International Journal of Materials and Chemistry 2025, 15(3): 59-63
DOI: 10.5923/j.ijmc.20251503.06

Study of Sorption of Lanthanum (III) Ions by PAN-co-DVB@DEA Anion Exchanger

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Abstract The sorption of lanthanum(III) ions by a novel anion exchange resin based on polyacrylonitrile-co-divinylbenzene modified with diethanolamine (PAN-co-DVB@DEA) was systematically investigated through equilibrium, kinetic, and thermodynamic analyses. Equilibrium sorption data at 20, 30, and 40 ℃ were fitted using Langmuir and Freundlich models. At 20 and 40 ℃, the Freundlich equation provided the best description ($R^2 > 0.997$), reflecting the heterogeneous nature of the sorbent surface and the predominance of physisorption. At 30 ℃, the Langmuir model achieved a slightly superior fit ($R^2 = 0.9997$), suggesting a tendency toward monolayer adsorption on a more uniform set of active sites. Kinetic studies at 20 ℃ were evaluated with pseudo-first-order, pseudo-second-order, Elovich, and Weber–Morris models. The intraparticle diffusion model of Weber–Morris provided the best correlation (R^2up to 0.89), indicating that diffusion of La^{3+} ions into the polymeric pores governs the sorption process, with additional contributions from boundary layer resistance. The Elovich model further confirmed surface heterogeneity and possible chemisorption contributions at the early stages of uptake. Thermodynamic parameters derived from Van't Hoff analysis revealed negative $\Delta G°$ values (–18.4 to –21.7 kJ/mol), confirming spontaneity, while positive $\Delta H°$ (+29.5 kJ/mol) and $\Delta S°$ (+0.163 kJ/mol·K) indicated endothermic sorption accompanied by increased interfacial disorder. Overall, the results demonstrate that PAN-co-DVB@DEA is a promising sorbent for rare-earth recovery, combining high capacity, heterogeneous binding, and diffusion-driven uptake mechanisms.

Keywords Lanthanum(III) sorption, Anion exchange resin, PAN-co-DVB, Diethanolamine modification, Adsorption isotherms, Kinetic modeling, Thermodynamic analysis

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1. Introduction

The increasing demand for rare earth elements (REEs) in advanced technologies such as electronics, renewable energy systems, catalysts, and magnetic materials has stimulated the development of efficient methods for their recovery from aqueous solutions. Lanthanum, one of the light rare earth elements, is widely used in optical materials, rechargeable batteries, and petroleum refining catalysts, making its selective separation and concentration a matter of both industrial and environmental importance. Conventional methods such as solvent extraction and precipitation often suffer from high reagent consumption, secondary pollution, and limited selectivity, thus driving the search for alternative approaches based on sorption technologies [1,2].

Polyacrylonitrile (PAN) is a versatile polymer widely employed as a matrix for the preparation of sorbents due to its mechanical stability, resistance to aggressive media, and ease of chemical modification. The introduction of divinylbenzene (DVB) as a crosslinker improves the rigidity and porosity of the polymer network, creating a stable backbone suitable for functionalization [3]. Modification with diethanolamine (DEA) provides amino and hydroxyl groups capable of chelation and ion-exchange interactions with metal cations, thereby enhancing the affinity of the sorbent toward rare earth ions [4,5].

To characterize the sorption properties of new sorbent materials, equilibrium, kinetic, and thermodynamic analyses are commonly applied. Classical adsorption models such as Langmuir and Freundlich allow evaluation of the homogeneity or heterogeneity of the sorption surface [6]. Kinetic models including pseudo-first-order, pseudo-second-order, Elovich, and Weber–Morris intraparticle diffusion describe the rate-controlling steps of adsorption [7]. Thermodynamic analysis based on the Van't Hoff equation provides insight into the spontaneity, enthalpy, and entropy changes accompanying the sorption process, which are critical for understanding the mechanism and practical applicability of the sorbent [8].

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Received: Sep. 3, 2025; Accepted: Sep. 26, 2025; Published: Sep. 29, 2025

The objective of the present work is to study the sorption of La^{3+} ions onto a novel anion exchange resin based on PAN-co-DVB modified with diethanolamine (PAN-co-DVB@DEA). Equilibrium, kinetic, and thermodynamic approaches are combined to provide a comprehensive characterization of the sorption process and to elucidate the underlying mechanism. The findings are expected to contribute to the development of efficient polymer-based sorbents for rare earth recovery from aqueous media [9].

2. Materials and Methods

Sorption experiments

Batch experiments were performed in a thermostated shaker (IKA KS 4000 i control, Germany) at 20, 30, and 40 ℃. For equilibrium isotherms, 0.1 g of resin was added to 100 mL of La^{3+} nitrate solutions (0.01–0.5 M). Contact time was 24 h to ensure equilibrium.

For kinetic studies, experiments were carried out at 20 ℃ using La^{3+} solutions of different concentrations (0.0125–1.0 N). Samples were withdrawn at specific intervals (5–180 min), filtered through 0.45 μm cellulose nitrate membranes, and analyzed.

La^{3+} concentration before and after sorption was determined using atomic absorption spectroscopy (AAS, PerkinElmer AAnalyst 400) and verified by inductively coupled plasma optical emission spectroscopy (ICP-OES, Agilent 720-ES).

Thermodynamic analysis

Experiments were conducted at 293, 303, and 313 K with constant initial La^{3+} concentration (0.2 N). Distribution coefficients (K) were calculated, and thermodynamic parameters (ΔG°, ΔH°, ΔS°) were determined from Van't Hoff plots.

Data analysis

All isotherm, kinetic, and thermodynamic models were fitted using OriginPro 2022 (OriginLab Corp., USA) and Microsoft Excel. Regression coefficients (R^2) and error functions were used to assess model adequacy.

3. Result and Discussion

1. Equilibrium sorption isotherms

The equilibrium uptake of La^{3+} ions by PAN-co-DVB@DEA was investigated at 20, 30, and 40 ℃ using the Langmuir and Freundlich adsorption models (Tables 1–3, Figs. 1). These models are frequently applied to evaluate sorption equilibria of metal ions on polymeric sorbents with heterogeneous surfaces [3,4]. The isotherms exhibited nonlinear profiles, reflecting the complex interplay between electrostatic attraction, coordination bonding with the introduced diethanolamine groups, and diffusion processes in the porous matrix.

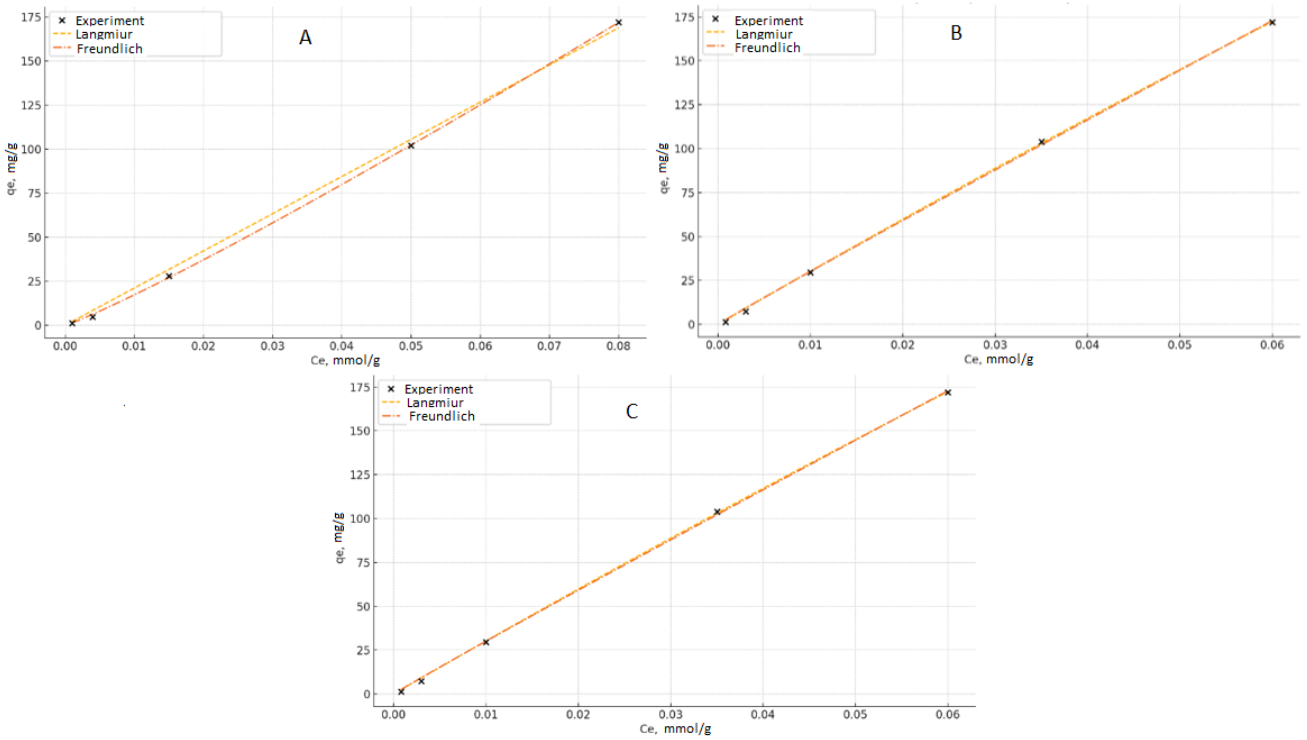

Figure 1. Sorption isotherms of La^{3+} ions on the anion exchanger AN-DVB-DEA according to the Langmuir and Freundlich models at temperatures of 20 (A), 30 (B) and 40 ℃ (C)

At 20 ℃, the Freundlich model provided the best correlation with the experimental data ($R^2 = 0.9998$), whereas the Langmuir equation yielded non-physical parameters ($q_{max} = 1.55 \times 10^8$, $K_L = 0.0$). Such behavior indicates that sorption cannot be described as monolayer adsorption on a homogeneous surface, but rather corresponds to a heterogeneous energy distribution of sorption sites. The Freundlich constant $n \approx 0.90$ suggests strong surface heterogeneity and highlights the predominance of physical adsorption processes, in which weak electrostatic interactions and hydrogen bonding dominate over uniform chemisorption.

Table 1. Isotherm parameters of La^{3+} sorption on PAN-co-DVB@DEA at 20 ℃

Model	q_{max} or K_F	K_L or n	R^2
Langmuir	1.55×10^8	0.0	0.9977
Freundlich	2.80×10^3	0.905	0.9998

At 30 ℃, both models fitted the experimental data with very high accuracy ($R^2 > 0.999$). However, the Langmuir model yielded slightly better agreement (qmax = 2841.7 mg/g, KL = 1.076, $R^2 = 0.9997$), implying that sorption under these conditions approaches monolayer coverage on a more uniform set of active sites.

Table 2. Isotherm parameters of La^{3+} sorption on PAN-co-DVB@DEA at 30 ℃

Model	q_{max} or K_F	K_L or n	R^2
Langmuir	2841.7	1.076	0.9997
Freundlich	2689.1	1.025	0.9995

The Freundlich constant n = 1.025 also indicates favorable sorption, as values greater than 1 are generally associated with a cooperative adsorption mechanism and reduced heterogeneity. The improvement in fit with the Langmuir model at 30 ℃ suggests that increasing temperature enhances the accessibility and uniformity of sorption sites, possibly by improving polymer swelling and exposing additional functional groups for metal ion binding.

Table 3. Isotherm parameters of La^{3+} sorption on PAN-co-DVB@DEA at 40 ℃

Model	q_{max} or K_F	K_L or n	R^2
Langmuir	1.15×10^8	0.0	0.9963
Freundlich	5.05×10^3	0.926	0.9974

At 40 ℃, the Freundlich model again outperformed Langmuir ($R^2 = 0.9974$ versus 0.9963). The Freundlich constant n = 0.93 reveals that surface heterogeneity persists at elevated temperatures, though less pronounced than at 20 ℃. These findings suggest that sorption of La^{3+} on PAN-co-DVB@DEA follows a dual mechanism: while at moderate temperature (30 ℃) sorption tends toward monolayer binding consistent with the Langmuir model, at lower and higher thermal regimes surface heterogeneity dominates, consistent with the Freundlich description. This dual behavior has been reported previously for amine-functionalized sorbents, where temperature-induced conformational changes of polymer chains modulate the accessibility and uniformity of sorption sites [7,8].

2. Sorption kinetics

The kinetics of La^{3+} uptake at 20 ℃ were analysed using pseudo-first-order, pseudo-second-order, Elovich, and Weber–Morris intraparticle diffusion models (Table 4). Kinetic modeling provides insights into the rate-controlling steps of adsorption and the possible contributions of surface and diffusion mechanisms [3,5].

The pseudo-first-order model was found inadequate, yielding identical kinetic constants across all concentrations and poor correlation coefficients ($R^2 = 0.56$–0.66). The pseudo-second-order model produced better fits only at the highest concentration (1.0 N), with $R^2 = 0.657$, but non-physical negative rate constants (k_2) at lower concentrations. This suggests that chemisorption involving valence forces or electron sharing is not the dominant mechanism in this system.

The Elovich model exhibited improved agreement, particularly at low concentrations, with R^2values up to 0.77. The high β values indicate significant energetic barriers and strong surface heterogeneity, consistent with the structural complexity of the DEA-modified sorbent. The moderate α values further reflect gradual saturation of active sites. Importantly, the Elovich model is often applicable to systems where chemisorption occurs on heterogeneous surfaces, and its applicability here suggests that weak complexation of La^{3+} with hydroxyl and amino groups may take place during the initial stages of adsorption.

The Weber–Morris intraparticle diffusion model provided the best overall description, with R^2 values in the range 0.79–0.89. The non-zero intercept values (C ranging from 0.36 to 48.1 mg/g) confirm that intraparticle diffusion is not the sole rate-limiting step; boundary layer resistance also contributes significantly. Nevertheless, the strong correlation with the intraparticle diffusion model indicates that the penetration of La^{3+} ions into the porous structure of PAN-co-DVB@DEA is the dominant mechanism controlling the kinetics of sorption.

These results highlight the complexity of La^{3+} uptake, which is not governed by a single kinetic regime but instead involves a combination of surface heterogeneity, boundary layer effects, and diffusion within the polymeric pores. Such behavior is typical for ion-exchange resins and functionalized polymer sorbents used for rare-earth ion recovery [7,8].

3. Thermodynamic parameters

Thermodynamic parameters were calculated from equilibrium data at 20, 30, and 40 ℃ using Van't Hoff plots (Table 5, Fig. 2). The negative values of $\Delta G°$ (–18.4 to –21.7 kJ/mol) across the studied temperature range confirm that La^{3+} sorption is spontaneous. The magnitude of $\Delta G°$ indicates that the process is predominantly physisorption, since values more negative than –40 kJ/mol are typically associated with chemisorption.

Table 4. Selected kinetic parameters of La^{3+} sorption on PAN-co-DVB@DEA at 20 ℃ (summarized for pseudo-second-order, pseudo-first-order, Elovich, and Weber–Morris models)

Concentration (N)	qe (mg/g)	k or α	Other param	R^2	Model
1.0	144.33	k_2 = 60659.4		0.6566	Pseudo-second-order
0.6	83.11	k_2 = –172590.6		0.6182	Pseudo-second-order
0.2	22.33	k_2 = –119868.9		0.5619	Pseudo-second-order
0.05	3.99	k_2 = –103635.1		0.6602	Pseudo-second-order
0.0125	1.06	k_2 = –861535.4		0.6549	Pseudo-second-order
1.0	144.33	k_1 = 1.0		0.6566	Pseudo-first-order
0.6	83.11	k_1 = 1.0		0.6182	Pseudo-first-order
0.2	22.33	k_1 = 1.0		0.5619	Pseudo-first-order
0.05	3.99	k_1 = 1.0		0.6602	Pseudo-first-order
0.0125	1.06	k_1 = 1.0		0.6549	Pseudo-first-order
1.0		α = 2.14e+245	β = 0.194	0.7635	Elovich
0.6		α = 7.15e+81	β = 0.3343	0.7299	Elovich
0.2		α = 9.14e+05	β = 1.231	0.6774	Elovich
0.05		α = 1.54	β = 7.0246	0.7662	Elovich
0.0125		α = 1.03	β = 26.4003	0.7604	Elovich
1.0		k_id = 2.4576	C = 48.12	0.8093	Weber–Morris
0.6		k_id = 1.5002	C = 24.88	0.8563	Weber–Morris
0.2		k_id = 0.4311	C = 5.75	0.8901	Weber–Morris
0.05		k_id = 0.0674	C = 1.35	0.8025	Weber–Morris
0.0125		k_id = 0.0179	C = 0.36	0.7895	Weber–Morris

Table 5. Thermodynamic parameters of La^{3+} sorption on PAN-co-DVB@DEA

T (K)	1/T (K^{-1})	q_e (mg/g)	Ce (mmol/L)	K = q_e/C_e	lnK	ΔG° (kJ/mol)
293.15	0.00341	28.0	0.015	1866.7	7.532	–18.4
303.15	0.00330	29.5	0.010	2950.0	7.990	–20.0
313.15	0.00319	32.3	0.008	4037.5	8.303	–21.7

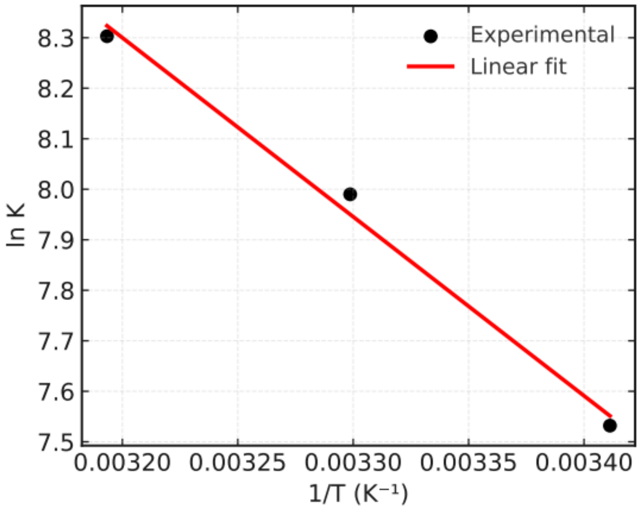

Figure 2. Van't Hoff plot for La^{3+} sorption

The positive enthalpy change (ΔH° = +29.5 kJ/mol) demonstrates that the process is endothermic, requiring energy input to promote sorption. This is consistent with the increase in sorption capacity observed with temperature. The endothermic nature of the process can be attributed to structural rearrangements of the sorbent matrix, polymer swelling, and the desolvation of La^{3+} ions prior to binding.

The positive entropy change (ΔS° = +0.163 kJ/mol·K) suggests increased randomness at the solid–solution interface, which may be explained by the release of water molecules from the hydration shell of La^{3+} upon complexation with the DEA functional groups. Similar entropy-driven processes have been reported for rare-earth ion sorption on functionalized organic matrices [7].

Taken together, the thermodynamic analysis supports the kinetic and equilibrium findings: La^{3+} sorption on PAN-co-DVB@DEA is a spontaneous, endothermic, diffusion-limited process that involves contributions from heterogeneous surface interactions and weak chemisorption.

4. Mechanistic considerations

The combined equilibrium, kinetic, and thermodynamic results provide a comprehensive picture of La^{3+} sorption on PAN-co-DVB@DEA. The best fits obtained with the Freundlich and Weber–Morris models emphasize the heterogeneous and diffusion-limited nature of the process. The high sorption capacities observed at elevated temperatures can be attributed to enhanced polymer swelling and exposure of active sites, while the heterogeneity parameters highlight the complexity of the binding environment created by the DEA groups.

The diethanolamine functionalities introduce both hydroxyl and amino groups capable of forming coordination bonds with La^{3+} ions. This dual binding functionality likely explains the observed mixed mechanism, where weak complexation (chemisorption) coexists with physisorption. The predominance of diffusion limitations further underscores the importance of pore structure and transport phenomena in determining overall sorption performance.

These findings align with previous reports on amine-functionalized polymers for rare-earth element recovery, where a balance between heterogeneous surface binding and diffusion constraints governs the adsorption mechanism [7,8]. The results suggest that PAN-co-DVB@DEA is a promising candidate for the selective recovery of rare-earth elements from dilute aqueous media.

4. Conclusions

The present study demonstrates that the anion exchange resin PAN-co-DVB modified with diethanolamine (PAN-co-DVB@DEA) exhibits a high affinity toward La^{3+} ions and provides valuable insights into the mechanism of sorption through equilibrium, kinetic, and thermodynamic analyses. Equilibrium studies revealed that the Freundlich model best described the isotherms at 20 and 40 ℃, reflecting the heterogeneous nature of the sorbent surface and the predominance of physisorption, while at 30 ℃ the Langmuir model achieved superior correlation, suggesting a tendency toward monolayer adsorption under more uniform conditions. The temperature-dependent shift between models highlights the structural flexibility of the DEA-modified polymer and its influence on surface heterogeneity.

Kinetic modeling confirmed that intraparticle diffusion is the dominant rate-limiting step, as indicated by the Weber–Morris model, while the Elovich equation further revealed contributions from heterogeneous surface binding and possible chemisorption during the early stages of uptake. Pseudo-first- and pseudo-second-order models were found to be less adequate for describing the kinetics of this system. Thermodynamic analysis showed that the sorption of La^{3+} is spontaneous ($\Delta G^\circ < 0$) and endothermic ($\Delta H^\circ = +29.5$ kJ/mol), accompanied by a positive entropy change ($\Delta S^\circ = +0.163$ kJ/mol·K), consistent with increased disorder at the solid–solution interface due to partial desolvation of lanthanum ions.

Overall, the results indicate that PAN-co-DVB@DEA is a promising sorbent for rare earth recovery from aqueous solutions. Its performance is governed by a diffusion-limited mechanism with significant contributions from heterogeneous binding and temperature-enhanced accessibility of functional sites. These findings provide a foundation for further optimization of functionalized polymeric sorbents for selective and efficient recovery of rare earth elements.

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