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Ce(III) Adsorption on Na-bentonite: Coupled Cation Exchange and Colloidal Stability

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Abstract

The interaction of rare earth elements with bentonite is increasingly important for predicting the long-term performance of engineered barrier systems exposed to contaminated aqueous environments. This study investigated the coupled adsorption, cation-exchange, and colloidal responses of Na-bentonite during Ce(III) uptake. Batch adsorption experiments (1 g L⁻¹ Na-bentonite, 10 mg L⁻¹ Ce³⁺, 25 °C, 0–320 min) revealed rapid Ce(III) uptake within the first 5 min, reflecting the high cation-exchange capacity and abundance of reactive surface sites. Among the evaluated kinetic models, the Avrami model provided the best description of the adsorption process ($R^2 = 0.999$), suggesting the simultaneous contribution of multiple adsorption pathways and diffusion-related mechanisms. Simultaneous ion-release analyses showed rapid Na⁺ and K⁺ release, whereas Ca²⁺ and Mg²⁺ concentrations remained nearly constant, indicating coupled cation-exchange and re-adsorption process. Dynamic light scattering, ζ -potential, and DLVO analyses consistently demonstrated only limited colloidal destabilization despite partial compression of the electrical double layer. The hydrodynamic diameter increased only slightly (979–1011 nm), while the ζ -potential remained nearly unchanged (−27.7 to −27.2 mV), indicating that electrostatic stabilization was largely preserved throughout the adsorption. The results indicate that Ce(III) adsorption is governed by coupled cation exchange and interfacial interactions, leading to only limited colloidal destabilization and regulating the physicochemical stability of Na-bentonite suspensions. These findings improved the understanding of

bentonite barrier behavior in waste disposal environments, where water can be exposed to rare earth contaminants.

Keywords: Rare earth elements; Cerium; Bentonite; Cation exchange; Colloidal stability

1. Introduction

Hazardous waste is a major source of environmental pollution and may cause long-term risks to ecosystems and human health (Yasmine et al., 2022; Ziane et al., 2022; Adnan et al., 2024; Bensafi et al., 2025). Landfilling is still the most common method for hazardous waste disposal worldwide (Mor and Ravindra, 2023). During landfill operation, water passing through the waste produces leachate containing dissolved inorganic and organic compounds that can affect the performance of engineered barrier systems (Ray et al., 2021). Since these barriers are expected to remain effective for thousands of years, their long-term stability is essential for preventing contaminant migration into surrounding soil and groundwater (Wilson et al., 2025).

Sodium bentonite, which is rich in montmorillonite, is widely used in landfill liners because of its low hydraulic conductivity ($<10^{-8}$ cm s⁻¹), high swelling capacity, and strong cation exchange capacity (Chen et al., 2025). These properties mainly depend on the diffuse double layer (DDL) around clay particles. A thicker DDL generally results in greater swelling and lower hydraulic conductivity. According to the Debye–Hückel theory (Debye and Hückel, 1923), increasing ionic strength or cation valence compresses the DDL. In addition, multivalent cations can replace interlayer Na⁺ through cation exchange (Fox et al., 2024). These changes reduce the swelling capacity of bentonite and may decrease the sealing performance of landfill liners.

Many studies have investigated how environmental factors such as pH (Prongmanee and Chai, 2019), surfactants (Shah et al., 2017), major cations (Xiang et al., 2022), antibiotics (Ortiz-Ramos et al., 2022), heavy metals (Ray et al., 2021), salinity (Navarro and Asensio, 2023), and acidic conditions (J. Liu et al.,

2025) affect the behavior of Na-bentonite. However, much less information is available on the effects of rare earth elements (REEs). This is becoming more important because the use of REEs has increased rapidly in recent years, leading to their release into different environmental compartments. In some waste streams, REE concentrations may be similar to or even higher than those of common heavy metals such as Cu and Pb (Van Gosen et al., 2014).

Cerium (Ce^{3+}) is the most abundant rare earth element and is commonly used in catalysts, ceramics, alloys, electronics, and other industrial products (Ramasamy et al., 2018). Hazardous wastes, especially those related to mining and mineral processing, may contain high concentrations of cerium and other REEs that can enter soils and groundwater through leaching (Zhang et al., 2024). Although Ce adsorption on clay minerals has been reported, limited information is available on how Ce^{3+} affects adsorption, cation exchange, and colloidal stability at the same time. Most previous studies have mainly focused on adsorption capacity or equilibrium behavior, while the relationship between adsorption, cation exchange, and colloidal stability has not been studied in detail.

Understanding these processes is important because Ce^{3+} may change the surface charge, compress the diffuse double layer, and influence particle interactions during adsorption. These changes can affect the swelling behavior and hydraulic performance of bentonite, which is critical for the long-term stability of landfill barrier systems.

In this study, the adsorption of Ce^{3+} onto Na-bentonite was investigated using kinetic models along with measurements of exchangeable cation release. Dynamic light scattering (DLS), ζ -potential measurements, and DLVO analysis were used to evaluate the changes in colloidal stability during adsorption. By combining these approaches, this study elucidates the relationship between Ce^{3+} adsorption, cation exchange, and colloidal stability, and provides a better understanding of the behavior of Na-bentonite exposed to rare earth contaminants.

2. Materials and Methods

2.1 Materials

Cerium nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) of analytical grade was used in this study, purchased from Carlo Erba Reagents (France). Na-bentonite was purchased from Azichem S.r.l. (Italy). Milli-Q water, produced by an Elga Purelab Option-Q system (electrical conductivity = $0.5 \mu\text{S cm}^{-1}$), was used to prepare the solutions.

2.2 Properties of Na-bentonite

The swelling index was determined according to ASTM D5890 (Wireko et al., 2020). The specific surface area was measured using the Brunauer–Emmett–Teller (BET) method (Brunauer et al., 1938). Before BET analysis, exchangeable cations were replaced with NH_4^+ following ASTM D7503–D7510 (Xiang et al., 2022). Moisture content was determined by drying the samples at 105°C to constant weight (Olu-Owolabi and Unuabonah, 2011). The point of zero charge (pH_{pzc}) was measured using the pH-drift method (Wang et al., 2021). The physicochemical properties and exchangeable cation contents of the Na-bentonite are summarized in Table 1.

Table 1. Physicochemical properties and exchangeable cations of the Na-bentonite used in this study

Parameter	unit	value
Na	meq/100g	41.9
Ca	meq/100g	16.7
Mg	meq/100g	6.5
K	meq/100g	3.2
CEC	cmol(+)/kg	64
^a Alkalinity coefficient		1.9
pH _{zpc}		2.9

Swelling index	mL/2g	26.7
Specific surface area	m ² /g	31
Moisture	%	12.6

$$.^a \text{Alkalinity coefficient} = \frac{\Sigma \text{Na}^+ + \Sigma \text{K}^+}{\Sigma \text{Ca}^{2+} + \Sigma \text{Mg}^{2+}}$$

X-ray diffraction (XRD) patterns were collected using a Rigaku MiniFlex 600 diffractometer with Cu K α radiation ($\lambda = 0.154$ nm) over a 2θ range of 10–80°. Mineral phases were identified using Match! software and quantified by Rietveld refinement. Particle morphology and elemental composition were examined by scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM–EDS). Bulk chemical composition was determined by wavelength-dispersive X-ray fluorescence (WDXRF). The hydrodynamic diameter and ζ -potential of Na-bentonite suspensions were measured by dynamic light scattering (DLS) using a Horiba SZ-100 particle analyzer.

2.3 Batch adsorption experiments

The adsorption of Ce³⁺ onto Na-bentonite was investigated as a function of contact time using batch experiments. A 1000 mg L^{−1} Ce³⁺ stock solution was prepared by dissolving 3.1 g of Ce(NO₃)₃·6H₂O in Milli-Q water and subsequently diluted to obtain a working solution containing 10 mg L^{−1} Ce³⁺. Preliminary aqueous speciation calculations were performed using Visual MINTEQ (version 4.0) to determine the pH range in which dissolved Ce(III) remains stable. The calculations indicated that Ce(III) remains predominantly dissolved below pH 6.5, whereas precipitation becomes thermodynamically favorable at higher pH values (Fig. S1). Based on these calculations, the initial solution pH was adjusted to 3.25 using 0.1 M HNO₃ to ensure that precipitation did not occur during the adsorption experiments. The solution pH was not controlled after the experiments had started. Batch experiments were carried out in 50 mL polypropylene centrifuge tubes containing 0.05 g of Na-bentonite and 50 mL of the Ce³⁺ solution, corresponding to an adsorbent dosage of 1 g L^{−1}. The initial solution pH was adjusted to 3.25 before adding the adsorbent. The suspensions were shaken at 150 rpm in a horizontal shaker at 25 ± 1 °C. Samples were collected after 0, 5, 10, 20, 40, 80, 160, and 320 min. The pH and electrical conductivity (EC) were

measured before and after each experiment. All experiments were performed in triplicate, and the reported values represent the corresponding mean values. After each reaction period, the suspensions were filtered through 0.45 μm syringe filters. The filtrates were immediately acidified with ultrapure 65% HNO_3 before elemental analysis. Dissolved concentrations of cations (Ce, Si, Fe, Ca, Mg, Na, and K) and anions (NO_3^- , Cl^- , F^- , SO_4^{2-} and PO_4^{3-}) were determined using inductively coupled plasma–mass spectrometry (ICP) and Ion Chromatography (IC), respectively.

2.5 Adsorption kinetics modeling

The amount of cerium adsorbed on the Na-bentonite surface at each time (q_t , mg g^{-1}) was determined according to the mass-balance equation (Eq. (1)):

$$q_t = \frac{C_i - C_t}{m} \times V \quad (1)$$

where C_i and C_t (mg L^{-1}) are the initial and time-dependent Ce concentrations, respectively; V (L) is the solution volume and m (g) is adsorbent mass.

The adsorption data were analyzed using six kinetic models in both linear and nonlinear forms, including the pseudo-first-order (PFO), pseudo-second-order (PSO), Elovich, diffusion–chemisorption (DC), Avrami, and Bangham models. The equations of the kinetic models are summarized in Table 2.

Table 2. Kinetic models used in this study

Model	Equation	
PFO	$\ln(q_e - q_t) = \ln(q_e) - k_1 t$	(Lagergren., 1898)
PSO	$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{t}{q_e}$	(Ho and McKay, 1999)
Elovich	$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t)$	(Chien and Clayton, 1980)
DC	$\frac{t^5}{q_t} = \frac{t^5}{q_e} + \frac{1}{k_D}$	(Sutherland, 2004)
Avrami	$\ln\left(\ln\left(\frac{q_e}{q_e - q_t}\right)\right) = n_{av} \ln k_{av} + n_{av} \ln t$	(Avrami, 1940)
Bangham	$\log(\log\left(\frac{C_0}{C_0 - q_t \cdot m}\right)) = \log\left(\frac{k_0 \cdot m}{2.303V}\right) + \sigma \cdot \log t$	(Aharoni et al., 1979)

2.6 DLVO calculations

The DLVO theory was applied to evaluate the interaction energy between Na-bentonite particles. The interaction energy results from the balance between attractive van der Waals forces and electrostatic double-layer repulsion (García-García et al., 2009). The total interaction energy was calculated according to Eqs. (2)–(5) (Martines et al., 2008)

$$V_T = V_R + V_A \quad (2)$$

$$V_A = -\frac{Ar}{12D} \quad (3)$$

$$V_R = \frac{64\pi r n_0 k_B T}{\kappa^2} \gamma^2 e^{-\kappa D} \quad (4)$$

$$\kappa = \left(\frac{1000 e^2 N_A}{\varepsilon_0 \varepsilon_r k_B T} \sum Z_i^2 M_i \right)^{.5} \quad (5)$$

where V_T , V_A and V_R are the total potential energy, attractive potential energy and repulsive potential energy, respectively. A is Hamaker constant, n_0 is the number of ions per cubic meter, e is the elementary charge (1.6×10^{-19} C), N_A is Avogadro's constant (6×10^{23}), ε_0 is the vacuum dielectric constant (8.9×10^{-12} C² J⁻¹ K⁻¹), ε_r is the dielectric constant of water, T is the absolute temperature, r is the radius of the particle, D is the distance between the surfaces of the particles, $1/\kappa$ is the Debye length, Z_i is the charge of the background ion, M_i is the concentration of the background ion and γ is a parameter dependent on the surface potential that is obtained by Eq. (6):

$$\gamma = \tanh\left(\frac{Ze\Psi_\delta}{4k_B T}\right) \quad (6)$$

Because the ζ -potential does not represent the true surface potential, the surface potential was calculated using Eq. (7) proposed by van Olphen (1964)

$$\Psi_0 = 0.1725 \frac{T}{v} \sinh^{-1}\left(\frac{1256.81 \times \rho'}{\sqrt{n\varepsilon T}}\right) \quad (7)$$

where Ψ_0 is the estimated surface potential (mV), ρ' is the ratio of cation exchange capacity (CEC) (cmol(+)/kg) to the specific surface area, ν is the ion valence, and n is the ion concentration in the bulk solution.

3. Results and discussion

3.1. Characterization of Na-bentonite

XRD pattern shown in Fig. 1 indicates that montmorillonite is the dominant mineral phase in the Na-bentonite sample. The characteristic basal reflection observed at $2\theta \approx 6.2^\circ$ corresponds to the (001) plane, indicating an interlayer spacing of approximately 14.24 Å. Reflections at approximately 20° and 36.5° are assigned to the (100) and (110) planes, respectively, confirming the layered structure of montmorillonite. The diffraction peak at approximately 62° assigned to the (060) plane further indicates the dioctahedral character of montmorillonite (Gupt et al., 2020). Minor amounts of quartz and calcite were also identified, with characteristic reflections at approximately 26.6° and 29.4° (2θ), respectively.

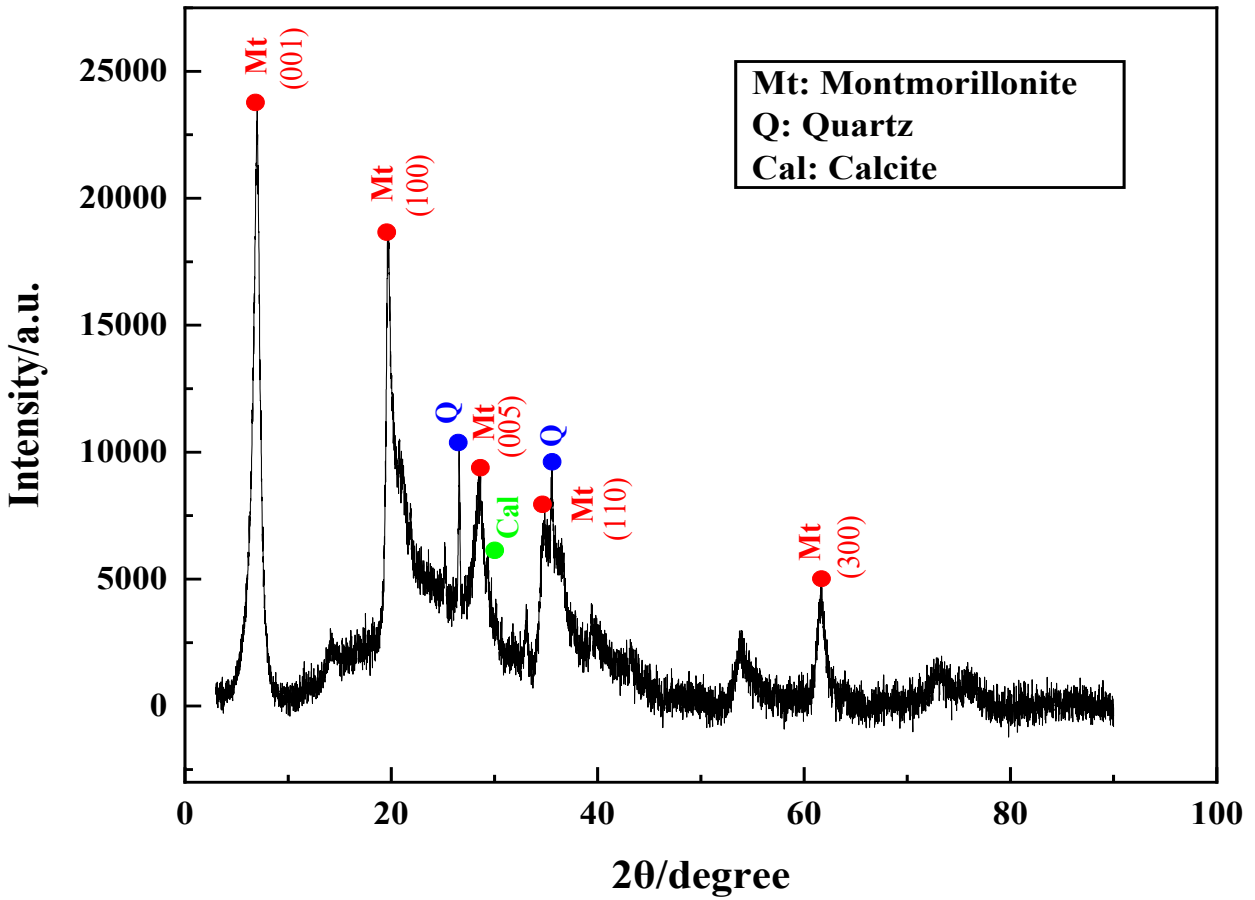


Fig. 1. XRD diffraction pattern of Na-bentonite

XRF analysis (Table 3) showed that SiO_2 and Al_2O_3 were the major oxides, indicating that the sample was mainly composed of aluminosilicate minerals. The presence of Na_2O , together with smaller amounts of Fe_2O_3 , MgO , and CaO , is consistent with the mineralogical composition of Na-bentonite. Based on the oxide composition, the structural formula of the Na-bentonite was estimated as $\text{Na}_{0.3}\text{Ca}_{0.08}(\text{Si}_{3.74}\text{Al}_{0.26})(\text{Al}_{1.32}\text{Fe}^{3+}_{0.36}\text{Mg}_{0.20})\text{O}_{10}(\text{OH})_2$ (Mihaljevič et al., 2006).

Table 3. Chemical analysis (Wt%) of Na-bentonite as determined by XRF

Oxides	SiO_2	Al_2O_3	Na_2O	MgO	K_2O	TiO_2	CaO	Fe_2O_3	LOI	TOT
Wt %	56.16	20.14	2.3	1.9	0.12	1.7	1.8	7.1	8	99.22

SEM micrographs of the Na-bentonite sample at different magnifications (Fig. 2) show aggregated particles with irregular shapes, rough surfaces, and plate-like morphology characteristic of smectite minerals. The particles exhibited a wide size distribution, reflecting the natural heterogeneity of the clay. Based on measurements of 200 particles, the mean particle size was $55.19 \pm 25.30 \mu\text{m}$.

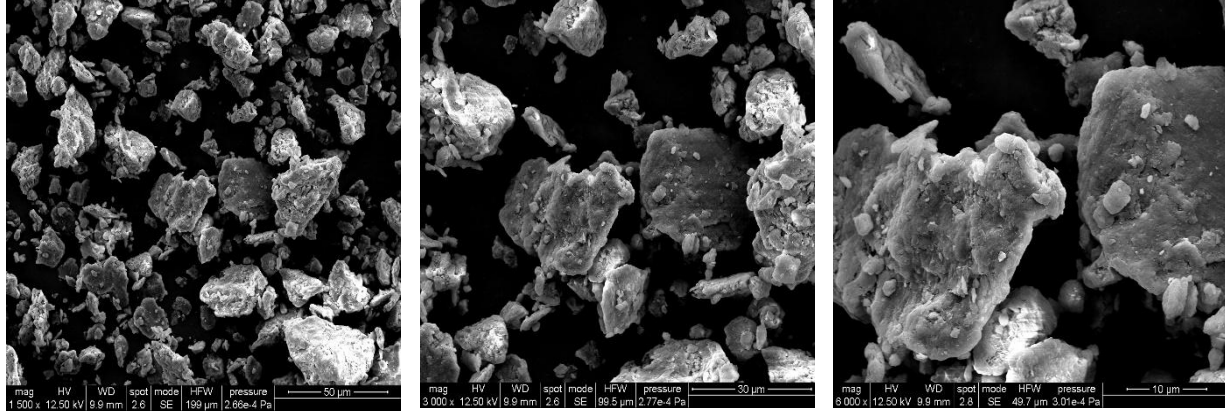


Fig. 2. Scanning electron microscope images of Na-bentonite

SEM-EDS analyses were performed at seven different locations on the Na-bentonite surface. The average elemental compositions obtained from these analyses are presented in Table 4. Oxygen, silicon, aluminum, sodium, magnesium, potassium, calcium, and iron were identified as the major elements in the samples.

Table 4. Elemental composition (Wt%) of Na-bentonite as determined by EDS

Elements	C	O	Na	Mg	Al	Si	Ca	Ti	Fe	Cu
Wt %	33.27	43.46	1.50	1.34	3.87	10.99	0.50	0.26	4.59	0.26

3.2. Cerium adsorption tests

Adsorption experiments were conducted at different contact times to evaluate the adsorption kinetics (Fig. 3). As shown in Fig. 4, Ce^{3+} adsorption was rapid during the first 5 min, removing most of the dissolved cerium from the solution. Previous studies on soils have also reported rapid Ce^{3+} adsorption within the first few minutes, including at contact times shorter than 5 min (D. Li et al., n.d.).

During the adsorption process, the solution pH increased from 3.25 to approximately 5.6 within the first 5 min and gradually approximately 6.3 at the end of the experiment. The increase in pH can be attributed to

protonation reactions at clay surface sites (Duc et al., 2005), cation exchange involving H^+ , Ce^{3+} , Na^+ , and K^+ (Sun et al., 2024), and the release of carbonate species from the clay structure (Wang et al., 2020).

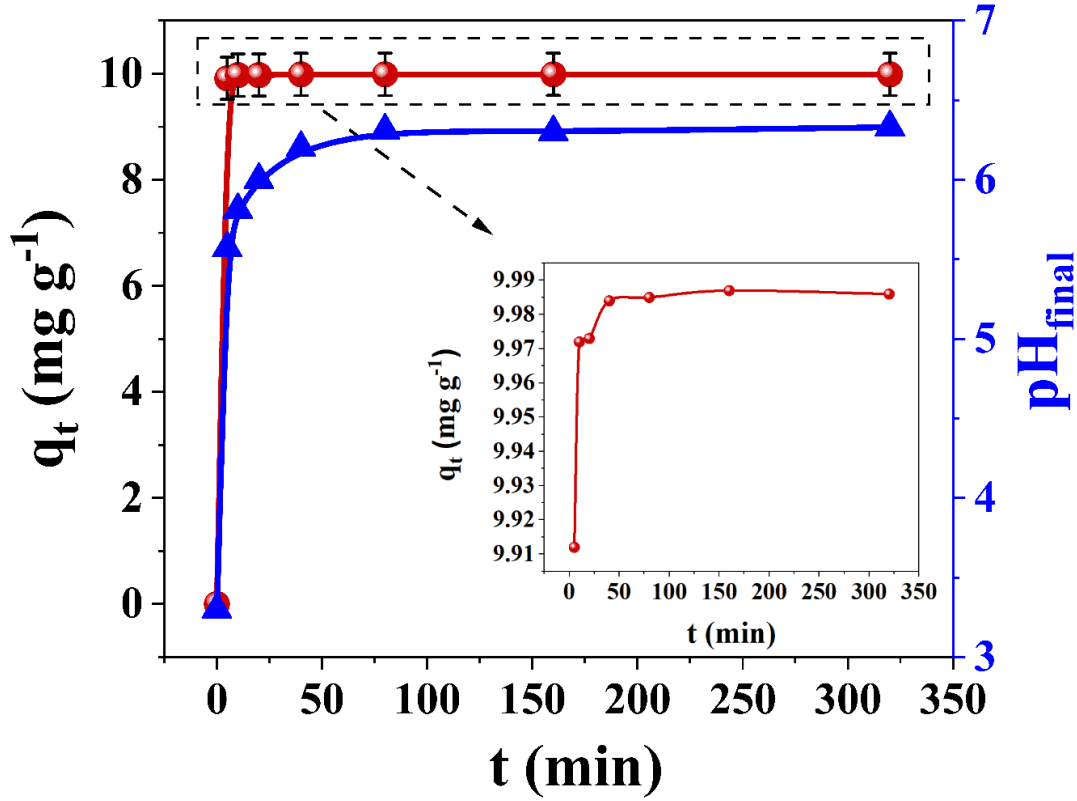
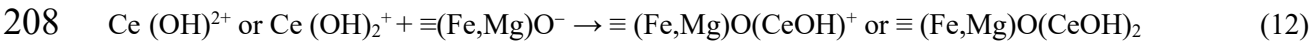


Fig. 3. Time-dependent variation of adsorbed Ce^{3+} and pH during batch adsorption

Equilibrium was reached within 5 minutes, suggesting the high adsorption capacity of Na-bentonite, which can be attributed to its large cation exchange capacity (CEC) and strong affinity toward Ce^{3+} ions. The surface of montmorillonite contains hydroxyl groups associated with Si, Al, and Fe atoms, which can deprotonate to form $\equiv SiO^-$, $\equiv AlO^-$, and $\equiv FeO^-$ functional groups, providing active sites for metal ion sorption. The reactions between Na-bentonite particles and Ce^{3+} free ions in the system can be explained by Reactions (8)-(12) (PL Brown, 2016):





209 The different sorption sites for cerium ions, which act as cation exchangers, are also highlighted.

210 **3.3. Kinetic modeling**

211 The experimental adsorption data were fitted using the kinetic models described in Section 2.5, and their
 212 performance was compared using the calculated equilibrium adsorption capacity (q_e), coefficient of
 213 determination (R^2), and error metrics, including RMSE, SSE, χ^2 , and AIC. The fitting curves are shown in
 214 Fig. S2, and the resulting kinetic parameters are listed in Table 5. Higher R^2 values and lower error values
 215 indicate better agreement between the experimental and calculated data (de Oliveira et al., 2023).

216 **Table 5. Kinetics parameters for Ce (III) adsorption onto Na-bentonite.**

Model		Parameters					
		Constant		Statistical			
Nonlinear	PFO	k_1	q_e	R^2	SSE	χ^2	RMSE
		0.993	9.98	0.99	2.3×10^{-4}	3.8×10^{-5}	5.3×10^{-3}
	PSO	k_2	q_e	0.99	3.5×10^{-4}	5.9×10^{-5}	6.5×10^{-3}
	Elovich	β	α	0.99	0.14	.024	0.13
		7.44	1.29×10^{29}				
	DC	k_D	q_e	0.99	8.89×10^{-4}	1.48×10^{-4}	0.01
		584	10				
Linear	Avrami	n_{av}	k_{av}	q_e	1.1×10^{-4}	2.2×10^{-5}	3.6×10^{-3}
		0.39	2.62	0.99			
	Bangham	k_0	σ	0.99	1.8×10^{-3}	3.03×10^{-4}	0.014
		9.92	0.001				
	PFO	k_1	q_e	0.38	39.15	16.7	2.2
		0.01	0.056				
	PSO	k_2	q_e	0.99	9.4×10^{-6}	-105.07	0.001
Linear		59.4	9.99				
	Elovich	β	α	0.47	45.68	17.94	2.38
		0.78	47.94				
	DC	k_D	q_e	0.99	1.8×10^{-6}	-118.45	4.7×10^{-4}
		1410	10.00				
	Avrami	n_{av}	k_{av}	q_e	1.08	-12.02	0.36
		0.03	10.27	0.69			
Linear	Bangham	k_0	σ	0.71	0.048	-36.92	0.077
		3.2	0.16				

3.3.1. PFO

The linear PFO model showed a poor fit to the experimental data, with a low R^2 value (0.38) and a calculated equilibrium adsorption capacity ($q_e = 0.056 \text{ mg g}^{-1}$) that differed considerably from the experimental value (Table 5). In contrast, the nonlinear model provided a much better fit, with a high R^2 value (0.998) and a calculated q_e (9.98 mg g^{-1}) that was close to the experimental value. The relatively high k_1 value indicates that Ce^{3+} adsorption proceeded rapidly during the initial stage of contact.

3.3.2. PSO

Both the linear and nonlinear PSO models showed excellent agreement with the experimental data, with high R^2 values, low error statistics (SSE, RMSE, χ^2 , and AIC), and calculated q_e values close to the experimental value (Table 5). The relatively high k_2 value is consistent with the rapid uptake of Ce^{3+} observed during the first 5 min of the experiment.

3.3.3. Elovich

The linear Elovich model showed a poor fit to the experimental data, whereas the nonlinear model provided a much better fit (Table 5). The relatively high α value indicates a rapid initial adsorption rate, whereas the low β value suggests that the adsorption rate decreases gradually as the surface coverage increases. These results are consistent with the rapid Ce^{3+} uptake observed during the early stage of the adsorption process and with previous studies on rare-earth adsorption systems (Nizam et al., 2024).

3.3.4. D-C

Among the linear kinetic models, the D–C model showed the best performance, with $R^2 = 0.998$, $\text{SSE} = 1.8 \times 10^{-6}$, $\text{RMSE} = 4.7 \times 10^{-4}$, and the lowest AIC value (-118.45) (Table 5). These results indicate that the adsorption kinetics cannot be explained by a single process and suggest that both diffusion and chemisorption contribute to Ce^{3+} adsorption onto Na-bentonite.

3.3.5. Avrami

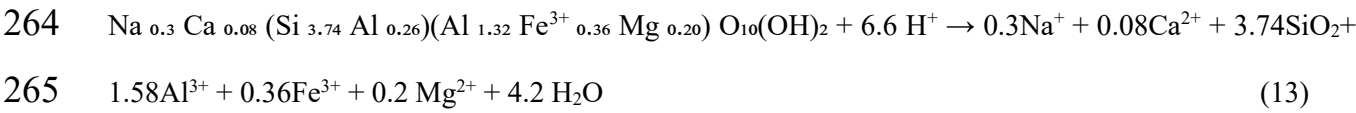
The nonlinear Avrami model provided the best fit to the experimental data, with $R^2 = 0.999$, $RMSE = 3.6 \times 10^{-3}$, $SSE = 1.1 \times 10^{-4}$, and $\chi^2 = 2.2 \times 10^{-5}$ (Table 5). It also showed the smallest difference between the calculated and experimental equilibrium adsorption capacities (Δq_e), outperforming the PFO, PSO, Elovich, and D-C models. The Avrami exponent ($n_{av} < 1$) indicates that Ce^{3+} adsorption was not controlled by a single kinetic mechanism but involved multiple processes. Considering the results obtained in this study, these processes most likely include cation exchange, surface complexation, and diffusion. Similar Avrami-type behavior has been reported for rare-earth adsorption on heterogeneous surfaces (Dotto et al., 2004).

3.3.6. Bangham

The Bangham model showed good agreement with the experimental data, with R^2 values higher than 0.99 and small Δq_e values (Table 5). These results indicate that intraparticle diffusion contributed to Ce^{3+} adsorption onto the Na-bentonite. However, the relatively low σ value suggests that pore diffusion was not the only rate-controlling process, indicating that additional surface and mass transfer processes also contributed to the overall adsorption kinetics.

3.4. Element release mechanism

To better understand the adsorption process, the release of structural elements (Si, Fe, and Mg) and exchangeable cations (Na^+ , K^+ , Ca^{2+} , and Mg^{2+}) was also evaluated. However, as reported by Zeng et al. (2024), montmorillonite can partially dissolve under acidic conditions. In the present study, the measured Si concentration reached a maximum of 4.5 ppm, indicating that clay dissolution was not significant. Silicate mineral dissolution, driven by protons and accompanied by Si release, is generally limited under near-neutral to slightly alkaline conditions (pH 6–9) (Blake and Walter, 1999; Chibesa et al., 2025). Similar observations were reported by Golubev et al. (2006) for smectite and by Köhler et al. (2003) for illite, kaolinite, montmorillonite, and other smectite minerals. According to Cappelli et al. (2018), the stoichiometry of Na-bentonite dissolution can be expressed as Reaction (13):



266 In practice, dissolution does not occur uniformly across the tetrahedral, octahedral, and interlayer sites of
267 clay structures (Zeng et al., 2024). The release of each element depends on its structural position and
268 chemical properties. The temporal evolution of these elements during Ce^{3+} adsorption is shown in Figs. 4
269 and 6, respectively.

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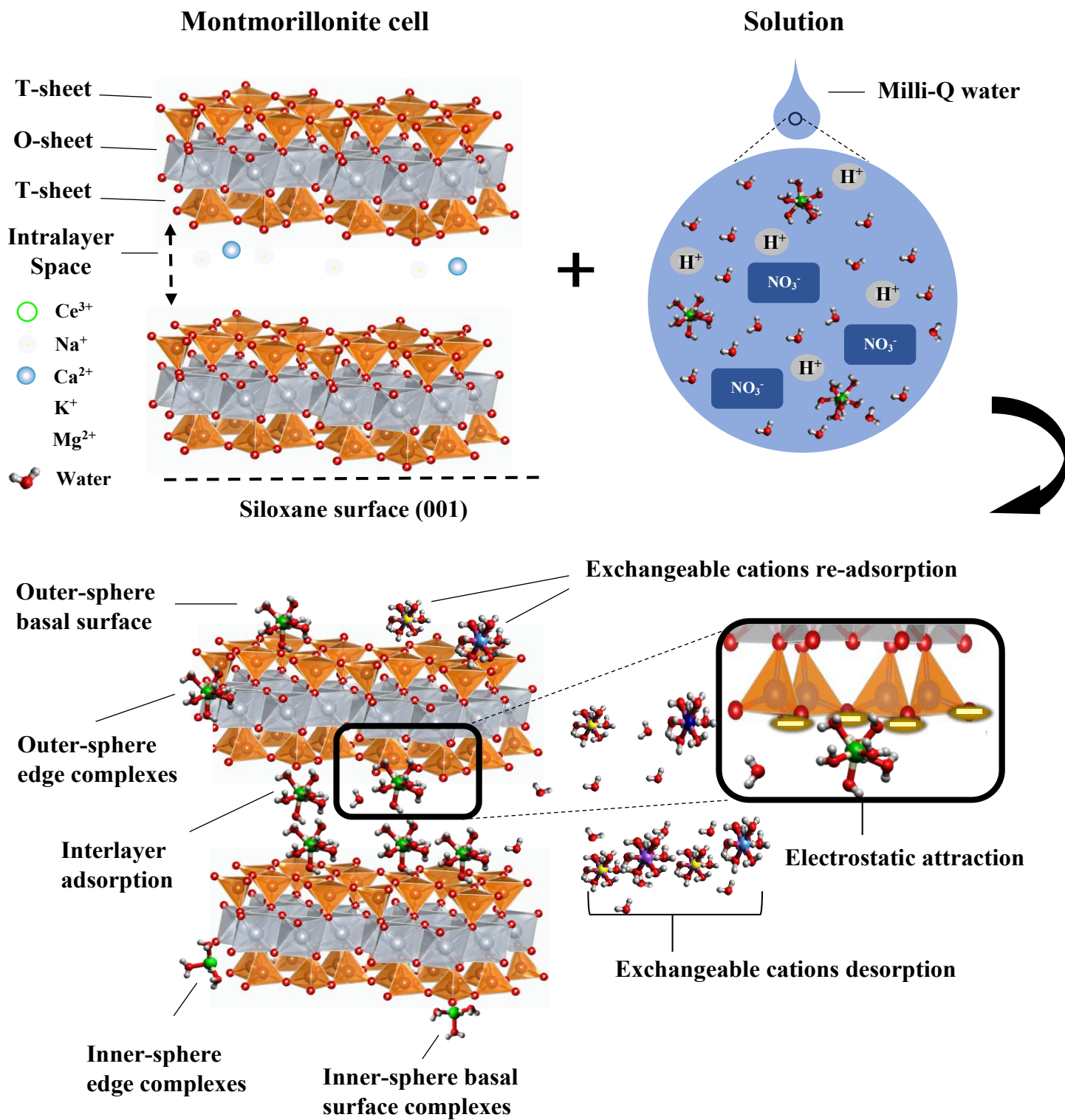
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280 Fig. 4. Schematic adsorption mechanism of cerium onto Na-bentonite and ion exchange of
 281 exchangeable cations.

Ce³⁺ ions can be retained by Na-bentonite through cation exchange and inner- and outer-sphere complexation (Fang et al., 2025). During this process, the structural and exchangeable cations may also be released into the solution. Figure 5 shows the concentrations of exchangeable cations released from Na-bentonite together with the adsorption of Ce³⁺ at different contact times. These results provide the basis for discussing the ion-exchange processes occurring during adsorption.

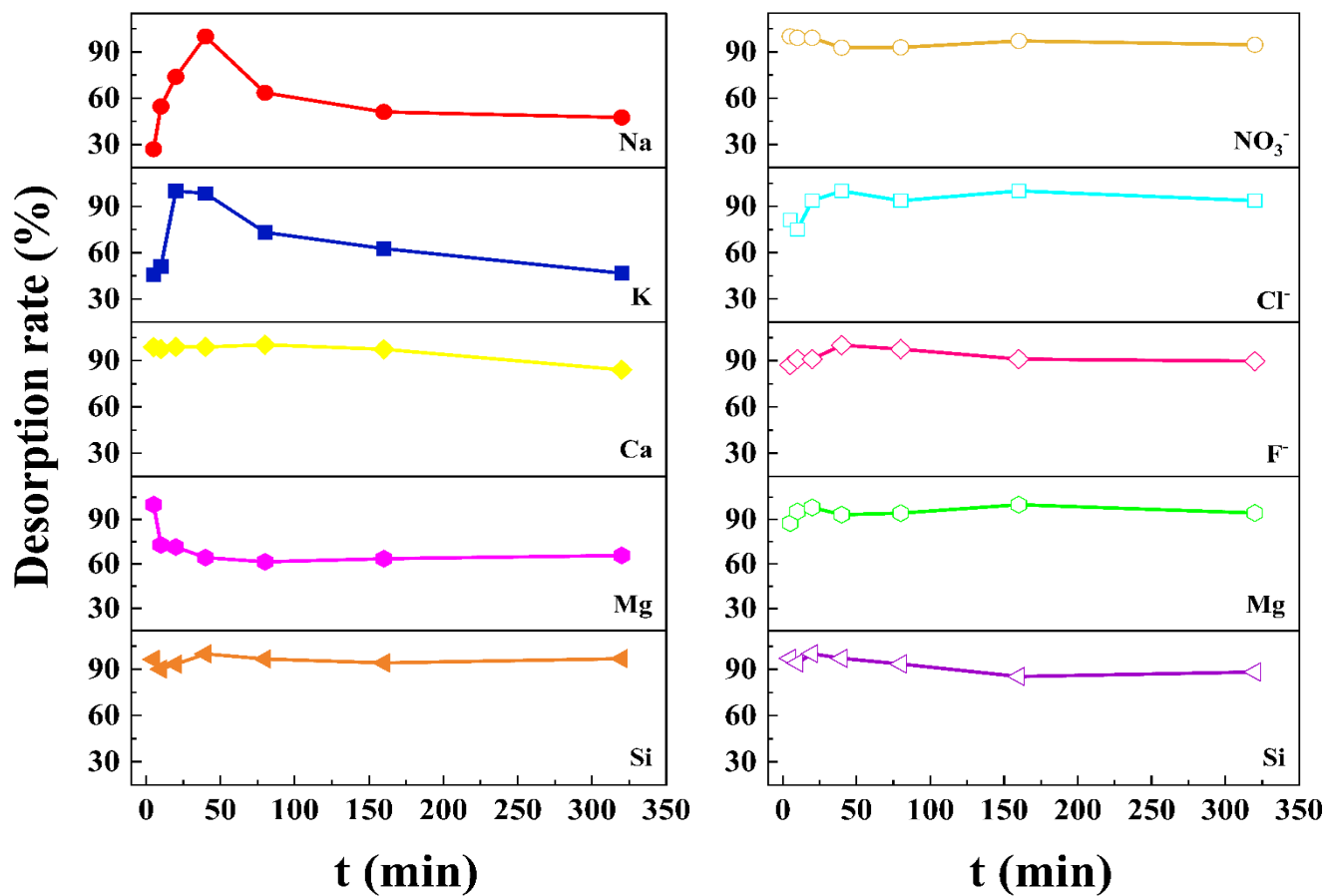


Fig. 5. Desorption of exchangeable cations (Na, K, Ca, Mg and Si) and anions (NO₃⁻, Cl⁻, F⁻, SO₄²⁻ and PO₄³⁻) from Na-bentonite and concurrent Ce³⁺ adsorption (Ce=10 mg L⁻¹, pH_{initial}=3.2, adsorbent dosage= 1 g L⁻¹).

From a physicochemical perspective, Na^+ is the most readily exchangeable interlayer cation in Na-bentonite (Neves et al., 2022). Accordingly, its concentration increased rapidly during the initial stage of the experiment and reached a maximum after about 40 min (Fig. 5). This release is mainly attributed to cation exchange with H^+ , Ce^{3+} , and Mg^{2+} (Reactions 14–16) (Rozalén et al., 2009; Yaghmaeiyan et al., 2022). Under the experimental conditions used here, proton-promoted dissolution is expected to play only a minor role (Ramos et al., 2011).



Most of the layer charge in montmorillonites originates from the octahedral sheets (Kumaragamage et al., 2021), which allows interlayer cations to remain hydrated and move relatively freely (Ghasemi and Sharifi, 2021). Cations with a higher charge than Na^+ are preferentially adsorbed at exchangeable sites on the clay (Rytwo et al., 1996).

K

As shown in Fig. 6, K^+ exhibited a release pattern similar to that of Na^+ , with the maximum concentration reached slightly earlier. Similar behavior has also been reported for Na^+ - and K^+ -saturated smectites (Morida et al., 2023). Because K^+ is less hydrated than Na^+ , it interacts more strongly with negatively charged clay surfaces and can inhibit clay swelling under partially dehydrated conditions (Tan, 2010; Mancinelli et al., 2007; Liu et al., 2010). After reaching the maximum concentration, both Na^+ and K^+ gradually decreased, and the mechanisms responsible for this behavior are discussed in the following sections.

Ca^{2+} and Mg^{2+}

Furthermore, no significant leaching of Ca^{2+} or Mg^{2+} was observed. The concentration of Ca^{2+} remained nearly constant during the initial 80 min, after which it exhibited a moderate decline. In contrast, Mg^{2+}

showed an initial decrease up to 80 min, followed by stabilization, indicating preferential adsorption, even exceeding that of Ca^{2+} . Although Sposito et al. (1983) reported that montmorillonite generally prefers Ca^{2+} adsorption over Mg^{2+} , Rytwo et al. (1996) noted that a reduction in $|\phi_0|$ diminishes Ca^{2+} adsorption more significantly than Mg^{2+} adsorption. As shown in Fig. 6, the surface potential initially decreased during the early stage and subsequently increased during the intermediate stage, corresponding to the onset of Ca^{2+} adsorption. Mg^{2+} adsorption within the interlayer may reduce the available interlayer space and consequently limit Ca^{2+} incorporation (Levy and Shainberg, 1972). Additionally, the preference of bentonite for Ca^{2+} and Mg^{2+} adsorption depends on its structural characteristics and surface charge density (Suarez and Zahow, 1989).

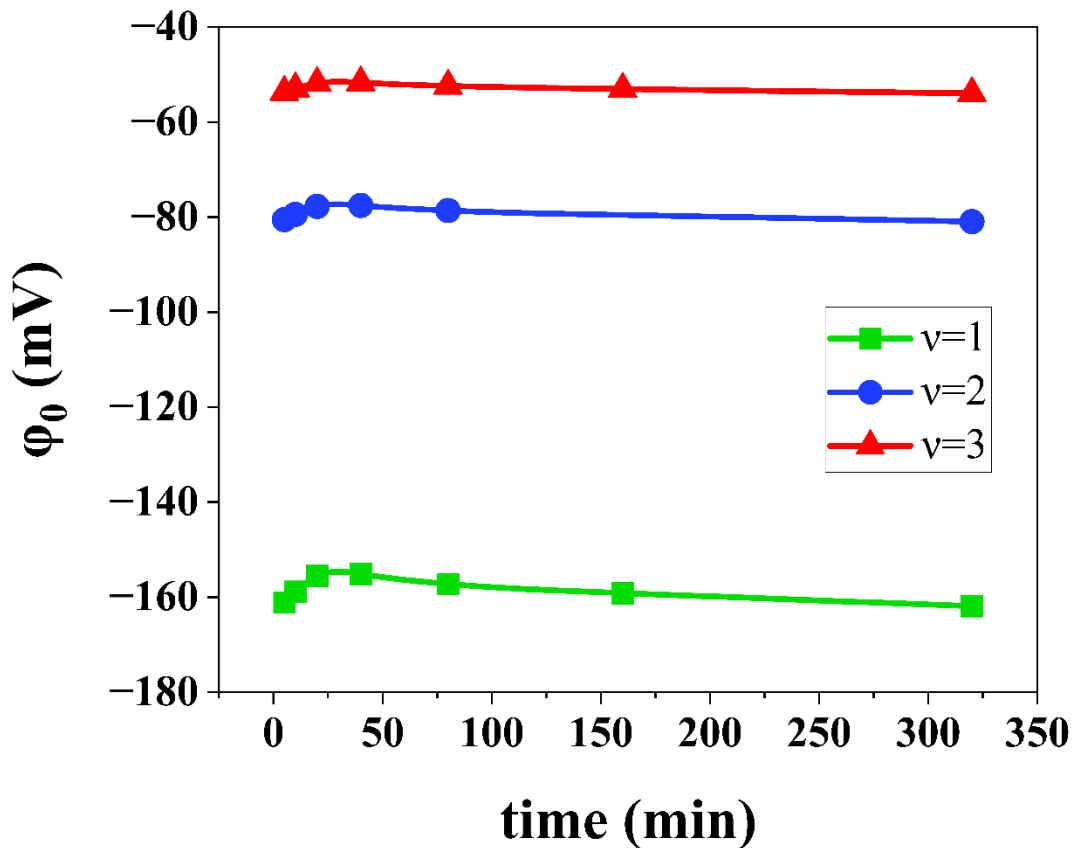


Fig. 6. Calculated surface potential of Na-bentonite in the presence of monovalent (green square), divalent (blue circle), and trivalent cations (red triangle)

Si and anions

In contrast to the exchangeable cations, dissolved Si showed only minor variations throughout the experiment, and approximately $95 \pm 5\%$ remained in solution. Dissolved silica originates mainly from the limited dissolution of SiO_2 , producing orthosilicic acid (H_4SiO_4), the dominant aqueous species below pH 8.5 (Krauskopf, 1966; Potysz and Bartz, 2022).



Because H_4SiO_4 is electrically neutral, its interaction with the negatively charged bentonite surface is weak, resulting in minimal adsorption (Luxton et al., 2006; Jordan et al., 2009). This behavior is consistent with the concentration profiles shown in Fig. 6, where Si and the measured anions remained largely in solution during the experiment. Among the anions, phosphate showed slightly greater retention than monovalent anions, reflecting its relatively stronger affinity for clay surfaces and ability to form inner-sphere surface complexes (Schell and Jordan, 1959).

3.5 Zeta Potential and Clay Mineral Swelling

The swelling behavior of clay minerals is important in many applications, including environmental management, oil and gas wellbore stability, geological hazard assessment, and the development of clay-based materials (Zhang et al., 2022). The ζ -potential, hydrodynamic diameter, and polydispersity index (PDI) were measured to assess the changes in the surface properties and colloidal behavior of Na-bentonite during Ce^{3+} adsorption (Delgado et al., 1986; Laguta and Shiknazarov, 2025). Figure 7 shows the changes in the ζ -potential, particle size (DLS), and PDI during Ce^{3+} adsorption onto Na-bentonite.

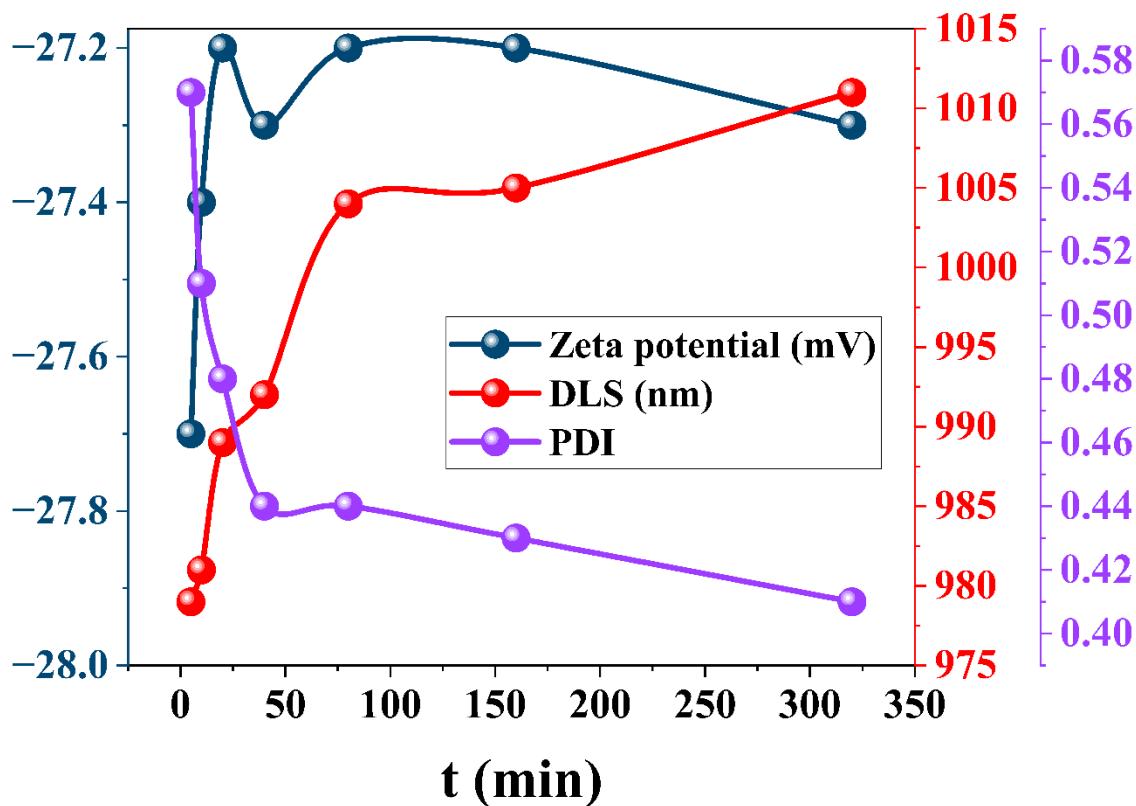


Fig. 7. ζ -Potential, DLS particle size, and PDI of Na-bentonite as functions of time.

During the experiments, the hydrodynamic diameter of the Na-bentonite particles increased slightly from 979 to 1011 nm ($\sim 3.3\%$), whereas the PDI decreased. This indicates limited particle association and a more uniform particle-size distribution. Similar changes have been reported for clay suspensions in the presence of multivalent cations, where charge screening can promote particle association (Gao et al., 2019). At intermediate contact times, cation re-adsorption may have affected interparticle and interlayer interactions through hydration effects. The adsorbed cations also screened part of the negative surface charge, which reduced the diffuse double-layer thickness and allowed limited particle association (Gao et al., 2019). At later stages, continued cation adsorption may have promoted closer particle association (Montes-H et al.,

2003). The increase in particle size remained small throughout the experiment, and no extensive aggregation was observed. The DLS measurements were obtained for particles smaller than 5 μm , and the PDI remained below 0.7, which is within the range generally considered acceptable for DLS measurements (Q. Li et al., 2021). The ζ -potential changed only slightly, from -27.7 to -27.2 mV. This change was within the experimental and instrumental uncertainty. Thus, the electrostatic repulsion between the particles was largely maintained during Ce^{3+} adsorption, and complete colloidal destabilization did not occur. A schematic representation of the proposed colloidal behavior of Na-bentonite during Ce^{3+} adsorption is shown in Fig. 8. It shows the partial compression of the diffuse double layer and the resulting limited particle association, while the suspension remained largely stable.

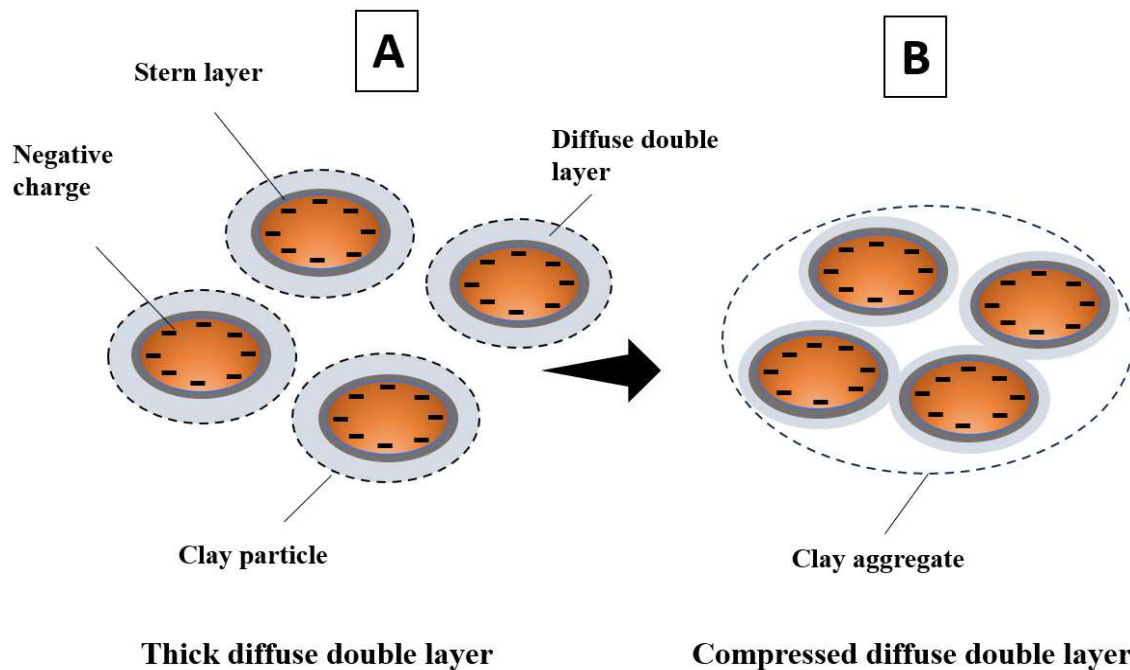
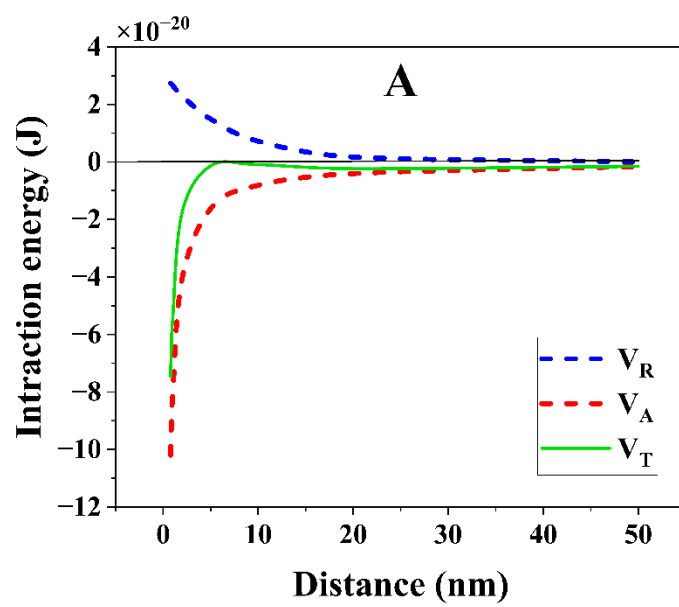


Fig. 8. Proposed colloidal behavior of Na-bentonite during Ce^{3+} adsorption: (A) stable dispersion of clay particles with an expanded diffuse double layer, and (B) partial double-layer compression promoting limited particle aggregation.

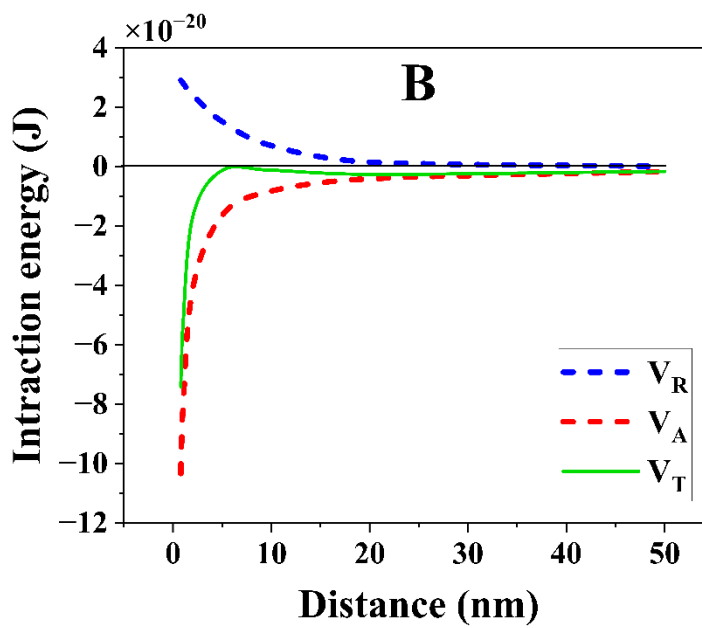
3.6 DLVO theory

The DLVO profiles (Fig. 9) show the balance between attractive van der Waals interactions and electrostatic repulsion in the Na-bentonite suspension. The van der Waals interaction remained attractive over the entire separation range, whereas electrostatic repulsion decreased with increasing interparticle distance. The resulting energy barrier limited particle association but did not completely overcome the attractive interaction, indicating slight colloidal destabilization.

The DLVO results agreed with the DLS and ζ -potential measurements. At 40 min, the lower energy barrier indicated a greater tendency for particle association, consistent with the slight increase in hydrodynamic diameter. However, the nearly constant ζ -potential showed that sufficient electrostatic repulsion remained to prevent extensive aggregation. Similar effects of multivalent cations on double-layer compression and particle association have been reported for clay suspensions (Li et al., 2020; Q. Li et al., 2021). The limited change in ζ -potential also suggests that aggregation was not controlled solely by charge neutralization. Cation-mediated interactions and rearrangement of the electrical double layer may have contributed to the observed particle association, as reported for Na-montmorillonite systems (Michot et al., 2013). Overall, Ce^{3+} adsorption reduced the electrostatic barrier and promoted limited particle association, but the remaining electrostatic repulsion was sufficient to maintain the overall colloidal stability of the Na-bentonite suspension.



390



391

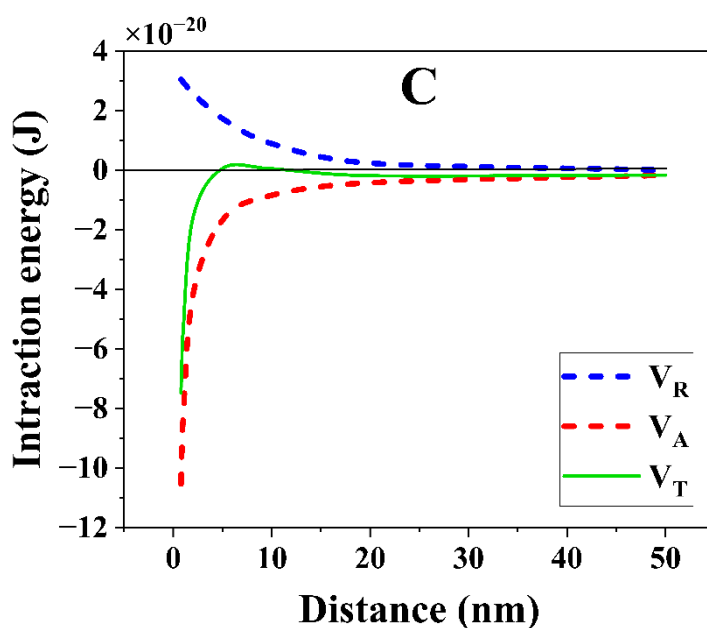


Fig. 9. Temporal evolution of the DLVO interaction energy profiles at 5 min (A), 40 min (B) and 320 min (C).

The gradual decrease in the energy barrier over time indicates partial compression of the electrical double layer and increased particle association, whereas the remaining electrostatic repulsion prevents extensive aggregation.

3.7 Comparative evaluation with previous studies

To better position the present findings within the existing literature, previous studies on adsorption, interfacial processes, and colloidal behavior in bentonite and montmorillonite systems were comparatively evaluated (Table 6).

Table 6. Comparative summary of previous studies and the present study

Study	Ion/element studied	Main focus	Key finding
Gao et al. (2019)	Cu ²⁺ , Ca ²⁺ , Mg ²⁺	Ion-specific aggregation	Divalent cations promoted aggregation through electrical double-layer compression and ion-specific surface interactions

Li et al. (2024)	Ca ²⁺	Particle aggregation	Ca ²⁺ promoted edge-to-edge and face-to-face associations in montmorillonite
Liu et al. (2025)	Na ⁺ , K ⁺ , Mg ²⁺ , Ca ²⁺ , Cs ⁺	Hydration and colloidal stability	Ion valence and hydrated ionic radius strongly influenced hydration-layer stability and colloidal behavior
Chen et al. (2024)	Hydrated interlayer ions	DLVO and swelling	Hydration repulsion and double-layer interactions influenced clay swelling
Klika et al. (2016)	Ce ³⁺ / Ce ⁴⁺	Ce sorption and oxidation	Ce sorption involved ion exchange and surface complexation and was affected by oxidation state
Chen et al. (2012)	La ³⁺	Adsorption on GMZ bentonite	La ³⁺ adsorption was rapid and accompanied by exchange of interlayer cations
Guo et al. (2009)	Eu ³⁺	Adsorption and surface complexation	Eu ³⁺ adsorption involved cation exchange and surface complexation
Bradbury et al. (2005)	Eu ³⁺ /Cm ³⁺	Surface complexation modeling	Sorption was described by coupled cation exchange and inner-sphere complexation
Present study	Ce ³⁺	Adsorption, ion exchange, and colloidal behavior	Ce ³⁺ adsorption was accompanied by cation exchange and limited changes in particle size and ζ -potential

The present results are consistent with those of previous studies showing that multivalent and rare-earth cations can modify clay behavior through cation exchange, surface interactions, and electrical double-layer compression. However, Ce³⁺ adsorption in the present Na-bentonite system caused only limited particle association, as shown by the small increase in hydrodynamic diameter and the nearly constant ζ -potential. The combined kinetic, ion-release, DLS, ζ -potential, and DLVO results indicated that Ce³⁺ adsorption was accompanied by cation exchange and changes in interparticle interactions, while the overall colloidal stability was largely maintained.

Conclusions

This study investigated the adsorption of Ce³⁺ onto Na-bentonite together with the associated cation exchange and changes in colloidal behavior. Ce³⁺ adsorption was rapid, reaching near-equilibrium within the first few minutes of contact. Among the tested kinetic models, the Avrami model provided the best fit, indicating that the adsorption process involved heterogeneous surface reactions together with diffusion-related processes. The release of dissolved species showed that Ce³⁺ adsorption was accompanied by significant Na⁺ and K⁺ release, confirming that cation exchange was an important adsorption mechanism. In contrast, Ca²⁺ concentrations changed only slightly, whereas Mg²⁺ was rapidly removed during the early stage of the experiment. Only minor changes in particle size and ζ -potential were observed, indicating

limited particle association, whereas the overall colloidal stability of the suspension was maintained. The DLVO calculations supported these observations by showing that Ce^{3+} adsorption reduced the electrostatic energy barrier through partial compression of the diffuse double layer, increasing the tendency for particle association without causing complete colloidal destabilization.

Overall, the combined kinetic, ion-release, DLS, ζ -potential, and DLVO results show that Ce^{3+} adsorption on Na-bentonite involves coupled adsorption, cation exchange, and interparticle interactions. These findings improve the understanding of the physicochemical behavior of Na-bentonite in the presence of rare-earth ions and provide useful information for evaluating bentonite as a barrier material in environmental and waste management applications.

Declaration

Ethical Approval

Not applicable.

Funding Declaration

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Availability of Data and Materials

The data generated or analyzed during the current study are available from the corresponding author on request.

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