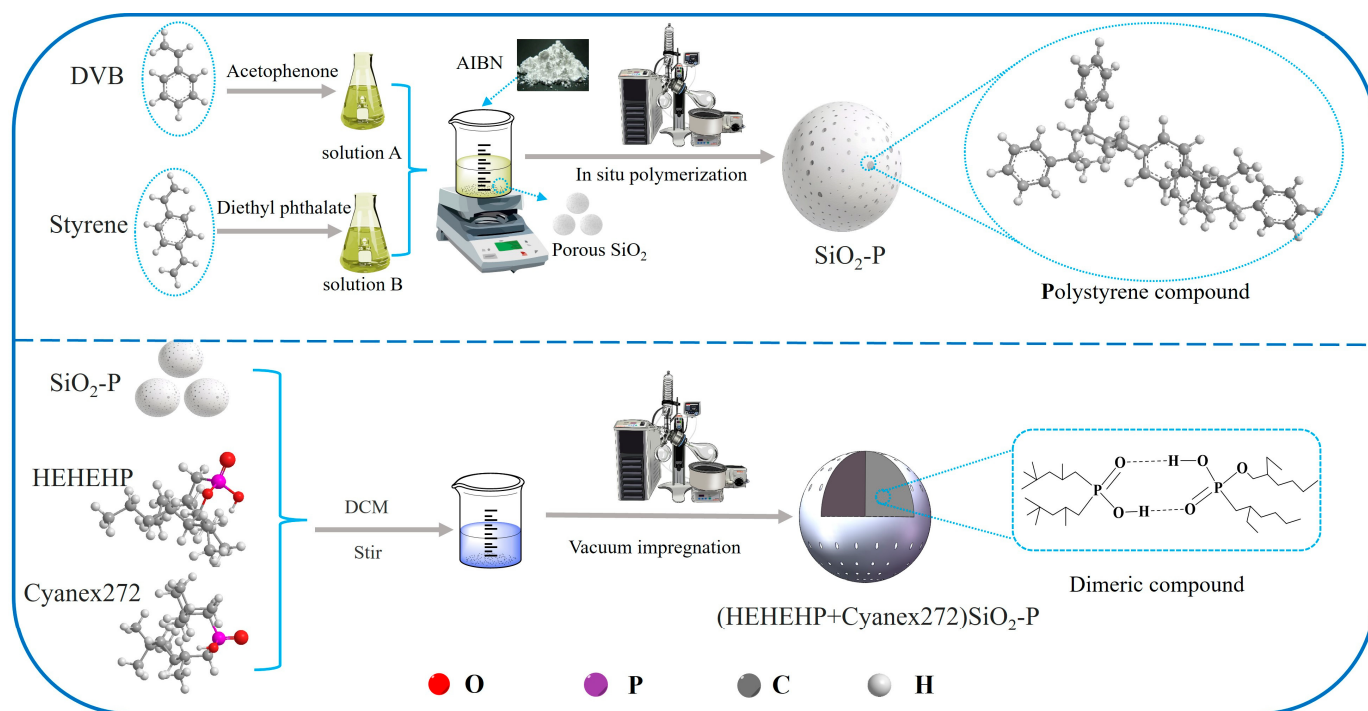


Figure 11. Flowchart of the synthesis process for $\text{SiO}_2\text{-P}$ and $(\text{HEHEHP} + \text{Cyanex272})/\text{SiO}_2\text{-P}$.

Then, to check the success synthesis of the resin and evaluate its physical and chemical properties, a series of methods were used to characterize the resin, including thermogravimetric differential scanning calorimetry (TG-DSC, STA 449 F3, Selb, Germany), Fourier-transform infrared spectrometry (FT-IR, Shimadzu IR Tracer 100, Kyoto, Japan), Brunauer–Emmett–Teller (BET, ASAP 2460, Norcross, GA, USA), scanning electron microscopy–energy spectrometry (SEM-EDS, Tescan Mira Lms, Brno, Czech Republic), and X-ray photoelectron spectroscopy (XPS, ESCALAB 139+, Thermo Science, Waltham, MA, USA).

3.3. Batch Experiments

Firstly, solutions of La, Ce, Pr, and Nd with a concentration of approximately 50 mM were prepared as the mother liquor. A total of 0.05 g $(\text{HEHEHP} + \text{Cyanex272})/\text{SiO}_2\text{-P}$ resin and 2.5 mL of solution were put in a 5 mL sealed glass vial and shaken at 160 rpm in a constant temperature water bath oscillator for 24 h (NTS-4000 B, EYELA, Tokyo, Japan). The removal or adsorption efficiency E (%), adsorption capacity Q (mg/g), distribution factor K_d (mL/g), and separation factor $SF_{A/B}$ were calculated by Equations (1)–(4).

$$E = \frac{(C_0 - C)}{C_0} \times 100\% \quad (1)$$

$$Q = (C_0 - C) \times \frac{V}{m} \quad (2)$$

$$K_d = \frac{(C_0 - C)}{C} \times \frac{V}{m} \quad (3)$$

$$SF_{A/B} = \frac{K_{dA}}{K_{dB}} \quad (4)$$

where C_0 (mg/L) and C (mg/L) are the initial and equilibrium concentrations of elements, respectively; V (mL) means the volume of the working solution; and m (g) is the mass of resin. All the batch experiments were conducted with two parallel samples simultaneously, ensuring that the test error was less than 5%.

3.4. Column Experiments

The core component of the column experimental setup was a double-layer glass column that could withstand high temperatures and strong acids. The inner layer was filled with functional resin (HEHEHP + Cyanex272)/SiO₂-P, while the outer layer was connected to a constant-temperature circulating water system. Other components included a peristaltic pump (BT 100FC, Kang Rui, Baoding, China), a constant-temperature device (MP-5H, Blue-pard Company, Shanghai, China), and an automatic collector (DC-1500C, EYELA, Tokyo, Japan). Various types of flexible and rigid tubes are used to connect these components. The feed liquid is loaded into clean beakers, and the effluent is collected using a 10 mL small flexible tube. Figure S11 presents the exterior view of the device. Details of the other column experiments can be found in the Supplementary Materials.

3.5. DFT Calculations

The Gaussian16 program was used for density functional theory (DFT) calculations. This scheme achieves efficient and accurate calculations of lanthanide complexes through the SDD (Simplified Due Diligence) ECP + 6-311G(d) hybrid basis set, and combines the IEFPCM solvent model to fully reproduce the experimental environment. All key parameters have been verified for convergence, and the calculation process adheres to the best practices in quantum chemistry, ensuring the results are repeatable and comparable [52]. The binding energy of metal ions and ligands was calculated from the single point energy of each optimized configuration, as expressed in Equation (5) [44]:

$$E_{\text{binding energy}} = (E_{\text{complex}} + E_{\text{H}_2\text{O}}) - (E_{\text{hydrated ion}} + E_{\text{ligands}}) \quad (5)$$

where E_{complex} , $E_{\text{H}_2\text{O}}$, $E_{\text{hydrated ion}}$, and E_{ligands} refer to the total energy (kcal/mol) of the ligand–metal complex, water molecules, hydrated metal ions, and ligands, respectively.

4. Conclusions

In this study, a synergistic extraction resin (HEHEHP + Cyanex272)/SiO₂-P was synthesized for the removal of trace impurities in light RE from high-concentration lanthanum solutions, enabling the production of ultra-high-purity lanthanum compounds. Batch experiments demonstrated that the resin achieved maximum separation factors for Ce³⁺/Pr³⁺/Nd³⁺ over La³⁺ through synergistic effects. The 1:1 blend ratio of HEHEHP and Cyanex272 optimized interfacial properties via hydrogen-bonded dimers, balancing basicity and steric effects to significantly enhance selectivity. All adsorbed ions were desorbed using 1 M HNO₃. The column experimental results showed that under ambient conditions, the resin enabled efficient separation of the light RE in the initial two stages, producing high-purity La³⁺ solutions (impurity removal > 98%) with a single column. The purification capacity reached 120.6 mg/g, surpassing most reported values. Characterization and DFT calculations confirmed that the adsorption mechanism involved ion exchange (P-OH) and coordination (P=O) interactions, with higher selectivity for LREE over La. An innovative method of removing impurities through adsorption was adopted for purification. This approach is more advanced than the traditional process of adsorption–desorption and multi-stage series purification, significantly enhancing work efficiency while reducing economic and time costs. This work presents an effective strategy for rare earth purification, offering strong industrial application potential.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/inorganics13090296/s1>, References [53,54] are cited in the Supplementary Materials.

Author Contributions: Conceptualization, M.H., S.N. and M.F.H.; Methodology, M.H.; Validation, S.N.; Formal analysis, M.H.; Investigation, M.H.; Resources, S.N. and Y.W.; Data curation, M.H. and J.L.; Writing—original draft, M.H.; Writing—review & editing, S.N.; Supervision, S.N. and L.C.; Funding acquisition, S.N. All authors have read and agreed to the published version of the manuscript.

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