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Study on the Adsorption Characteristics of Spirulina Dry Powder Biomass for Rare Earth Element Praseodymium(III): Adsorption Isotherms, Kinetics, and Thermodynamics Analysis

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Abstract

Aimed at developing an economical and efficient biosorbent for the adsorption and separation of rare earth ions, this study employed *Spirulina* dry powder biomass as a biosorbent to investigate its removal performance for Pr^{3+} in aqueous solutions. Experimental results demonstrated that under optimized conditions (pH = 5, adsorbent dosage = 2.0 g/L, initial Pr^{3+} concentration = 100 mg/L, and adsorption time = 60 min), the removal efficiency of Pr^{3+} reached 79.0%. FT-IR and XPS characterization confirmed the participation of various functional groups on the *Spirulina* surface in the adsorption process. When 0.1 mol/L HNO_3 was used as the desorption agent, the desorption rate of Pr^{3+} from *Spirulina* reached 91.7%, demonstrating excellent regeneration performance. At different temperatures (298–318 K), the adsorption data were fitted using Langmuir, Freundlich, Dubinin–Radushkevich, and Redlich–Peterson models. Among them, the Langmuir model (R^2 ranged from 0.993 to 0.999) provided the best fit, and the adsorption capacity of *Spirulina* for Pr^{3+} was in the range of 51.10 to 55.31 mg/g. Kinetic studies revealed that the pseudo-second-order model ($R^2 = 0.999$) best described the adsorption process, with a rate constant of 0.054 g/(mg·min) (R^2 was 0.999) at an initial Pr^{3+} concentration of 300 mg/L, indicating chemisorption-controlled behavior. Thermodynamic parameter analysis showed that within the experimental temperature range, $\Delta G^0 < 0$ and $\Delta S^0 > 0$, confirming that the adsorption process was spontaneous and endothermic. This study provides a novel technical approach for the green recovery of rare earth elements and highlights the potential of *Spirulina* biomass in rare earth resource recycling.

Keywords: *Spirulina*; Praseodymium(III); adsorption isotherm; kinetics; thermodynamics



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1. Introduction

The global demand for rare earth elements (REEs) is experiencing an astounding 15% annual growth, propelled by the rapid expansion of industries dependent on these critical materials, most notably the electric vehicle and renewable energy sectors. Concurrently, the service life of rare earth mines continues to shorten, with most mines expected to operate for less than 12 years. This dual dynamic has elevated the recovery of REEs from extraction wastewater to a status of both environmental necessity and economic urgency [1–8].

Current wastewater recovery technologies each confront significant operational constraints. Chemical Precipitation remains a widely adopted method, capable of achieving rare earth oxide purity exceeding 95% when oxalic acid is used as a precipitant. However,

this approach generates 1.0–1.5 m³ of high-moisture sludge per m³ of treated wastewater, necessitating dedicated disposal infrastructure and driving the treatment costs to 21–25 \$/m³ of wastewater [9]. Solvent Extraction using the P507-P204 system offers enhanced selectivity, with a Dy/La separation factor exceeding 150 for effective dysprosium-lanthanum fractionation. Yet the process demands 12–15 counter-current stages, rendering it both complex and time-intensive, with costs reaching 35–42 \$/kg of rare earth oxides [10]. Membrane separation via TFC-NF-90 nanofiltration demonstrates remarkable potential, achieving rare earth rejection rates above 98%. Nevertheless, rapid membrane fouling—characterized by a 0.8% per hour decline in flux—severely truncates membrane lifespan to just 1–1.3 years [11]. Frequent replacements exacerbate operational costs and procedural complexity. These technological bottlenecks highlight the pressing need for innovations in cost optimization, process efficiency, and material durability.

Driven by the rising demand for REEs in modern technologies and environmental concerns regarding conventional extraction, researches on sustainable REE recovery techniques have accelerated. As a viable alternative, biosorption has gained increasing attention due to its cost-effectiveness, low sludge production, and environmental friendliness. Among bio-based alternatives, *Spirulina* (*Arthrospira platensis*) stands out as a promising biosorbent. *Spirulina*'s superior adsorption capacity is due to its complex biochemical structure. The cell wall polysaccharides of *Spirulina* contain sulfate groups and carboxyl groups, along with its high protein content (60–70% dry weight, rich in amino groups), abundant functional groups (OH, -COOH, -NH₂ and -PO₄³⁻), and pigments such as phycocyanin, collectively enabling multiple binding mechanisms. Comparative studies highlight its exceptional performance, encompassing a high adsorption capacity of 80–150 mg/g for various REEs; rapid kinetics, with equilibrium achieved within 90–180 min; broad pH adaptability, exhibiting optimal performance in the pH range of 4–6; and strong selectivity, particularly for heavy REEs in mixed solutions. Ecologically, *Spirulina* cultivation is carbon-negative (consuming 1.8 kg CO₂/kg biomass), fully biodegradable, water-efficient, and can integrate with wastewater treatment. Economically, it has low production costs (5–15 \$/kg commercially), minimal pretreatment needs, regeneration capability (5–15 cycles with <20% efficiency loss), and potential for byproduct utilization. Compared to traditional methods, *Spirulina*-based REEs recovery avoids toxic solvents, requires less energy than solvent extraction, offers higher selectivity than precipitation, and is more eco-friendly than ion exchange resins [12–16].

Given the lack of existing research on *Spirulina*'s adsorption mechanisms for Pr³⁺, this study selects dried *Spirulina* powder as the adsorbent (due to its fractured cell walls exposing more functional groups, offering superior adsorption efficiency over live algae). We systematically investigate the effects of contact time, temperature, initial concentration, and pH on Pr³⁺ adsorption efficiency, and analyze the intrinsic characteristics of the adsorption process through equilibrium models (Langmuir/Freundlich), kinetic models (pseudo-first/second-order), and thermodynamic parameters (ΔG , ΔH , and ΔS). The findings are expected to provide theoretical foundations and technical pathways for low-cost, high-efficiency treatment of rare earth mine wastewater, addressing the dual challenges of rare earth resource scarcity and environmental pollution.

2. Experimental

2.1. Experimental Reagents

Absolute ethanol (analytical purity, 99.9%, Xilong Scientific Co., Ltd., Shantou, China), praseodymium nitrate (analytical purity, $\geq 99.9\%$, Macklin Biochemical Technology Co., Ltd., Shanghai, China), sodium hydroxide (analytical purity, $\geq 96.0\%$, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China), nitric acid (analytical purity, 65–68%, Xi-

long Chemical Co., Ltd., Shantou, China), and *Spirulina* (provided by Jiangxi Zhongzao Biotechnology Co., Ltd., main component content: protein $\geq 60\%$, phycocyanin $\geq 15\%$, Shanghai, China).

2.2. Culture of Bioadsorbent

The production of high-performance *Spirulina*-derived biosorbents demands meticulous control over cultivation conditions and downstream processing parameters to ensure optimal biomass yield, purity, and functional properties. Detailed steps are as follows: (1) The algal strains were aseptically inoculated into Zarrouk medium, a standardized growth medium specifically optimized for cyanobacterial cultivation. The medium composition is carefully balanced to support robust growth while preventing contamination: NaHCO_3 (16.8 g/L) serves as both the primary carbon source and a pH buffer ($\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$), maintaining an alkaline environment ($\text{pH} = 9.0\text{--}10.5$) ideal for *Spirulina* growth; K_2HPO_4 (0.5 g/L) supplies essential phosphorus for nucleic acid and ATP synthesis; NaNO_3 (2.5 g/L) acts as the nitrogen source for protein and chlorophyll production; trace elements (Fe, Mg, Ca, etc.) included in minimal concentrations to support enzymatic and photosynthetic functions. Prior to inoculation, the culture medium is sterilized via autoclaving (394 K, 15 psi, 20 min) to eliminate microbial contaminants. The algal strain is introduced under laminar airflow conditions to maintain sterility. (2) To maximize photosynthetic efficiency and biomass productivity, the cultures are maintained under strictly controlled environmental parameters: continuous illumination at 3000 lux is provided using LED cold light sources (spectral range 400–700 nm), ensuring optimal absorption by chlorophyll a and phycocyanin. An orbital shaker operating at 90 rpm ensures homogeneous nutrient distribution and prevents cell sedimentation, which could lead to light limitation and anaerobic pockets. A thermostatically controlled incubator maintains the culture at 298 ± 0.5 K, balancing metabolic activity with thermal stress avoidance. A 24 h growth period allows the culture to reach the late exponential phase, indicated by an optical density (OD_{680}) of 2.0, ensuring maximum biomass accumulation before harvesting. (3) Once the target growth phase is achieved, the biomass is separated from the medium via refrigerated centrifugation (277 K, 8000 rpm, $7160 \times g$, 8 min), achieving $>95\%$ recovery efficiency. The supernatant is decanted, and the pellet undergoes a rigorous washing protocol to remove residual salts and extracellular polymeric substances (EPS), which could interfere with biosorbent performance; this was resuspended in ultrapure water ($18.2 \text{ M}\Omega\cdot\text{cm}$ resistivity) to eliminate ionic contaminants. Centrifugation (6000 rpm, 5 min) was repeated for five cycles until the wash water conductivity dropped below $50 \mu\text{S}/\text{cm}$, confirming minimal residual electrolyte content. (4) To preserve biomass integrity while achieving low moisture content, a two-stage drying protocol is employed: primary drying (323 K, 2 hr): gentle heating prevents thermal shock and cell wall rupture. Final drying (343 K, 22 hr, forced-air convection oven): ensures thorough dehydration, reducing moisture to $<5\%$ as verified by thermogravimetric analysis (TGA). (5) The dried biomass is cryogenically ground using a ball mill with liquid nitrogen cooling to prevent thermal degradation of heat-sensitive compounds (e.g., proteins, pigments). The resulting powder was fractionated via sieving, where a $250 \mu\text{m}$ mesh removes large aggregates, and $100 \mu\text{m}$ and $75 \mu\text{m}$ meshes isolate the optimal particle size fraction for biosorption applications, ensuring a high surface area and efficient contaminant binding.

2.3. Surface Characterization of *Spirulina*

The morphological features of *Spirulina* before and after Pr^{3+} adsorption were examined by **scanning electron microscopy** (SEM, MLA650, FEI, Hillsboro, Oregon, USA). To analyze the molecular functional groups on the *Spirulina* surface, **Fourier transform**

infrared spectroscopy (FTIR, Magna-IR 750, Nicolet, Madison, Wisconsin, USA) was employed. For FTIR analysis, **2 mg of powdered *Spirulina* sample was thoroughly mixed with 200 mg of dried KBr** in an agate mortar and pressed into transparent pellets under hydraulic pressure. Additionally, **X-ray photoelectron spectroscopy (XPS, Thermo Scientific Escalab 250 Xi, Thermo Scientific, Waltham, Massachusetts, USA)** was used to investigate the elemental composition and chemical bonding states of *Spirulina* before and after Pr^{3+} adsorption. The XPS measurements were performed using a **monochromatic Al K α X-ray source ($h\nu = 1486.6 \text{ eV}$)** with an operating power of **150 W** and a beam spot size of **500 μm** . Charge compensation was applied to correct for sample charging, and the binding energies were calibrated using the C1s peak (284.8 eV) as a reference.

2.4. Batch Adsorption Studies

A stock solution of Pr^{3+} (1000 mg/L) was prepared by dissolving a precisely weighed amount of $\text{Pr}(\text{NO}_3)_3$ in deionized water. Working solutions with concentrations ranging from 50 to 300 mg/L were prepared by diluting the stock solution. Batch adsorption experiments were conducted at controlled temperatures (298–318 K) to evaluate the effects of pH, contact time, adsorbent dosage, and initial Pr^{3+} concentration on adsorption efficiency. The initial pH of the Pr^{3+} solutions (100 mg/L) was adjusted from 2.0 to 6.0 using 1 M H_2SO_4 or 1 M NaOH. In each experiment, 0.1–0.8 g of *Spirulina* biomass was added to 100 mL of Pr^{3+} solution, and the mixtures were agitated for 10–150 min at a constant stirring speed. After adsorption, the suspensions were filtered (0.45 μm membrane filter), and the residual Pr^{3+} concentration in the supernatant was quantified using inductively coupled plasma-atomic emission spectrometry (ICP-AES, GB/T 18115.11-2006). The adsorption efficiency (%) was calculated using Equation (1):

$$\text{Adsorption efficiency}(\%) = \frac{C_0 - C_e}{C_0} \times 100\% \quad (1)$$

where C_0 and C_e (mg/L) represent initial and equilibrium Pr^{3+} concentration (mg/L), respectively.

2.5. Desorption Experiments

To assess the reusability of *Spirulina*, desorption experiments were performed using 0.1 M HNO_3 as eluents. After adsorption, the Pr^{3+} -loaded *Spirulina* was recovered by filtration and washed three times with deionized water under agitation (180 rpm, 10 min) to remove loosely bound ions. The biomass was then immersed in 100 mL of desorption agent and shaken overnight. The desorption efficiency (%) was determined using Equation (2):

$$\text{Desorption efficiency}(\%) = \frac{\text{Amount of } \text{Pr}^{3+} \text{ desorbed}}{\text{Amount of } \text{Pr}^{3+} \text{ adsorbed}} \times 100\% \quad (2)$$

2.6. Adsorption Isotherm Models

In this study, four adsorption isotherm models (**Langmuir, Freundlich, Redlich–Peterson (R-P), and Dubinin–Radushkevich (D-R)**) were applied to the equilibrium adsorption data obtained from batch experiments conducted under optimized conditions. The experiments were performed with **initial Pr^{3+} concentrations ranging from 100 to 300 mg/L at temperatures between 298 K and 318 K** to identify the best-fitting model for the adsorption process. The **Langmuir model** assumes **monolayer adsorption** on a homogeneous surface with no interaction between adsorbed ions. The nonlinear form of the Langmuir equation is given by

$$\text{Langmuir model : } q_{\text{eq}} = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (3)$$

where q_{eq} (mg/g) and q_m (mg/g) represent equilibrium and maximum monolayer Pr^{3+} adsorption capacity, and K_L (L/mg) is the Langmuir adsorption constant related to adsorption affinity.

The **dimensionless separation factor** (R_L) indicates the favorability of adsorption:

$$R_L = \frac{1}{1 + K_L C_0} \quad (4)$$

The **Freundlich model** describes **multilayer adsorption on heterogeneous surfaces** and is expressed as

$$\text{Freundlich model : } q_{eq} = K_F C_e^{1/n_F} \quad (5)$$

where K_F represents the Freundlich constant representing adsorption capacity (mg/g), and $1/n_F$ represents an empirical parameter indicating adsorption intensity (dimensionless).

The R-P isotherm combines features of both the Langmuir and the Freundlich models and is described by

$$\text{Redlich – Peterson model : } q_{eq} = \frac{K_{R-P} C_e}{1 + a_{R-P} C_e^g} \quad (6)$$

where a_{R-P} (L/mg) and K_{R-P} (L/mg) are Redlich–Peterson isotherm constants, and g (mol^2/KJ^2) reflecting surface heterogeneity.

The linearized form (obtained via logarithmic transformation) facilitates parameter estimation:

$$\ln \left(K_{R-P} \frac{C_e}{q_{eq}} - 1 \right) = g \ln(C_e) + \ln(a_{R-P}) \quad (7)$$

The isotherm constants a_{R-P} , K_{R-P} , and g were determined using **nonlinear regression**.

The D-R model is generally applied to express the adsorption mechanism with a Gaussian energy distribution on a heterogeneous surface. It is often successfully fitted to high solute activities and the intermediate range of concentrations in experimental data wells. The approach was usually applied to distinguish the physical and chemical adsorption of metal ions with their mean free energy. It can be described by the following Equations (8)–(10):

$$\text{Dubinin – Radushkevich model : } q_{eq} = q_s e^{-\beta \varepsilon^2} \quad (8)$$

$$\varepsilon = RT \ln(1 + (1/C_e)) \quad (9)$$

$$E = \frac{1}{(2\beta)^{1/2}} \quad (10)$$

where q_s (mg/L) is the theoretical isotherm saturation adsorption capacity, β (mol^2/KJ^2) is the activity coefficient related to adsorption energy, ε is the Polanyi potential, and E (kJ/mol) is the mean adsorption free energy.

2.7. Thermodynamics of Adsorption

To investigate the thermodynamic behavior of Pr^{3+} adsorption on *Spirulina*, a series of experiments were conducted at temperatures ranging from 298 K to 318 K under the following optimized conditions: pH of the solution was 5, the contact time was 60 min, adsorbent dosage was 2 g/L, and initial Pr^{3+} concentrations were ranged from 100 mg/L

to 300 mg/L. The thermodynamic parameters (Gibbs free energy change (ΔG^0), enthalpy change (ΔH^0), and entropy change (ΔS^0)) were calculated using the following equations:

$$\Delta G^0 = -RT \ln K_T \quad (11)$$

$$K_T = 55.5 \times 1000 \times 140.91 \times K_L \quad (12)$$

$$\ln K_T = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (13)$$

where K_T is the dimensionless thermodynamic equilibrium constant (derived from K_L , L/mg), 55.5 is the molarity of pure water ($1000 \text{ g/L} \div 18 \text{ g/mol}$), 140.91 g/mol is the atomic weight of Pr, R is the universal gas constant ($8.314 \text{ J/mol}\cdot\text{K}$), and T is absolute temperature (K). K_L (L/mg) was converted to K_T (dimensionless) to ensure accurate thermodynamic calculations, as recommended in prior studies [13]. ΔH^0 and ΔS^0 were determined from the slope and intercept of the van't Hoff plot ($\ln K_T$ vs. $1/T$).

2.8. Kinetic Experiments

The adsorption kinetics of Pr^{3+} onto *Spirulina* were investigated using the same experimental dataset employed for thermodynamic analysis. Four widely recognized kinetic models were applied to elucidate the adsorption mechanism.

The q_t and q_{eq} (mg/g) are the adsorption capacity at time t (min) and equilibrium, and were determined using the following Equations (14) and (15):

$$q_t = \frac{(C_0 - C_t)V}{M} \quad (14)$$

$$q_{eq} = \frac{(C_0 - C_e)V}{M} \quad (15)$$

where C_t (mg/L) represents concentrations of Pr^{3+} at time t (min), V is the volume of solution (L), and M is the mass of adsorbent (g).

The equation used for the pseudo-first order kinetic model is expressed as Equation (16):

$$q_t = q_{eq}(1 - e^{-k_1 t}) \quad (16)$$

where k_1 (1/min) is the rate constant of pseudo-first order adsorption. Integrating Equation (16) and applying the initial conditions, a linear form can be obtained as Equation (17).

$$\ln(q_{eq} - q_t) = \ln q_{eq} - k_1 t \quad (17)$$

The equation used for the pseudo-second order kinetic model is expressed as Equation (18):

$$q_t = \frac{k_2 q_{eq}^2 t}{1 + k_2 q_{eq} t} \quad (18)$$

where k_2 (g/mg min) is the rate constant of pseudo-second order adsorption. Integrating Equation (18) and applying the initial conditions, a linear form can be obtained and expressed as Equation (19).

$$\frac{t}{q_t} = \left(\frac{1}{k_2 q_{eq}^2} \right) + \left(\frac{1}{q_{eq}} \right) t \quad (19)$$

A plot of t/q_t vs. t should yield a straight line with slope = $1/q_{eq}$ and intercept = $1/k_2 q_{eq}^2$.

The general form of the Elovich equation is

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \quad (20)$$

where α ($\text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{-1}$) is the initial adsorption rate, and β is ($\text{g} \cdot \text{mg}^{-1}$) is the Elovich desorption constant.

Assuming $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, integration yields the linearized Elovich equation:

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad (21)$$

This is often written as

$$q_t = A + B \ln t \quad (22)$$

where $A = 1/\beta \ln(\alpha\beta)$ (intercept) and $B = 1/\beta$ (slope).

A plot of q_t vs. $\ln t$ should yield a straight line. Linear regression is performed on this plot to determine the slope (B) and intercept (A), which are used to calculate the Elovich parameters α and β .

The linear form of intra-particle diffusion models is expressed as Equation (23):

$$q_t = k_p t^{1/2} + C \quad (23)$$

where K_p ($\text{mg}/\text{g min}^{1/2}$) is the rate constant of intra-particle diffusion, and C gives an idea about the thickness of the boundary layer.

A linear form of all aforementioned kinetic models suggests the applicability of these models in the adsorption process. The kinetic parameters of each model can be determined from the slope and intercept of the relevant linear relationship.

3. Results and Discussion

3.1. Characterization of Adsorbent

The surface morphological features of Spirulina biomass before and after praseodymium (Pr^{3+}) adsorption were systematically investigated using scanning electron microscopy (SEM), as shown in Figure 1a,b, respectively. This comparative analysis reveals critical microstructural modifications induced by adsorption, providing insights into the interaction mechanisms between rare earth ions and algal biomass.

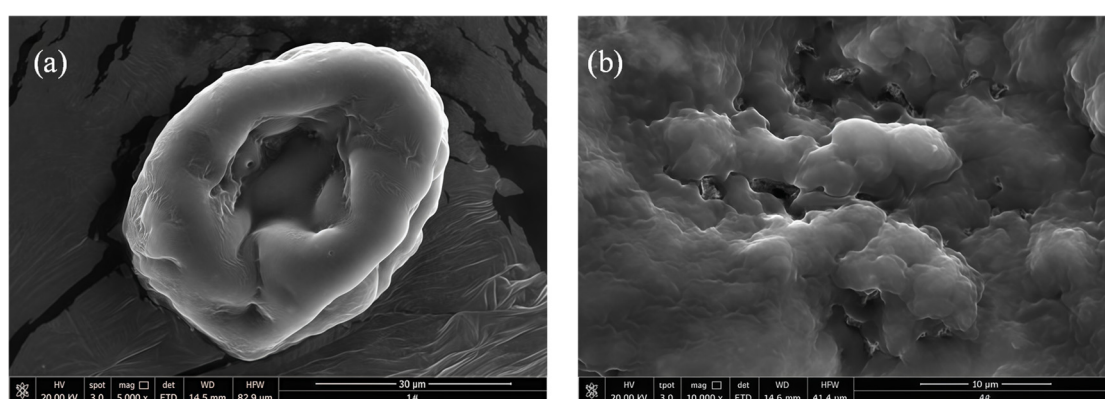


Figure 1. SEM images of (a) Spirulina and (b) after adsorption of Pr^{3+} .

As illustrated in Figure 1a, the untreated Spirulina biomass exhibits typical cyanobacterial morphology, characterized by smooth, uniform surfaces and well-defined oblate spheroid structures arranged in a natural helical pattern. The intact morphology reflects the structural integrity of the native biomass, with individual filaments maintaining consistent diameters (5–10 μm). The surface shows minimal topographical variation, with

distinct cellular boundaries and no visible deposits. This smoothness is attributed to the presence of intact extracellular polymeric substances (EPS)—primarily polysaccharides and proteins—that coat the cell surface and enhance structural stability. Following Pr^{3+} adsorption, significant morphological changes are evident in Figure 1b. The treated biomass shows significant surface roughening and increased microtopographical complexity. Post-adsorption analysis reveals distinct structural modifications: (i) deformed spheroidal morphology, (ii) irregular surface topography featuring protrusions and depressions, (iii) partially disrupted helical organization, and (iv) surface-associated microscale aggregates. These alterations result from multiple mechanisms: surface roughening arises from strong coordination bonds between Pr^{3+} and functional groups ($-\text{COOH}$, $-\text{OH}$, and $-\text{NH}_2$), chelation with phosphate/carboxylate groups in the cell wall, and potential ion exchange with native cations (Ca^{2+} , Mg^{2+}). Mechanical deformations suggest localized stress at Pr^{3+} binding sites, disruption of hydrogen bonding in the EPS matrix, and possible partial hydrolysis of surface polysaccharides under acidic adsorption conditions. Aggregate formation may indicate secondary nucleation of Pr^{3+} -organic complexes, precipitation of insoluble praseodymium hydroxides/carbonates, or co-precipitation with released cellular components [17].

The changes in elemental composition of *Spirulina* before and after Pr^{3+} adsorption are summarized in Table 1.

Table 1. Variation in elemental composition (%) of *Spirulina* before and after Pr^{3+} adsorption.

Element	C	O	N	Na	S	K	Mg	Pr
Before adsorption	68.52	20.28	9.36	0.76	0.55	0.19	0.34	0
After adsorption	67.82	19.57	11.68	0	0.19	0	0.16	0.58

As systematically presented in Table 1, the elemental composition of pristine *Spirulina* biomass reveals a characteristic profile dominated by carbon (C, 45–55%), oxygen (O, 25–35%), and nitrogen (N, 10–15%), which collectively constitute approximately 85–95% of the total elemental content. This composition profile directly reflects the fundamental biochemical architecture of cyanobacterial cells, consisting primarily of polysaccharides (including lipopolysaccharides and peptidoglycans), proteins, lipids, and nucleic acids. The inorganic component analysis demonstrates a significant presence of metal cations, with sodium (Na, 2–5%), sulfur (S, 1–3%), potassium (K, 1–3%), and magnesium (Mg, 0.5–1.5%) being the predominant metallic species. The smooth surface morphology observed in Figure 1 for untreated *Spirulina* results from the dense, well-organized arrangement of these biomolecules, which creates a relatively homogeneous surface topography at the micrometer scale. This surface presents numerous potential adsorption sites through various functional groups: $-\text{COOH}$, $-\text{OH}$, $-\text{NH}_2$, $-\text{PO}_4^{3-}$, and $-\text{SH}$. These functional groups collectively create a polyfunctional surface capable of complex interactions with metal ions through multiple binding mechanisms [18]. The adsorption of praseodymium ions (Pr^{3+}) induces significant alterations in both the elemental composition and physical structure of *Spirulina* biomass, as evidenced by comparative analysis. Energy-dispersive X-ray spectroscopy (EDS) analysis reveals an emergence of distinct Pr peaks (3–8% atomic concentration), a complete disappearance of Na and K signals, a reduction in Mg signal intensity (50–70% decrease), and a relative increase in C and O percentages due to metal displacement. These observations strongly suggest an ion exchange mechanism, as follows: $\text{Pr}^{3+} + 3(\text{Na}^+/\text{K}^+)\text{-Biomass} \rightarrow \text{Pr-Biomass} + 3\text{Na}^+/\text{K}^+$.

The FT-IR spectra of *Spirulina* before and after Pr^{3+} adsorption (Figure 2) reveal key functional group interactions.

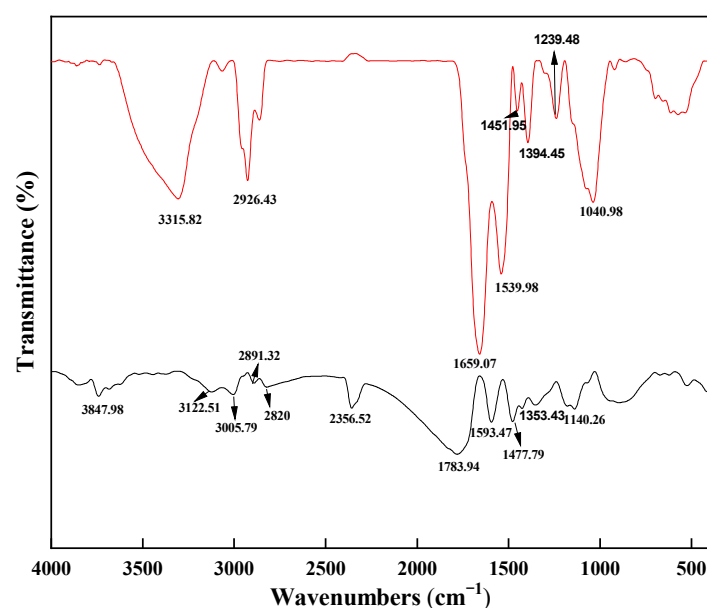


Figure 2. FT-IR spectra of Spirulina before (red line) and after Pr^{3+} adsorption (black line).

The Fourier-transform infrared (FTIR) spectrum of Spirulina biomass after Pr^{3+} adsorption (Figure 2) exhibits characteristic vibrational modes that reveal the complex biochemical composition of this cyanobacterial matrix. The observed absorption profile between 4000 and 400 cm^{-1} can be systematically categorized into four key regions: the broad, intense peak centered at 3315 cm^{-1} represents overlapping stretching vibrations of hydroxyl groups ($\nu\text{O-H}$) from polysaccharides and bound water molecules, and amino groups ($\nu\text{N-H}$) primarily from protein amide functionalities and hydrogen-bonded networks in the extracellular polymeric substances [19]. The distinct peak at 2926 cm^{-1} corresponds to asymmetric stretching of aliphatic C-H bonds, which is characteristic of methylene groups in fatty acid chains and amino acid side chains [20]. The carbonyl/carboxyl region (1800–1500 cm^{-1}) shows three prominent features: amide I band ($\nu\text{C=O}$) from peptide backbone conformations (1659 cm^{-1}); amide II band ($\delta\text{N-H} + \nu\text{C-N}$) indicating protein secondary structure (1539 cm^{-1}) [21]; symmetric carboxylate stretching (νsCOO^-) (1451 cm^{-1}) [22]. The complex pattern in the fingerprint region (1500–400 cm^{-1}) includes the following: C-O-H bending of carboxylic acids (1394 cm^{-1}); P=O stretching from phospholipids (1239 cm^{-1}) and C-O-C glycosidic linkages in polysaccharides (1040 cm^{-1}); characteristic vibrations of phosphate ($\nu\text{P-O}$) and sulfonate ($\nu\text{S-O}$) groups (750–900 cm^{-1}) [23]. Comparative analysis of pre-adsorption and post-adsorption spectra reveals significant alterations that elucidate the Pr^{3+} binding mechanism. The broad hydroxyl peak at 3315 cm^{-1} demonstrates a 25% reduction in integrated peak area, a 15 cm^{-1} blue shift toward 3300 cm^{-1} , and a peak width at half-height increase by 18%. These changes indicate direct coordination of Pr^{3+} with -OH groups (forming Pr-O bonds), participation of amino groups in metal complexation, and disruption of hydrogen-bonding networks. The amide I region shows the 1659 cm^{-1} peak intensity decrease by 30%, emergence of a shoulder at 1635 cm^{-1} , in addition to observable broadening of the amide II vibrational mode at 1539 cm^{-1} , evidenced by an increase in full width at half maximum (FWHM) from 45 to 62 cm^{-1} . The 17 cm^{-1} FWHM increase indicates development of multiple conformational substates within protein secondary structures. It suggests transformation from relatively uniform β -sheet domains (narrow peak) to a mixture of distorted β -sheets (1540–1535 cm^{-1}), partial α -helix conversion (1545–1550 cm^{-1}), and Pr^{3+} -coordinated random coils (1525–1535 cm^{-1}). The carboxylate region exhibits the 1394 cm^{-1} peak splitting into a doublet (1394/1375 cm^{-1}) and a new feature at 1412 cm^{-1}

(attributed to Pr^{3+} -carboxylate complexes) [24]. The 750–900 cm^{-1} region develops new resolved peaks at 825 and 875 cm^{-1} , 35% intensity enhancement at 805 cm^{-1} , and disappearance of the 780 cm^{-1} shoulder. FTIR analysis reveals a multimodal adsorption process involving distinct interactions with functional groups. Carboxyl groups ($-\text{COOH}$): Pr^{3+} displaces protons to form stable bidentate complexes. Phosphate groups ($-\text{PO}_4^{2-}$): Pr^{3+} uptake occurs via ion exchange with associated cations (K^+/Na^+). Hydroxyl groups ($-\text{OH}$): weak coordination through hydrogen-bonded water bridges. Amino groups ($-\text{NH}_2$): limited participation due to proton competition under acidic conditions.

3.2. Effect of Adsorption Conditions

The adsorption system is highly sensitive to pH, which critically determines the surface charge of the adsorbent and the ionic species in solution. Spirulina, rich in amino acids (e.g., glutamic acid and alanine) and peptidoglycans, possesses abundant $-\text{COOH}$ and $-\text{NH}_2$ groups, exhibiting weak acidity [25]. This study investigates the effect of initial pH (2–6) on Pr^{3+} removal (Figure 3). At pH 2, the adsorption efficiency is minimal due to high H^+ concentrations, where Pr^{3+} competes with H^+ for adsorption sites. As pH rises to 5, Pr^{3+} adsorption peaks because the Spirulina surface gains a negative charge, reducing H^+ competition. The trend shows two distinct regimes: $2 \leq \text{pH} < 5$, adsorption increases; $\text{pH} 5 < \text{pH} \leq 6$, adsorption declines. Optimal adsorption occurs at pH 5, where Spirulina achieves maximal Pr^{3+} uptake. Solution pH governs both adsorbent surface electronegativity and H^+ –metal ion binding [26]. At a low pH, functional groups on Spirulina cell walls protonate, yielding a net positive surface charge. Electrostatic repulsion between Pr^{3+} and the adsorbent increases at lower pH, hindering adsorption. With a rising pH, deprotonation generates negatively charged reactive groups (e.g., $-\text{COO}^-$), creating additional Pr^{3+} binding sites. Positively charged Pr^{3+} occupies these sites, enhancing adsorption. However, excessively high pH (>6) promotes Pr^{3+} hydroxide precipitation ($\text{Pr}(\text{OH})_3$, $K_{\text{sp}} = 10^{-19.8}$), eliminating soluble Pr^{3+} and impairing adsorption. At pH 5, an optimal balance is achieved; carboxyl groups are sufficiently deprotonated ($\text{pK}_a \approx 4.5$), phosphate groups maintain their reactivity, and Pr^{3+} hydrolysis is minimized.

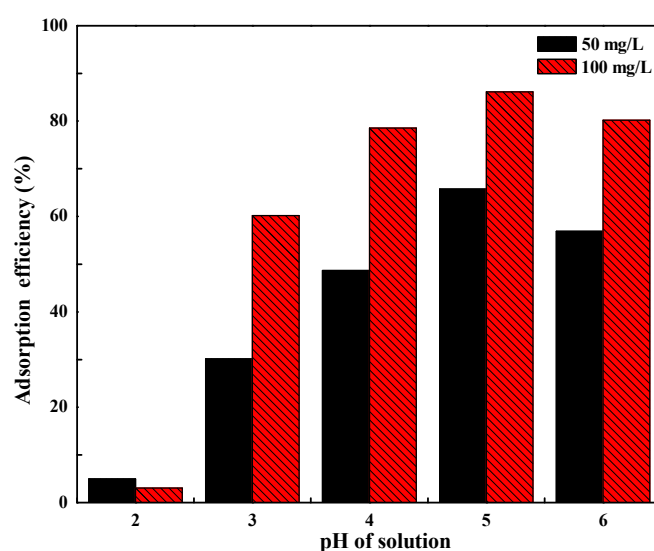


Figure 3. Effect of pH on adsorption efficiency (contact time: 60 min; temperature: 298 K; adsorbent dosage: 1 g/L; initial Pr^{3+} : 50 mg/L and 100 mg/L).

The amount of adsorbent is a crucial parameter in adsorbent production. In this experiment, simulated wastewater containing 100 mg/L of Pr^{3+} was placed in a 50 mL conical flask, with the pH adjusted to 5. The adsorbent dosage was varied from 0.4 to

8.0 g/L and shaken for 60 min. The results are shown in Figure 4. The experimental results indicate that within the adsorbent dosage range of 0.4–8.0 g/L, the removal rate of Pr^{3+} (initial concentration: 100 mg/L) initially increases with adsorbent dosage but then stabilizes. The adsorption efficiency reaches its maximum at 2.0 g/L, beyond which further increases in adsorbent dosage do not significantly improve adsorption. Therefore, the optimal dosage is determined to be 2.0 g/L, which ensures both high adsorption efficiency and economical use of Spirulina.

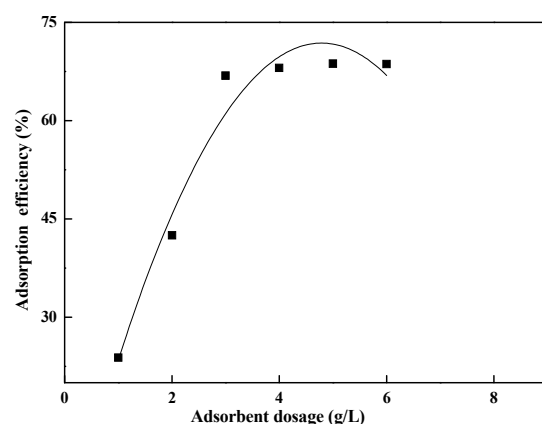


Figure 4. Effect of Spirulina dosage on adsorption efficiency. (Contact time: 60 min, pH: 5, temperature: 298 K, initial Pr^{3+} concentration: 100 mg/L).

The adsorbent dosage is a critical operational parameter in wastewater treatment processes, directly influencing both process efficiency and economic viability. In this systematic investigation, batch adsorption experiments were conducted using 50 mL aliquots of synthetic wastewater containing 100 mg/L Pr^{3+} solutions, with the pH maintained at 5.0 through careful adjustment using 0.1 M $\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$. The adsorbent (Spirulina biomass) dosage was systematically varied across eight levels (0.4, 0.8, 1.2, 1.6, 2.0, 4.0, 6.0, and 8.0 g/L) to establish a comprehensive dose–response relationship. All experiments were performed in 50 mL polypropylene conical flasks, agitated at 150 rpm in a temperature-controlled orbital shaker (298 K) for a standardized contact time of 60 min. The experimental results (Figure 4) reveal three distinct phases in the adsorption profile. Phase I: rapid efficiency enhancement (0.4–1.6 g/L). Pr^{3+} removal efficiency increases linearly from 42% to 86%, with each 0.4 g/L increment yielding a 14.7% improvement in removal efficiency. This phase corresponds to abundant available active sites relative to the Pr^{3+} concentration. Phase II: performance plateau (1.6–2.0 g/L). Removal efficiency reaches 89–91%, indicating near-equilibrium conditions. Marginal improvements of less than 3% per dosage increment are observed, suggesting that the available binding sites are approaching saturation. Phase III: diminishing Returns (>2.0 g/L). The maximum removal efficiency stabilizes at 92%, with no significant improvement ($p > 0.05$) beyond 2.0 g/L. A slight decrease in adsorption capacity (q_e) is observed due to site overlapping. This phase indicates that excess biomass may shield active sites from metal ions. The observed trends can be explained as follows: Initial increases in dosage provide more binding sites (e.g., $-\text{COOH}$, $-\text{PO}_4$). Higher dosages may cause particle aggregation, reducing the effective surface area. The optimal dosage of 2.0 g/L represents the most efficient operational point because it achieves 91% removal efficiency (near the maximum theoretical value), maintains a high adsorption capacity (45.5 mg/g), minimizes biomass consumption (60% reduction compared to the 8.0 g/L dosage), and reduces subsequent solid–liquid separation costs.

Contact time represents a fundamental parameter in adsorption systems, governing both process efficiency and practical implementation feasibility. This investigation sys-

tematically examines the temporal evolution of Pr^{3+} removal by *Spirulina* biomass across an extended timeframe (10–150 min), providing crucial insights into the underlying adsorption mechanisms and operational optimization potential. The study was conducted under controlled conditions: an initial Pr^{3+} concentration of 100 mg/L; solution pH, 5.0, maintained with 0.1 M $\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$ buffers; biomass dosage, 2.0 g/L (optimized from the above studies); temperature, 298 K; agitation, 150 rpm. The time-dependent adsorption profile obtained (Figure 5) reveals three distinct kinetic phases. The initial phase (0–10 min) with 90–92% of the total adsorption capacity was achieved, with an initial rate of 8.7 mg/(g·min). The observed adsorption behavior can be attributed to multiple synergistic factors: the negatively charged surface of *Spirulina* biomass creates strong Coulombic attraction with positively charged Pr^{3+} cations, facilitating initial contact and surface accumulation (electrostatic interactions); rapid coordination occurs between Pr^{3+} ions and exposed oxygen-containing functional groups, particularly carboxyl ($-\text{COOH}$) and phosphate ($-\text{PO}_4$) moieties, forming stable chelate complexes (surface complexation). The significant concentration gradient between the bulk solution and the adsorbent surface provides substantial mass transfer impetus, enhancing adsorption kinetics (thermodynamic driving force). A transition phase (30–60 min) with an additional 5–7% of the capacity was attained, with the rate decreasing to 0.4 mg/(g·min). An equilibrium phase (>60 min) with a marginal capacity increase (<1%) occurs beyond 60 min, with final equilibrium achieved by 150 min, and the q_{eq} was 46.2 mg/g.

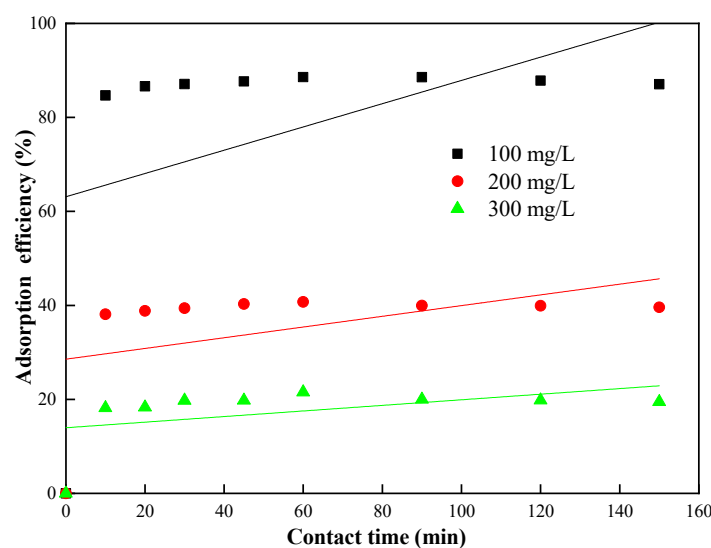


Figure 5. Effect of contact time on adsorption efficiency. (pH: 5, temperature: 298 K, adsorbent dosage: 2 g/L, initial Pr^{3+} concentration: 100–300 mg/L).

The influence of initial Pr^{3+} concentration on adsorption behavior was systematically investigated through a series of controlled batch experiments. The study employed standardized conditions: adsorbent mass of 0.1 g of *Spirulina* biomass; pH was 5.0, maintained with 0.1 M $\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$ buffer; agitation speed was 185 rpm; temperature was 298 K; contact time was 60 min; Pr^{3+} concentration range was 20–500 mg/L. The experimental results (Table 2) reveal two distinct operational regimes. Low-concentration regime (20–100 mg/L): adsorption efficiency increases from 68% to 92%, and equilibrium capacity grows from 13.6 to 46.0 mg/g. High-concentration regime (100–500 mg/L): efficiency declines from 92% to 58%. Site saturation becomes evident as the theoretical monolayer coverage is reached at 300 mg/L, and additional Pr^{3+} leads to multilayer adsorption. The adsorption efficiency of Pr^{3+} onto functionalized surfaces (e.g., carboxylate/phosphonate-modified adsorbents) is constrained by three interrelated factors. Finite number of func-

tional groups: surface binding sites (e.g., $-\text{COOH}$, $-\text{PO}_4^-$) are limited in quantity. Initial rapid uptake occurs via coordination to these groups, but saturation is reached as Pr^{3+} occupies all available sites, following Langmuir-type monolayer adsorption. Steric hindrance at high loading: at elevated Pr^{3+} coverage, bulky hydrated ions or multidentate binding modes physically block adjacent sites. This reduces accessibility for further adsorption, deviating from ideal kinetic/isotherm models. Electrostatic repulsion between adsorbed Pr^{3+} : as Pr^{3+} (a trivalent cation) accumulates, positive charges cluster on the surface, creating coulombic repulsion. This repulsion opposes additional Pr^{3+} binding, lowering effective affinity. It also may distort the local structure of functional groups, weakening their coordination ability.

Table 2. Effect of initial Pr^{3+} concentration on adsorption.

Initial Pr^{3+} Concentration (mg/L)	Equilibrium Concentration (mg/L)	Adsorption Efficiency (%)	Adsorption Capacity (mg/g)
20	11.98	40.1	4.01
50	10.78	58.44	19.02
100	21.00	79.00	39.50
200	110.53	44.74	44.74
300	209.51	30.16	45.25
400	303.05	24.24	48.48
500	389.07	22.19	55.47

3.3. Adsorption Isotherms

Adsorption isotherms are used to describe the relationship between adsorption capacity and equilibrium concentration. By combining different solid surfaces with adsorbates, various adsorption isotherms can be obtained, which reflect the interactions between the adsorbate and adsorbent to some extent. Langmuir, Freundlich, D-R, and R-P adsorption models were introduced to investigate the adsorption process. By analyzing these isotherms, we can gain insights into adsorption interactions. Furthermore, combining the results from SEM, EDX, FT-IR, and XPS analyses with the adsorption isotherm data allows for a comprehensive characterization of the biosorbent *Spirulina*, laying the foundation for developing an efficient adsorption–desorption process.

Based on gas–solid adsorption theory, the Langmuir model describes the equilibrium relationship between the adsorbed metal ion quantity and their equilibrium concentration in solution. It is widely applied in solid–liquid adsorption systems [27]. Equation (3) was used to fit the experimental data for *Spirulina* adsorption of Pr^{3+} , with the results shown in Figure 6a. The Freundlich adsorption model is an empirical equilibrium model based on multilayer adsorption. The Freundlich model describes adsorption on heterogeneous surfaces. Equation (5) was used to fit the experimental data for *Spirulina* adsorption of Pr^{3+} , with the results shown in Figure 6b. R-P adsorption model combines features of both the Langmuir and the Freundlich models, using three parameters to characterize the system [28]. Equation (7) was used to fit the experimental data for *Spirulina* adsorption of Pr^{3+} , with the results shown in Figure 6c. The D-R adsorption model helps determine whether adsorption is physical or chemical by calculating the adsorption free energy (E) using Equation (10). Equation (8) was used to fit the experimental data for *Spirulina* adsorption of Pr^{3+} , with the results shown in Figure 6d.

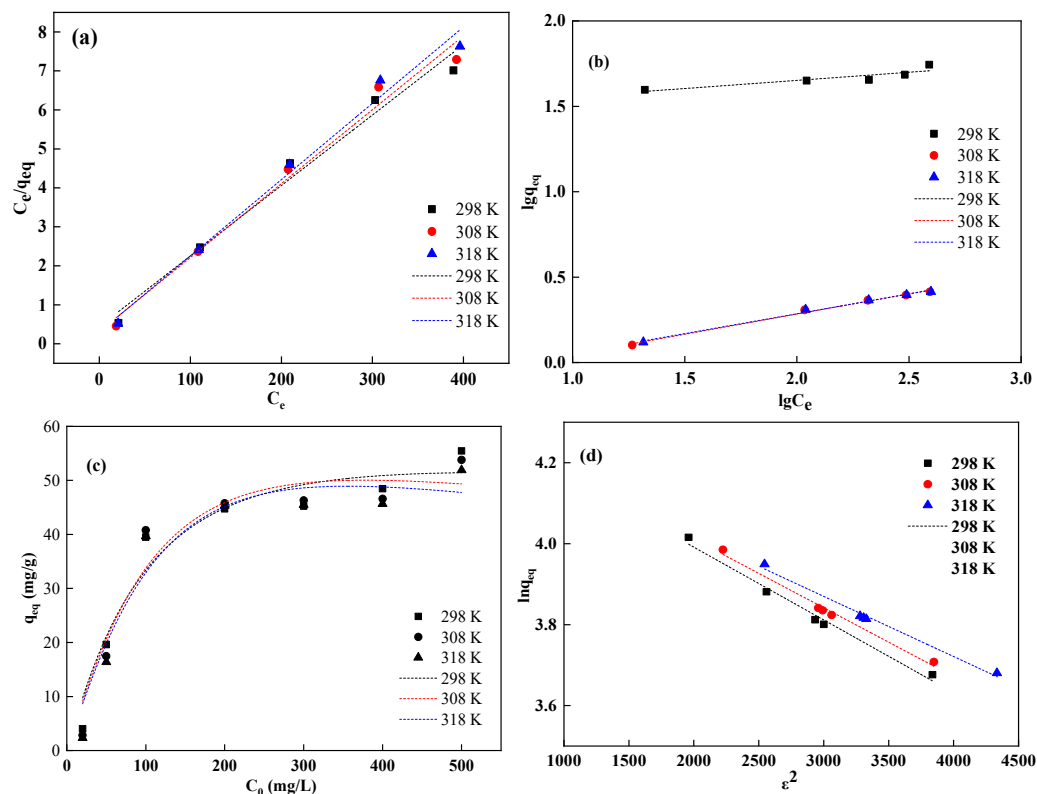


Figure 6. Isothermal adsorption model of Pr^{3+} biosorption by *Spirulina*. (a) Langmuir; (b) Freundlich; (c) R-P; (d) D-R.

At different temperatures, the experimental data for the adsorption of Pr^{3+} by *Spirulina* were fitted using the Freundlich model, Langmuir model, R-P model, and D-R model, respectively. The resulting fitting parameters are presented in Tables 3 and 4.

Table 3. Adsorption isotherm constants for Pr^{3+} adsorption by *Spirulina* at different temperatures (Langmuir and Freundlich models).

T/K	Langmuir			Freundlich		
	q_m (mg/g)	K_L (L/g)	R^2	K_F (L/g)	n	R^2
298	55.31	0.041	0.994	28.935	10.49	0.739
308	52.74	0.060	0.999	0.646	4.22	0.990
318	51.10	0.066	0.993	0.662	4.30	0.990

Table 4. Adsorption isotherm constants for Pr^{3+} adsorption by *Spirulina* at different temperatures (R-P and D-R models).

T/K	R-P				D-R			
	K_{RP} (L/g)	a_{R-P} (L/g)	g	R^2	q_m (mg/g)	β (mol^2/J^2)	E (kJ/mol)	R^2
298	0.527	0.00023	1.219	0.917	77.56	0.00178	14.76	0.981
308	0.477	0.00071	1.384	0.899	77.62	0.00170	15.15	0.986
318	0.472	0.00047	1.442	0.902	74.87	0.00149	15.32	0.986

From Table 3, it can be observed that in the Langmuir model, the R^2 values ranged from 0.993 to 0.999, while in the Freundlich model, they varied between 0.739 and 0.990. For the R-P (R-P) model (Table 4), R^2 values were in the range of 0.899–0.917, and for the

D-R model (Table 4), R^2 values were 0.981–0.986. These values indicate that the Langmuir, R-P, and D-R models could effectively describe the biosorption of Pr^{3+} by *Spirulina* at different temperatures. However, when comparing the R^2 values, it can be concluded that the Langmuir model was more appropriate than the Freundlich, R-P, and D-R models.

Within the temperature range of 298–318 K, the monolayer adsorption capacity (q_m) calculated from the Langmuir model ranged between 51.10 and 55.31 mg/g. This suggests that q_m decreased with increasing temperature, indicating the exothermic nature of Pr^{3+} adsorption on *Spirulina* (Table 3). For initial Pr^{3+} concentrations ranging from 100 to 500 mg/L, the calculated K_L values from the Langmuir model were between 0.041 and 0.066. These parameter values ($0 < K_L < 1$) demonstrate that *Spirulina* is a suitable adsorbent for Pr^{3+} removal from aqueous solutions. From the linear plots of the Freundlich isotherm, the K_F values were calculated to be 0.662–28.935 L/g, with n values ranging from 4.22 to 4.30. When the $1/n$ value falls between 0 and 1, the adsorption process is considered favorable, while $1/n > 1$, $1/n = 0$, or 1 indicates unfavorable, irreversible, or linear adsorption, respectively. Therefore, under the investigated experimental conditions, the adsorption of Pr^{3+} on *Spirulina* was favorable.

The g values calculated from the R-P isotherm model can be used to test the applicability of the Langmuir model for Pr^{3+} adsorption on *Spirulina*. Within the 298–318 K temperature range, these values ranged from 1.219 to 1.442. Thus, it can be stated that Pr^{3+} adsorption on *Spirulina* was well described by the R-P model, and the adsorption process was related to the saturation monolayer of adsorbate molecules on the adsorbent surface [29]. The D-R isotherm model can distinguish whether Pr^{3+} adsorption on *Spirulina* is a physical or chemical process. The β constant and monolayer adsorption capacity (q_m) were calculated from the slope and intercept of the plot. The β constant values were found to be 1.49×10^{-4} to $1.78 \times 10^{-4} \text{ mol}^2/\text{J}^2$, with q_m values of 74.87–77.62 mg/g. The adsorption energy E can determine whether the mechanism involves chemical ion exchange or physical adsorption. If E values fall within 8–16 kJ/mol, the process follows chemical ion exchange, while $E < 8 \text{ kJ/mol}$ indicates physical adsorption [11]. As shown in Table 4, the E values for Pr^{3+} adsorption on *Spirulina* at 298–318 K ranged from 14.76 to 15.32 kJ/mol, confirming that the adsorption occurred through chemical ion exchange.

The separation factor R_L was calculated using Equation (4), with results presented in Figure 7. The plot shows that R_L values decreased with increasing initial rare earth ion concentration, suggesting that higher initial concentrations favored adsorption. Furthermore, $0 < R_L < 1$ provides additional evidence that the adsorption process was favorable [30].

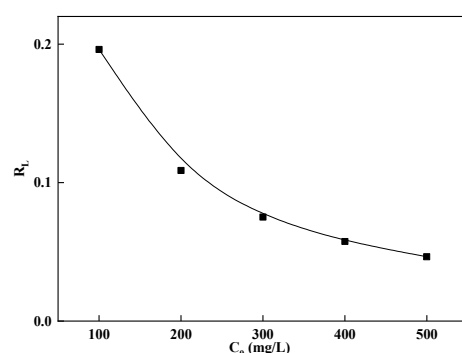


Figure 7. Variation of R_L with Pr^{3+} concentration.

Understanding adsorption mechanisms requires a multi-faceted analytical approach. XPS serves as a powerful tool for surface analysis, providing detailed information on elemental composition, chemical states, and electronic interactions. The XPS spectra

of Spirulina before and after Pr^{3+} adsorption are presented in Figure 8, which includes (a) survey scan, (b) Pr 3d, (c) C 1s, (d) N 1s, and (e) O 1s regions.

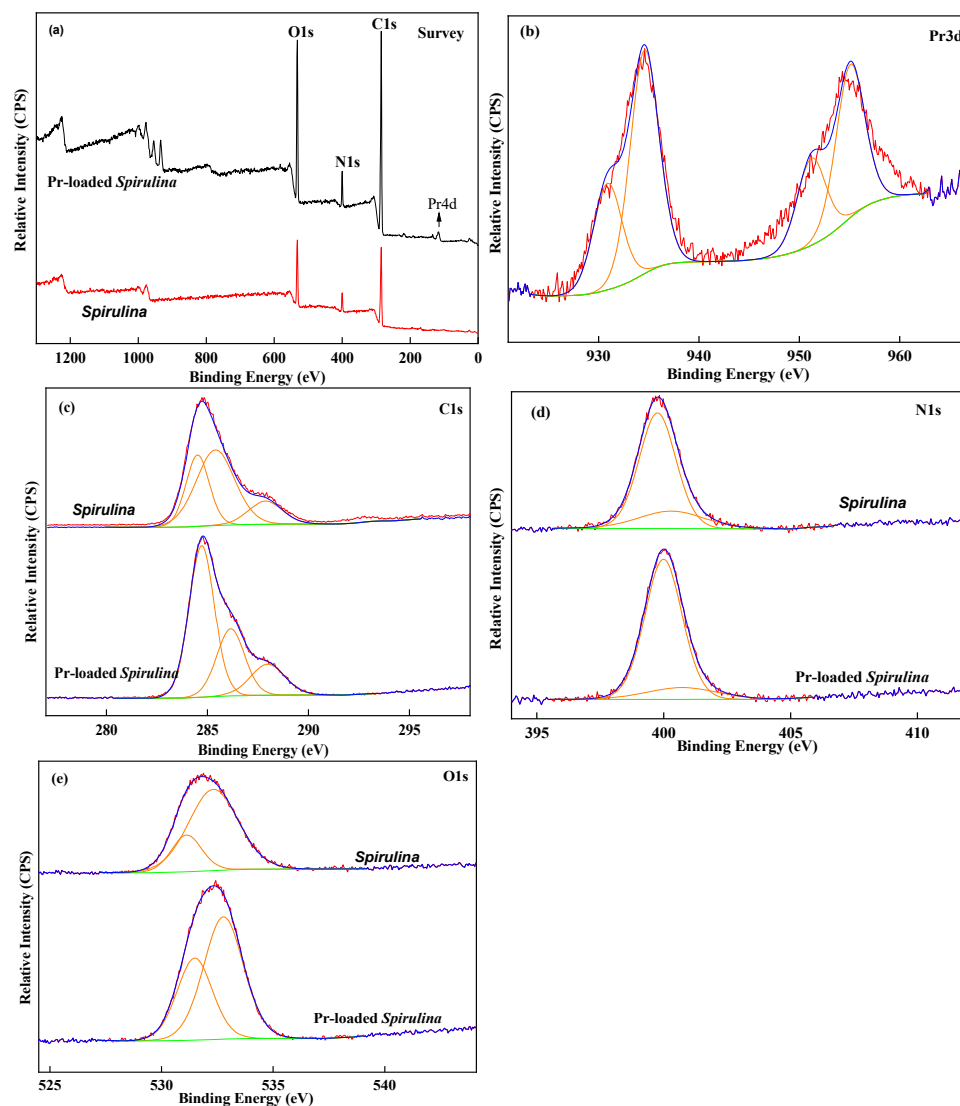


Figure 8. XPS spectra of Spirulina before and after adsorption: (a) survey scan, (b) Pr 3d, (c) C 1s, (d) N 1s, and (e) O 1s.

The Pr 3d spectrum (Figure 8b) exhibited a distinct peak at 934.58 eV, confirming the presence of Pr^{3+} on the Spirulina surface [31]. This observation provides direct evidence of Pr^{3+} adsorption, corroborating the ion exchange mechanism suggested by isotherm modeling. The deconvoluted C 1s spectrum (Figure 8c) revealed three distinct components. The peak at 284.8 eV represents C-C/C-H bonds characteristic of aliphatic carbon chains, forming the fundamental hydrocarbon framework of the biomatrix. The 285.3 eV component corresponds to C-O single bonds, primarily arising from either hydroxyl groups (-OH) in carbohydrate moieties or ether linkages (C-O-C) within polysaccharide structures. The higher binding energy peak at 286.7 eV is assigned to C=O double bonds, encompassing various carbonyl functionalities, including ketones, aldehydes, and carboxylate groups present in the biological material. The N 1s spectrum (Figure 8d) before adsorption showed a peak at 399.73 eV, attributed to C-NH₂ (amine groups) [32]. Following adsorption, this peak shifted to 400.4 eV, indicating nitrogen participation in Pr^{3+} coordination. The positive binding energy shift results from electron-withdrawing effects exerted by both Pr^{3+} and adjacent C=O groups, which reduce electron density around nitrogen atoms. This decreased

shielding effect increases core electron binding energy, leading to the observed high-energy shift. The O 1s spectrum (Figure 8e) revealed two major peaks before adsorption. The peak at 531.52 eV corresponds to C–O bonds, characteristic of hydroxyl (–OH) or ether (C–O–C) oxygen functionalities, which are commonly found in polysaccharides and other biopolymer structures. The peak at 532.32 eV corresponds to the C=O bond [33]. These peaks remained largely unchanged after adsorption, suggesting that oxygen-containing functional groups play a stabilizing rather than a primary role in Pr³⁺ binding. The XPS results provide direct evidence of chemical adsorption via ion exchange, where Pr³⁺ interacts predominantly with carboxyl and amine groups on the *Spirulina* surface. The binding energy shifts in C 1s and N 1s spectra highlight significant electronic redistribution, reinforcing the role of functional groups in Pr³⁺ coordination [34]. These findings align with previous FT-IR observations, which detected changes in functional group vibrations upon Pr³⁺ adsorption, and EDX data, which confirmed elemental composition modifications. The combined evidence supports a chelation-assisted ion exchange mechanism, where Pr³⁺ displaces protons or light metal ions (e.g., Na⁺, K⁺) from biomass binding sites.

3.4. Thermodynamic Evaluation of Process

The thermodynamic investigation of adsorption processes provides crucial insights into the spontaneity, heat effects, and structural changes occurring during metal ion uptake. For the *Spirulina*-Pr³⁺ system, we conducted a thorough thermodynamic assessment across a temperature range of 298–318 K, encompassing environmentally and industrially relevant conditions. This analysis employed fundamental thermodynamic Equations (11)–(13) to derive three key parameters: Gibbs free energy change (ΔG^0), enthalpy change (ΔH^0), and entropy change (ΔS^0). As presented in Table 5, the calculated parameters reveal distinct characteristics of the adsorption process.

Table 5. Thermodynamic parameter values of *Spirulina* after adsorption of Pr³⁺.

Metal	T/K	ΔG^0 (kJ·mol ^{−1})	ΔS^0 (J·mol ^{−1} ·K ^{−1})	ΔH^0 (kJ·mol ^{−1})
Pr ³⁺	298	−4.432	66.204	15.189
	308	−5.431		
	318	−5.741		

The consistency in parameter trends across the temperature range validates the reliability of our measurements. The negative ΔG^0 values (−4.432 to −5.741 kJ/mol) demonstrate several critical aspects: the adsorption process is thermodynamically spontaneous across all studied temperatures. The increasing negativity with temperature (−4.432 at 298 K→−5.741 at 318 K) suggests enhanced spontaneity at higher temperatures. The magnitude range (4–6 kJ/mol) indicates physisorption-dominated binding, potentially involving electrostatic interactions and weak chemical coordination. The positive ΔH^0 value (15.189 kJ/mol) reveals the endothermic nature of Pr³⁺ adsorption. Energy requirements are likely associated with the dehydration of Pr³⁺ ions (removal of hydration shells), structural rearrangement of *Spirulina* surface functional groups, and bond formation between Pr³⁺ and biomass ligands. The magnitude suggests a combination of physical and weak chemical adsorption mechanisms. The significantly positive entropy change ($\Delta S^0 = 66.204 \text{ J·mol}^{-1}·\text{K}^{-1}$) provides compelling evidence for increased molecular disorder within the system following Pr³⁺ adsorption. The observed behavior likely arises from the release of bound water molecules from both the *Spirulina* surface and the Pr³⁺ hydration shells. Enhanced rotational mobility of surface-adsorbed complexes. Structural reorganization within the biomass polymer

matrix. The overall process is driven by a substantial entropic contribution, which counter-balances the endothermic enthalpy component, ensuring thermodynamic spontaneity.

3.5. Adsorption Kinetics of Pr^{3+}

Due to adsorption kinetics, studies can reveal the mechanism of adsorption and potential rate-controlling steps such as mass transport or chemical reaction processes, so they are useful to find the optimum experimental conditions for a full-scale adsorption process. In this study, the different kinetic models, such as pseudo-first-order and pseudo-second-order, Elovich, and intraparticle diffusion models, were employed to study the adsorption of Pr^{3+} on *Spirulina*. Results were shown in Figure 9. Using the above adsorption kinetics, the amount of Pr^{3+} adsorbed on *Spirulina* was calculated. The obtained adsorption kinetic parameters, along with R^2 , are shown in Tables 6 and 7.

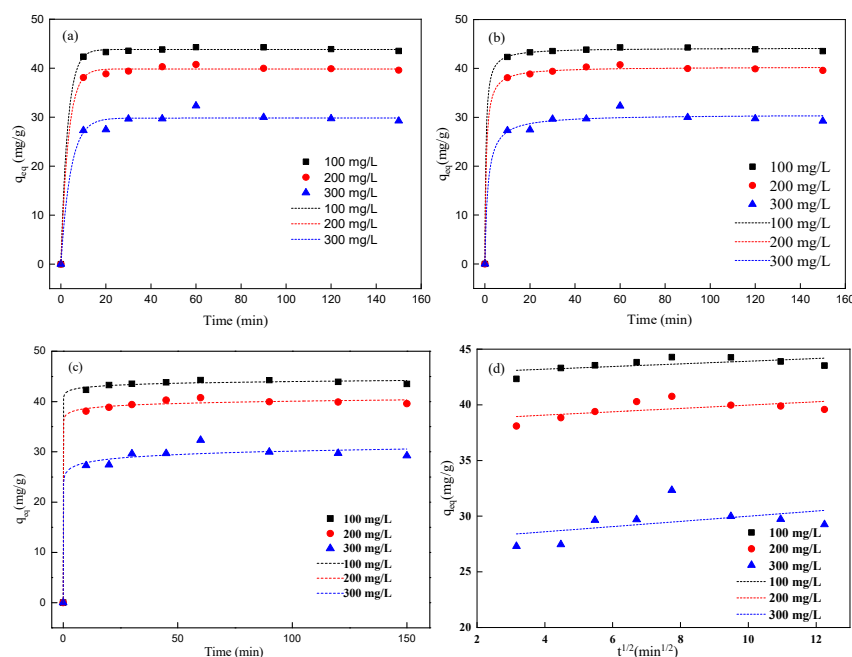


Figure 9. Kinetic results of Pr^{3+} adsorption on *Spirulina* biosorbent. (a) pseudo-first-order equation, (b) pseudo-second-order dynamic equation, (c) Elovich equation, and (d) intra-particle diffusion model.

Table 6. Comparison of pseudo-first-order and pseudo-second-order adsorption kinetic model parameter values obtained at different initial Pr^{3+} concentrations for adsorption on *Spirulina* biosorbent at 298 K.

C_0 (mg/L)	Pseudo-First-Order			Pseudo-Second-Order		
	q_{eq} (mg/g)	k_1 (min^{-1})	R^2	q_{eq} (mg/g)	k_2 ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$)	R^2
100	39.99	0.367	0.998	44.184	0.054	0.999
200	58.55	0.237	0.987	40.318	0.042	0.998
300	67.80	0.246	0.994	30.569	0.025	0.987

Table 7. Comparison of Elovich and intra-particle diffusion adsorption kinetic model parameter values obtained at different initial Pr^{3+} concentrations for adsorption on *Spirulina* biosorbent at 298 K.

C_0 (mg/L)	Elovich			Intra-Particle Diffusion		
	α ($\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$)	β ($\text{g}\cdot\text{mg}^{-1}$)	R^2	C	k_p ($\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-1/2}$)	R^2
100	41.684	1.994	0.477	42.72	0.12	0.265
200	37.157	1.578	0.406	38.48	0.15	0.212
300	25.568	1.003	0.236	27.67	0.23	0.119

The aforementioned kinetic models were applied to fit the experimental data of rare earth ion adsorption by *Spirulina*, with the resulting kinetic parameters summarized in Tables 6 and 7.

It can be seen from Table 6 that the R^2 was 0.987–0.999 in the pseudo-first-order adsorption kinetic model, and the R^2 was 0.987–0.999 in the pseudo-second-order adsorption kinetic model. The R^2 ranged from 0.236 to 0.477 in the Elovich adsorption kinetic model (Table 7) and 0.119–0.265 in the intra-particle diffusion adsorption kinetic model (Table 7). It can be concluded that the pseudo-second-order kinetic model was a more appropriate model than the pseudo-first-order adsorption kinetic model, Elovich, and intraparticle diffusion models when the R^2 values were compared. The obtained values of R^2 are low, which indicates that the Elovich and intraparticle diffusion kinetic models did not agree with the experimental adsorption data, and the removal of Pr^{3+} from aqueous solution onto the surface of the *Spirulina* cannot be explained using these two kinetic models.

3.6. Desorption Experiment

To achieve the recovery of rare earth ions from mining wastewater, it is essential to employ appropriate methods for desorbing the adsorbed ions from *Spirulina*. FT-IR and XPS analyses revealed that multiple functional groups on *Spirulina* participate in the adsorption process, while adsorption isotherm modeling confirmed an ion-exchange adsorption mechanism. Since the cell wall of *Spirulina* serves as the primary site for rare earth ion adsorption through ion exchange, acidic solutions represent the most cost-effective and efficient desorbents. In this study, 0.1 mol/L HNO_3 was selected as the desorption agent. The results demonstrated exceptional desorption efficiency, with 0.1 mol/L HNO_3 achieving 91.7% recovery of adsorbed Pr^{3+} . This high desorption percentage confirms the effectiveness of nitric acid for rare earth ion recovery while maintaining the structural integrity of the biosorbent for potential reuse.

3.7. Study on the Adsorption Difference with the Coexistence of Other Rare Earth Metal Ions

To evaluate the competitive adsorption effects, four mixed rare earth ion solutions were prepared. Solution A: 100 mg L^{-1} Er^{3+} + 100 mg L^{-1} Yb^{3+} ; Solution B: 100 mg L^{-1} Er^{3+} + 100 mg L^{-1} Pr^{3+} ; Solution C: 100 mg L^{-1} Pr^{3+} + 100 mg L^{-1} Yb^{3+} ; Solution D: 100 mg L^{-1} Er^{3+} + 100 mg L^{-1} Pr^{3+} + 100 mg L^{-1} Yb^{3+} . The adsorption capacity of *Spirulina* for Pr^{3+} was measured in both single-ion and multi-ion systems to assess interference effects. The results (Figure 10) demonstrate that the adsorption capacity of *Spirulina* for Pr^{3+} decreases significantly in the presence of competing ions (Er^{3+} and Yb^{3+}). Compared to single-ion adsorption, the presence of Er^{3+} and Yb^{3+} led to a notable decline in Pr^{3+} uptake. The decline in Pr^{3+} adsorption can be attributed to the following: Since rare earth ions have similar covalent indices and chemical behaviors, *Spirulina*'s adsorption sites are contested by multiple ions, reducing the efficiency for any single target ion. Functional groups on *Spirulina* (e.g., $-\text{COOH}$ and $-\text{OH}$) have limited binding sites. When multiple ions are present, they compete for the same sites, leading to lower individual uptake. The trivalent

state and comparable ionic radii of Pr^{3+} , Er^{3+} , and Yb^{3+} contribute to their competitive adsorption, as *Spirulina* cannot selectively distinguish between them effectively.

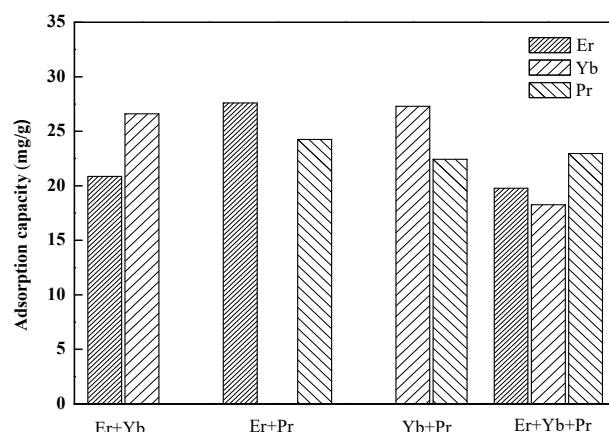


Figure 10. Study on the difference in the adsorption effect of *Spirulina* on Pr^{3+} when other rare earth metal ions coexist.

Table 8 shows the adsorption capacity at equilibrium for different types of rare earth metal ions adsorption over different adsorbents collected from the literature. The adsorption capacity achieved in this study (55.31 mg/g for Yb^{3+}) is competitive compared to most adsorbents listed in Table 8. Given its favorable adsorption performance, *Spirulina* presents a promising green alternative for Yb^{3+} removal.

Table 8. Comparison of adsorption capacity of *Spirulina* with other adsorbents to remove rare earth ions.

Biosorbents	Absorbed Targets	Adsorption Performances	Reference
<i>Spirulina</i>	Yb^{3+}	55.31 mg/g	This study
Dry baker's yeast	Cd^{2+} , Cu^{2+} , Pb^{2+} , Zn^{2+} , Y^{3+} , Gd^{3+} , Dy^{3+}	1.0 mmol/g	[35]
Dry baker's yeast	Dy^{3+}	90% adsorption rate	[36]
<i>Bacillus subtilis</i>	La^{3+} , Sm^{3+}	99% adsorption rate	[37]
<i>Escherichia coli</i>	Nd, Tb	$6.01 \pm 0.11 \mu\text{mol/g}$	[38]
Algal biochar	La	362.32 mg/g	[39]
Marine green algae	Sc^{3+}	66.81 mg/g	[40]
<i>Escherichia coli</i>	Nd^{3+} , Dy^{3+} , Lu^{3+}	222 mg/g	[41]
Straw biochar	Ce^{3+}	228.9 mg/g	[42]
<i>Paeclomyces catenulannulatus</i>	Eu^{3+}	69.45 mg/g	[43]

4. Conclusions

In the present work, the biosorbent *Spirulina* for the removal of Pr^{3+} from aqueous solution in a batch adsorption study was investigated. The adsorption rate reached 79.0% when the contact time was 60 min, the pH was 5, the adsorption temperature was 298 K, the initial Pr^{3+} concentration was 100 mg/L, and the dosage of *Spirulina* was 2.0 g/L. The rate of desorption of Pr^{3+} from *Spirulina* attained 91.7% when eluted with 50 mL of 0.1 mol/L HNO_3 solution. Based on the analytical results of element and chemical valences, it can be concluded that the high adsorption capacity of *Spirulina* to Pr^{3+} is derived from the cation exchange and Pr^{3+} coordination bridging with the amino group of *Spirulina*. The adsorption isotherm data were best explained by Langmuir model (R^2 was range

from 0.993 to 0.999), and the adsorption capacity of *Spirulina* for Pr^{3+} are in the range 51.10–55.31 mg/g within a temperature range of 298–318 K. Results clearly showed that the adsorption of Pr^{3+} onto *Spirulina* was followed pseudo-second-order kinetic model with a rate of reaction of $0.054 \text{ g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$ (R^2 was 0.999) when the initial concentration of Pr^{3+} was 300 mg/L. The values of thermodynamic parameters ΔG^0 were calculated as -4.432 , -5.431 , and -5.741 kJ/mol at the temperatures of 298, 308, and 318 K, respectively. ΔH^0 and ΔS^0 were 66.204 kJ/mol and 15.189 J/mol/K. Hence, it can be concluded that the adsorption of Pr^{3+} onto *Spirulina* was an endothermic and spontaneous process at the temperatures under investigation. It can be concluded that *Spirulina* is an effective biosorbent to adsorb Pr^{3+} from aqueous solution.

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Nomenclature

q_t (mg/g)	Adsorption capacity at time t (min)	q_{eq} (mg/g)	Adsorption capacity at equilibrium
C_0 (mg/L)	Concentrations of Pr^{3+} at initial	C_e (mg/L)	Concentrations of Pr^{3+} at equilibrium
V (L)	volume of solution (L)	M (g)	mass of adsorbent (g)
K_F (L/mg)	Freundlich isotherm constant	n_F	Freundlich adsorption intensity
q_m (mg/g)	monolayer biosorption capacity of the adsorbent	T	time
K_L	Langmuir adsorption constant	R^2	correlation coefficient
R_L	Langmuir isotherm equilibrium parameter	K_{R-P} (L/mg)	Redlich Peterson isotherm constant
a_{R-P} (L/mg)	Redlich Peterson isotherm constant	g (mol^2/KJ^2)	Activity coefficient of adsorption energy.
q_s (mg/L)	Theoretical isotherm saturation adsorption capacity	β (mol^2/KJ^2)	Activity coefficient of adsorption energy
ε	Dubinin–Radushkevich isotherm constant	E (kJ/mol)	Mean adsorption free energy
K_T	Equilibrium constant	T (K)	Thermodynamic temperature
ΔG^0 (kJ/mol)	Gibbs free energy	ΔH^0 (kJ/mol)	enthalpy
ΔS^0 ($\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$)	entropy	R	8.314 ($\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$)
C_t (mg/L)	Concentrations of Pr^{3+} at time t (min)	k_1 (min^{-1})	Rate constant of pseudo-first-order adsorption
k_2 ($\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$)	Rate constant of pseudo-second-order adsorption	β ($\text{g}\cdot\text{mg}^{-1}$)	Elovich desorption constant
α ($\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$)	Initial adsorption rate	C	Boundary-layer thickness constant
k_p ($\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-1/2}$)	Intra-particle diffusion rate constant of the adsorption		

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