



Original Article

Sorption behavior of Eu(III) on Tamusu clay under strong ionic strength: Batch experiments and BSE/EDS analysis

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ABSTRACT

The europium sorption on Tamusu clay was investigated by batch sorption experiments and spectroscopic study under the condition of strong ionic strength. The results demonstrated that europium sorption on Tamusu clay increased rapidly with pH value, but decreased with the ionic strength of solution increased. The europium sorption also increased in the presence of humic acid, especially at low pH value. The sorption could be fitted by Freundlich isotherm model and the europium sorption on clay was spontaneous and endothermic reaction. Besides, the result indicates that ion exchange was the main process at low pH value, while inner-sphere surface complexation dominated the sorption process at high pH value. The Backscatter electron scanning/Energy Dispersive Spectrometer(BSE/EDS) and the effect of Na for europium sorption results further suggested that europium sorption on Tamusu clay mainly competed with Na at low pH value. Overall, the results in this research were of significance to understand the sorption behavior of europium on the geological media under high ionic strength.

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1. Introduction

With the development of the nuclear industry, especially the rapid development of nuclear energy, a large amount of high-level radioactive waste (HLW) is generated [1]. How to prevent the HLW from entering the human environment? The currently acceptable treatment scheme is the deep geological disposal scheme [2,3]. The key to deep geological disposal is the selection of geological media. Clay and granite formations are considered as the most likely potential geological host rocks in the world [4,5]. In China, Beishan granite has been chosen as candidate geological host rock in the 1980s [6]. Recently, Tamusu clay in Inner Mongolia is another important potential geological host rock in China which has advantages of good plasticity, widely distributed, low permeability, and strong ion exchange capacity [7]. As we well known, the sorption behavior of radionuclides on geological host rock is of great significance for the assessment of the safety performance of HLW geological repository [8]. Therefore, it is important to study

the sorption research of radionuclides on Tamusu clay to predict the behavior of radionuclides in the environment.

Trivalent actinides (such as Am) are widely concerned nuclides because of their long half-lives and highly radioactive toxicity. The lanthanide europium is generally considered chemical analogue for actinides because of similar chemical properties [9]. Sorption of europium on minerals has been investigated extensively in many research groups [8,10–25]. For example, E.Tertre. et al. [26] observed that the Eu sorption on kaolinite and montmorillonite increased as temperature increased. Z. Chen. et al. [27] found that the sorption behavior of Eu on attapulgite was strongly affected by pH value and ionic strength of solution. L. Songsheng. et al. [25] concluded that the presence of humic acid promoted sorption of Eu on Gaomiaozhi bentonite at low pH value and reduced Eu sorption at high pH. K. Fukushi. et al. [28] applied Backscatter electron scanning/ Electron Probe Micro Analysis(BSE/EPMA) to confirm that the Eu sorption on granite competed with Na most likely at pH = 4. The spectroscopic analyses such as extended X-ray adsorption fine structure (EXAFS) and time resolved laser fluorescence spectroscopy (TRLFS) has confirmed that the Eu sorption on minerals was involved in inner-sphere surface complexation [13,16–18,29,30]. Unfortunately, most of the Eu sorption experiments were

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performed on single mineral until now, only very few research were involved in complex mineral assemblages [28,31–34]. As we know, natural geological bodies always contain multiple minerals, so the sorption behavior of Eu on Tamusu clay is significant to understand and predict the behavior of actinides in the environment. In addition, most of the Eu sorption behavior on minerals were studied only at lower ionic strength [20,33,35,36]. Since Tamusu groundwater has high ionic strength ($I = 0.6$ M) [7,37], it is important to explore the sorption behavior of Eu on Tamusu clay under strong ionic strength.

Our research group has studied the sorption behavior of selenium and cesium on Tamusu clay [7,37]. In this work, the sorption behavior of Eu on Tamusu clay was investigated by batch sorption experiments under high ionic strength in acidic, neutral and alkaline. X-ray diffraction (XRD) and Fourier transform infrared (FT-IR) spectroscopy were applied to study the characteristics of Tamusu clay. Back scattered Electron Imaging (BSE) and Energy Dispersive Spectrometer (EDS) were applied to explore the sorption mechanism of Eu on Tamusu clay. Based on this work, we can better understand the behavior of Eu in the environment under high ionic strength.

2. Materials and methods

2.1. Materials and chemicals

All chemical were dissolved with ultrapure water (Resistivity was $18 \Omega \text{ m}$). The clay samples from the depth of 439 in Inner Mongolia Tamusu were crushed and screened orderly, and then the smaller than diameter $75 \mu\text{m}$ were chosen for experiment. Humic acid was purchased from Tianjin Liyuan Chemical Co., Ltd (China). HA contained water, non-volatile matter, iron and the content was 88%. HA was a solid powder with a diameter of 0.125 mm . HA was not further purified before used. Tamusu groundwater ($I = 0.6$ M) was sampled from the Inner Mongolia area and analyzed. The ion species and content of groundwater were shown in Table 1. The Eu stock solution (1 g/L) was prepared by dissolving $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in dilute nitric acid.

2.2. XRD, FT-IR, BSE/EDS research of Eu sorption

XRD was used to analyze the mineral composition of clay and FT-IR was used to measure the surface functional groups of clay. After the thin sections of clay were in contact with the Eu solution for 6 days, they were washed repeatedly with ultrapure water and dried at 70°C for 24 h. The thin sections results were analyzed using BSE/EDS.

2.3. Batch sorption experiment method

The sorption experiment was researched by batch experiments in Tamusu groundwater. The initial concentration of Eu was $6.58 \times 10^{-5} \text{ M}$. A 30 mL Eu solution and 10 mg clay samples were mixed in 50 mL Erlenmeyer flasks. The pH meter used in this work was PHS-3C type pH meter (Shanghai Yidian Scientific Instrument Co., Ltd) and completed the two-point calibration before measuring the pH value. The pH values were the initial pH of the solutions before sorption. The pH value range was 2.0–8.0. The negligible

volumes of concentrated HNO_3/NaOH were used to adjust the pH values of the solutions. After the mixture was shaken to reach sorption equilibrium (previous experiments have shown that the balance time was 4d), the clay and solution were completely separated by centrifuge at 5000 rpm/min for 10 min. The Eu concentrations in the solution were measured by using inductively coupled plasma optical emissions spectroscopy (ICP-OES, Thermo Elemental, USA). The sorption percentage, sorption capacity and the distribution coefficient are calculated as the following:

$$\text{Sorption\%} = (C_0 - C_e) / C_0 \times 100\% \quad (1)$$

$$K_d = \frac{C_0 - C_e}{C_e} \times \frac{V}{m} \quad (2)$$

$$q_e = (C_0 - C_e) \times V/m \quad (3)$$

where sorption% is the sorption rate, K_d is the distribution coefficient (mL g^{-1}) and q_e is the sorption capacity (mg g^{-1}). C_0 and C_e are the initial Eu concentration (mg L^{-1}) and equilibrium Eu concentration in the solution (mg L^{-1}), respectively. V and m represent for total volume of solution (mL) and amount of clay (g).

3. Results and discussion

3.1. Characterization studies

3.1.1. XRD

Fig. 1 shows the XRD of Tamusu clay and Table 2 shows the mineral content of clay. The mineralogical composition was analcime, dolomite, quartz, microcline. The main mineralogical composition of Tamusu clay was dolomite (48.3%).

3.1.2. FT-IR

Fig. 2 shows the FT-IR of original Tamusu clay. The wavenumber at $3020, 2630, 1440, 729 \text{ cm}^{-1}$ were characteristic of dolomite [38,39]. The absorption features at 1620 cm^{-1} was O–H bending vibration [40]. Surface T–O–T (T = Al, Si) was located the range of 420 cm^{-1} – 500 cm^{-1} and 950 cm^{-1} – 1250 cm^{-1} [41]. The results were in agreement with the XRD. No obvious change in FT-IR was found after Eu sorption on Tamusu clay.

3.2. Effect of time and solid-to-liquid

Fig. 3 shows the effect of time for Eu sorption on Tamusu clay. The sorption rate increased with the sorption time increased. On the fourth day of the reaction, sorption achieved equilibrium. As shown in Fig. 4, when the amount of clay in the solution increased, the number of sorption sites increased, so the Eu sorption increased when solid-to-liquid increased [38].

3.3. Effect of initial pH and ion strength

The effect of solution ion strength and initial pH for Eu sorption on Tamusu clay are shown in Fig. 5. At pH value was 2.0, the Eu sorption rate was closed to zero. The main mineral of the Tamusu clay was dolomite. The chemical composition of dolomite was $\text{CaMg}(\text{CO}_3)_2$, which was likely dissolved at low pH. Dolomite

Table 1
The main ion species and concentrations of Tamusu groundwater.

Ionic species	Cl^-	SO_4^{2-}	HCO_3^-	Na^+	Ca^{2+}	Mg^{2+}	K^+	pH
Ion concentration(mM)	375.18	79.12	4.26	460.68	19.21	17.24	0.91	7.83

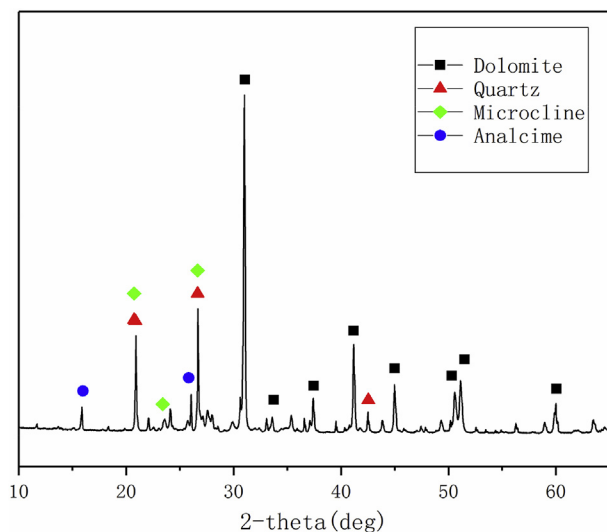


Fig. 1. XRD pattern of Tamusu clay.

Table 2

The content of Tamusu clay.

Phase name	Content (%)
Dolomite	48.3 ± 0.7
Quartz	17.9 ± 1.1
Pyrite	0.96 ± 0.11
Microcline	23 ± 4
Analcime	4.15 ± 0.12
Hydrotalcite, syn	0.45 ± 0.03
Muscovite-2M1	5.6 ± 0.6

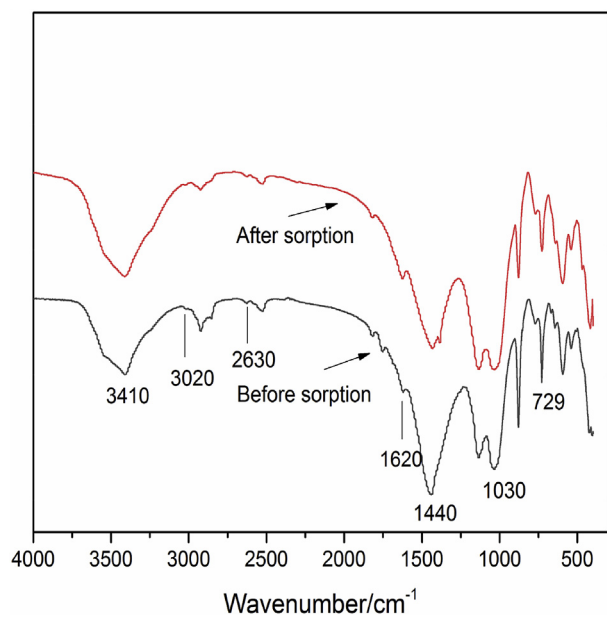


Fig. 2. FT-IR of Tamusu clay.

concentration of H^+ in the solution decreased. Therefore, the competitive effect of H^+ on the sorption sites was reduced, and the europium sorption increased. The sorption was strongly pH-dependent, meaning that Eu sorption was involved in inner-sphere surface complexation. In addition, the Eu sorption increased when solution ionic strength decreased at low pH value. In general, ion exchange is affected by solution ionic strength strongly. Therefore, the result indicated that ion exchange was the main sorption process when solution pH value was less than 6.0 and inner-sphere surface complexation was the main sorption process when solution pH value was greater than 6.0 [8,20].

3.4. Effect of HA

Humic acid is the macromolecular organic substance which exists widely in the environment. Humic acid may affect the sorption, migration, diffusion and toxicity of radionuclides in the environment [42]. Fig. 6 shows the effect of humic acid for Eu sorption on clay. The presence of humic acid promoted Eu sorption at low pH. The point of zero charge (PZC) of Tamusu clay was 8.45 and the clay surface was positively charged at low pH value [7]. HA possesses of phenolic, carboxylic and hydroxy functional groups. Part of hydroxyl, phenol and carboxyl groups of HA can interact with clay rock surfaces when pH value was less than 6.0 and the positive charge density of the clay rock surface decreased. The clay surface adsorbed HA can combine with Eu on clay surfaces at pH value < 6.0. Therefore, the sorption of Eu on clay increased in the presence of humic acid at low pH value. HA can promote the sorption of Eu on minerals at low pH value has been widely reported [16,21,43,44]. L. Songsheng et al. [25] confirmed that HA can combine with GMZ bentonite and the surface adsorbed HA can form strong complexes with Eu on bentonite surfaces at pH < 5.0. T. Yu et al. [21] researched the effect of HA for Eu sorption on natural red earth and found that the increase of Eu sorption on HA-NRE hybrids at low pH may be explained by a reduction in positive surface charge caused by the sorption of negatively charged HA at NRE surfaces.

3.5. Effect of Eu initial concentration and isotherm study

Fig. 7 shows the effect of Eu initial concentration for Eu sorption on clay. The sorption rate decreased when the Eu initial

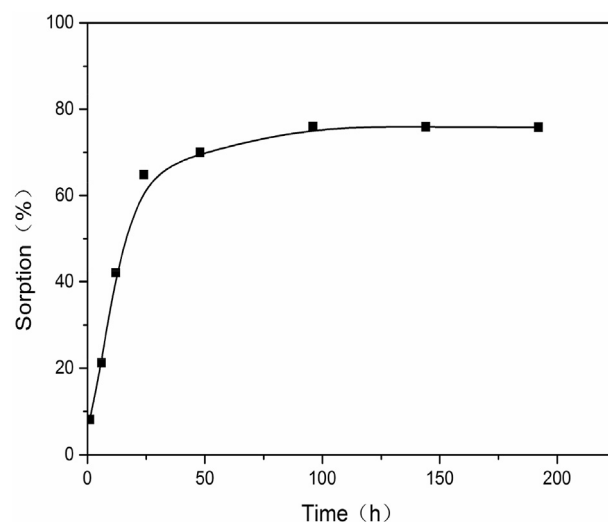


Fig. 3. Effect of time on the Eu sorption on clay.

($T = 298\text{ K}$, $\text{pH} = 5$, $C_0(\text{Eu}) = 6.58 \times 10^{-5}\text{ M}$, $m/V = 0.33\text{ g/L}$, and $V = 30\text{ mL}$).

dissolution may result in low Eu sorption at low pH value. The sorption of Eu increased rapidly with the pH value and then maintained high sorption rate when pH value was above 6.0. The pH-dependent of Eu sorption was explained by a decrease of H^+ competition. As the pH value of the solution increased, the

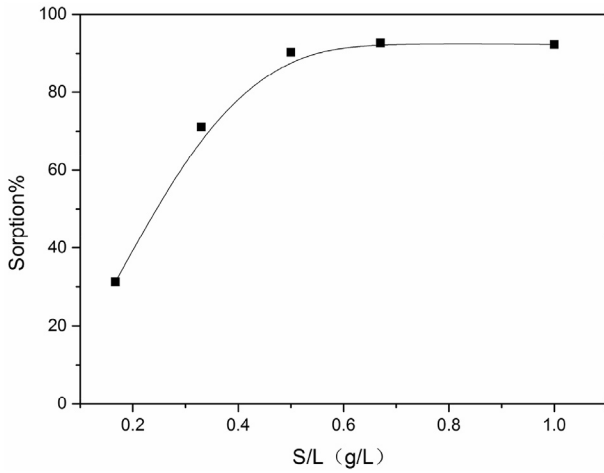


Fig. 4. Effect of solid-to-liquid on the Eu sorption on clay. ($T = 298\text{ K}$, $\text{pH} = 5$, $C_0(\text{Eu}) = 6.58 \times 10^{-5}\text{ M}$, $t = 6\text{ d}$, and $V = 30\text{ mL}$).

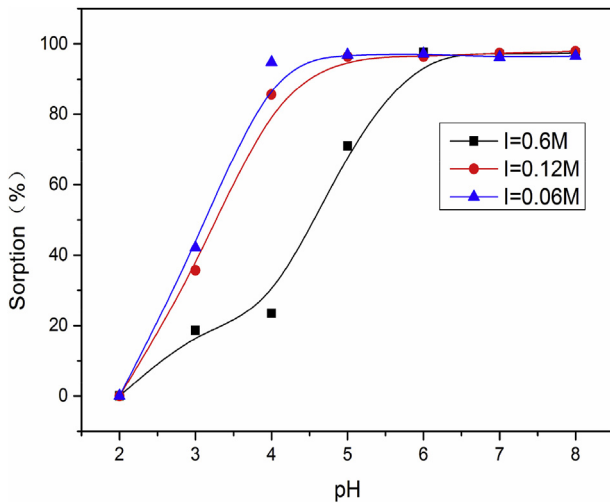


Fig. 5. Effect of ion strength and initial pH on the Eu sorption on clay rock. ($t = 6\text{ d}$, $C_0(\text{Eu}) = 6.58 \times 10^{-5}\text{ M}$, $T = 298\text{ K}$, $m/V = 0.33\text{ g/L}$, and $V = 30\text{ mL}$).

concentration increased. The trend was explained by the progressive saturation of sorption sites under high Eu initial concentrations.

The Langmuir model and the Freundlich model were applied to describe the sorption mechanism more adequately. The Langmuir model is extensively applied in single-layer sorption which assumes that the adsorbent surface is uniform and each adsorption site can only accommodate one adsorbate molecule [45,46]. The Freundlich model is an empirical formula for describing heterogeneous adsorption systems. If the solid surface is non-uniform, the exchange adsorption equilibrium constant is related to the surface coverage. It assumes that adsorbed on a heterogeneous surface and molecules that bind to the surface will affect nearby sites [47].

The linear form can be expressed as the following equations:

$$\frac{C_e}{q_e} = \frac{1}{q_L b_L} + \frac{C_e}{q_L} \quad (4)$$

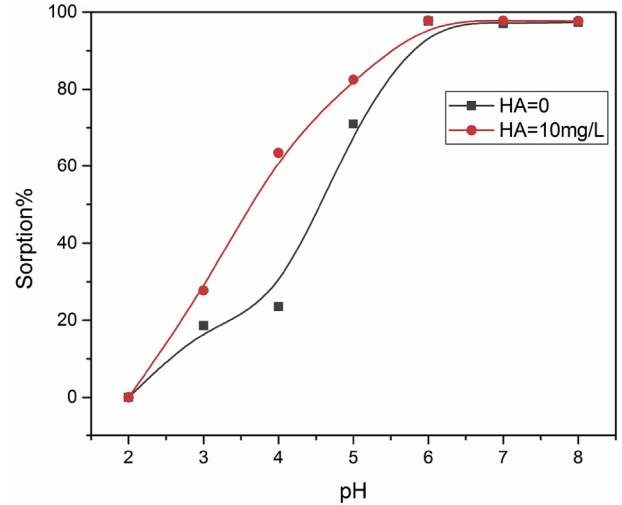


Fig. 6. Effect of HA on the Eu sorption on clay rock. ($t = 6\text{ d}$, $C_0(\text{Eu}) = 6.58 \times 10^{-5}\text{ M}$, $T = 298\text{ K}$, $m/V = 0.33\text{ g/L}$, $\text{HA} = 10\text{ mg/L}$ and $V = 30\text{ mL}$).

$$\text{Ln}q_e = \text{Ln}K_F + \frac{1}{n_F} \text{Ln}C_e \quad (5)$$

where q_e is the equilibrium sorption capacity (mg g^{-1}), C_e is the equilibrium Eu concentration in solution (mg L^{-1}), b_L is the Langmuir constant (L mg^{-1}) and q_L is the Langmuir monolayer sorption capacity (mg g^{-1}). K_F is the Freundlich constant that relates to the sorption capacity [$\text{mg g}^{-1} (\text{L mg}^{-1})^{1/n}$], and n_F is the Freundlich constant which indicates the sorption intensity.

The results of two models were shown in Table 3 and Fig. 8. Higher coefficient of determination ($R^2 > 0.99$) indicated that the europium sorption can be fitted by Freundlich isotherm model better. The result indicated that the europium sorption on Tamusu clay was primarily a heterogeneous sorption.

3.6. Effect of temperature

The radionuclide has a high heat release rate, and the HLW geological repository may be at high temperature, which affects the sorption behavior of Eu on clay rock. The effect of temperature for the europium sorption on Tamusu clay was researched in the range from 288K to 328K when pH value was 4.0 and 5.0. As shown in Fig. 9, the sorption rate increased rapidly with increasing temperature. The trend was consistent with previous research [26,48]. The thermodynamic parameters were shown in Table 4. The positive values of the change of enthalpy (ΔH) and the change of entropy (ΔS) showed that the Eu sorption was an endothermic reaction and increased confusion process. The negative values of the change of Gibbs free energy (ΔG) indicated that the sorption was spontaneous progress. Especially, ΔG became more negative with the temperature increased indicated that high temperatures can promote the Eu sorption on Tamusu clay.

The thermodynamic parameters were calculated using the following equations:

$$\text{Ln}K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (6)$$

$$\Delta G = \Delta H - T\Delta S \quad (7)$$

where ΔH is the change of enthalpy (KJ mol^{-1}), ΔS is the change

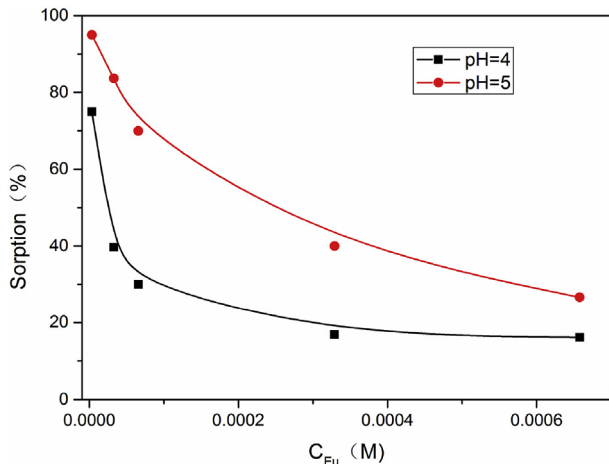


Fig. 7. Effect of initial concentration on the Eu sorption on clay. (pH = 4 and 5, $t = 6$ d, $T = 298$ K, $m/V = 0.33$ g/L, and $V = 30$ mL).

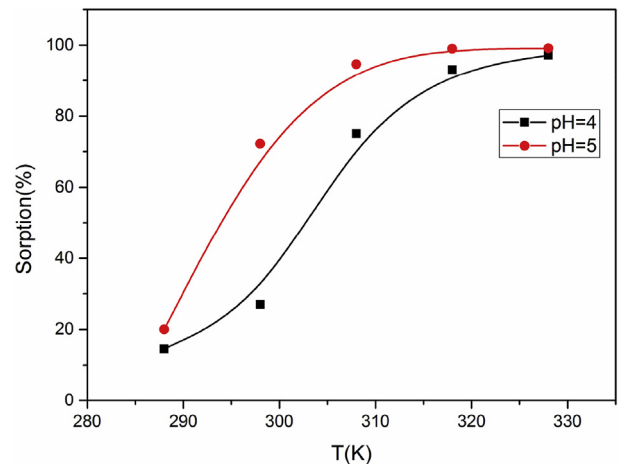


Fig. 9. Effect of temperature on the Eu sorption on clay rock. ($t = 6$ d, C_0 (Eu) = 6.58×10^{-5} M, $m/V = 0.33$ g/L, pH = 4 and 5 and $V = 30$ mL).

Table 3
Parameters of the Langmuir and Freundlich isotherms for the sorption of Eu on Tamusu clay.

Eu Sorption on Tamusu clay	Langmuir model			Freundlich model		
	q_L /(mg g ⁻¹)	b_L /(L mg ⁻¹)	R^2	K_F /[(mg g ⁻¹)(L mg ⁻¹) ^{1/n}]	n_F	R^2
pH = 4	57.8	0.0357	0.71	3.3535	1.7743	0.99
pH = 5	100	0.25	0.97	12.453	2.2173	0.997

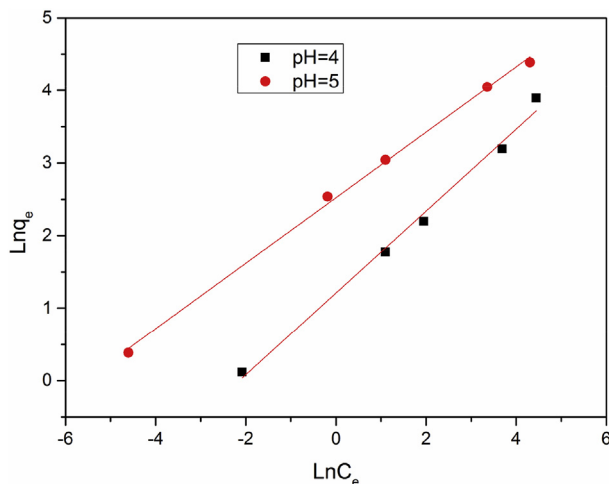


Fig. 8. Fitting result of Freundlich model.

of entropy (ΔS , KJ mol⁻¹ K⁻¹) and ΔG is the change of Gibbs free energy (KJ mol⁻¹). T is temperature (K), R is thermodynamic constant (KJ mol⁻¹ K⁻¹) and K_d is distribution coefficient (mL/g).

3.7. BSE/EDS analysis and effect of Na ionic strength

Fig. 10 shows the BSE image and elemental distributions of K, Na, and Eu in the original clay (Fig. 10 a–d) and after the sorption with the Eu solution (Fig. 10 e–h). We repeated BSE/EDS experiment at least twice and the experimental results are similar. Almost no difference was found in the distribution and content of K between those before and after the reaction (Fig. 10 b and f). A significant increase in Na distribution can be observed in BSE image (Fig. 10 c and g). Eu was evenly distributed throughout the BSE image (Fig. 10

h). Table 5 shows the element content of BSE before and after sorption. The wt% of Eu increased from zero to 3.53% after sorption. The Na content also increased from 1.97% to 3.61% in this area. Therefore, the region where Na increased corresponded to the Eu distribution region, meaning that Eu sorption was correlated with Na most likely. In addition, the similarity of the distribution of Na and Eu after sorption suggested that Eu was most likely to compete with Na [1,9]. Similar analyses could be found by related articles. K. Fukushi et al. [9] applied BSE/EPMA to research the changes in element distribution and content after Eu sorption. They observed that the increasing regions where the distribution of Eu and Na were closed and confirmed that the Eu sorption on granite competed with Na most likely at pH = 4. As shown in Fig. 11, the Eu sorption decreased with the ionic strength of Na increased at pH value was 5.0. The result further proved that the Eu sorption on Tamusu clay competed with Na most likely at low pH. The reason was that the content of Na⁺ in the solution was 0.46 mM, which was much higher than other cations.

4. Conclusions

Dolomite was the main mineralogical composition of Tamusu clay (48.3%) and the ion strength of Tamusu groundwater was 0.6 M. Batch experiments showed that the Eu sorption on Tamusu clay increased rapidly as pH value increased. As the ion strength of solution decreased, the sorption rate increased at low pH. The result indicated that ion exchange was the main sorption process at low pH and inner-sphere surface complexation dominated the sorption process at high pH. The europium sorption increased in the presence of humic acid at low pH. As the initial concentration of europium increased, the sorption rate decreased. The europium sorption could be fitted by Freundlich isotherm model. Thermodynamic parameters (ΔG and ΔH) indicated that the europium sorption was a spontaneous and endothermic process. The BSE/EDS and the effect of Na results indicated that Eu sorption was

Table 4
The thermodynamic parameters for the sorption of Eu on the clay.

	$\Delta H(\text{kJ mol}^{-1})$	$\Delta S(\text{KJ mol}^{-1}\text{K}^{-1})$	$\Delta G (\text{kJ mol}^{-1})$			
			288 (K)	298 (K)	308 (K)	318 (K)
pH = 4	115.495	0.45	-14.189	-18.69	-23.194	-27.7
pH = 5	151.55	0.582	-16.06	-21.88	-27.7	-33.52

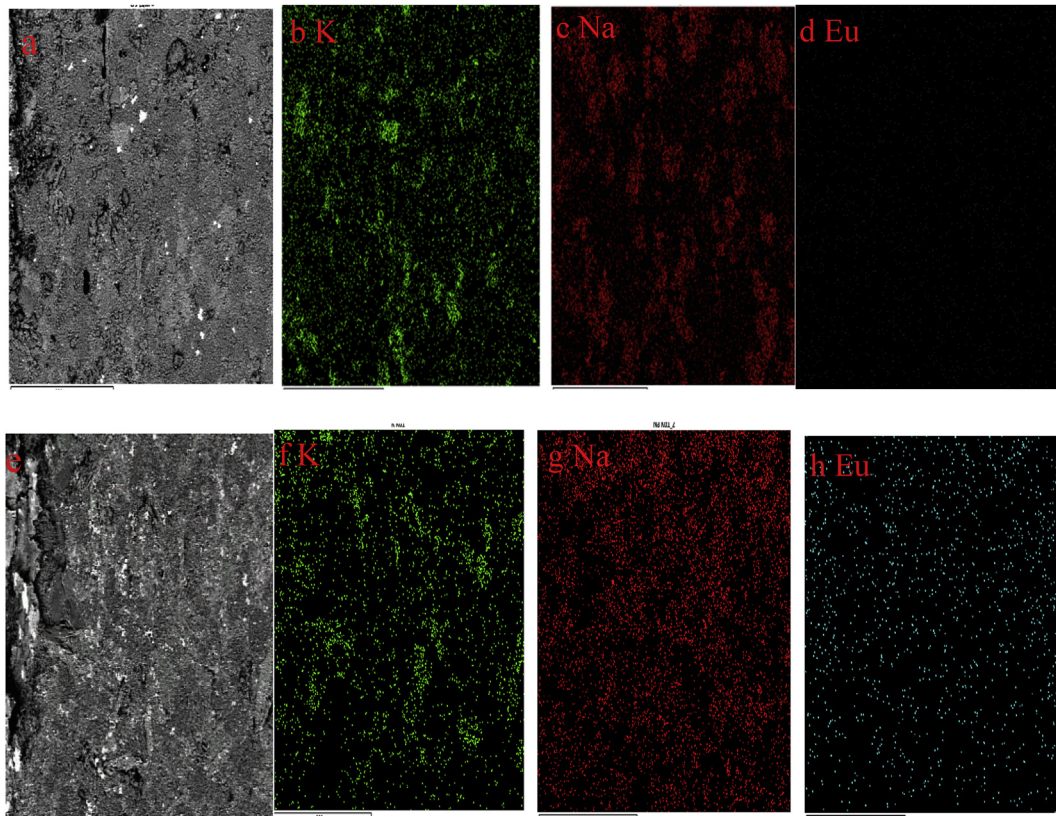


Fig. 10. BSE, K, Na, and Eu distribution images in Tamusu clay before (a–d) and after (e–h) the reaction with Eu(III) at pH 5.

Table 5
Element content of BSE before sorption and after sorption.

Before sorption		After sorption	
Element	wt%	Element	wt%
C	11.60	C	13.09
O	47.24	O	41.05
Na	1.97	Na	3.61
Mg	2.40	Mg	2.05
Al	3.83	Al	4.00
Si	19.50	Si	19.53
S	2.27	S	1.73
K	1.18	K	1.67
Ca	8.15	Ca	6.33
Fe	1.34	Fe	1.56
Eu	0.00	Eu	3.53
		Cl	1.85

correlated with Na most likely. Overall, the results reported in this work help understand the sorption behavior of Eu on clay materials under high-salt groundwater in deep geological environments.

Declaration of competing interest

The authors declare that they have no known competing

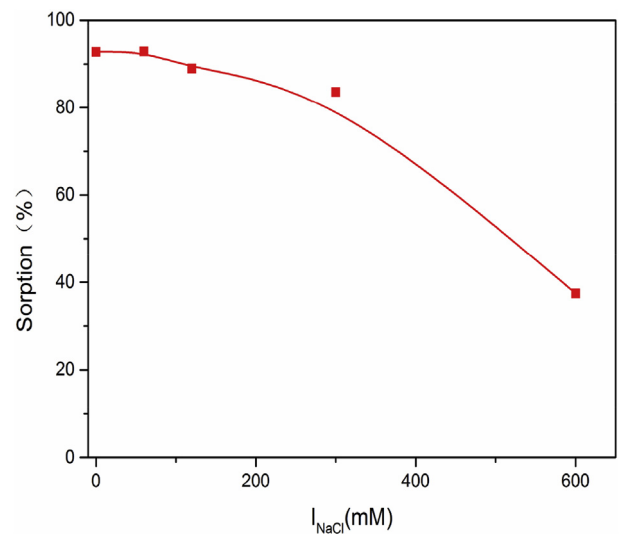


Fig. 11. Effect of I_{NaCl} on the Eu sorption on clay rock. ($t = 6 \text{ d}$, $C_0 (\text{Eu}) = 6.58 \times 10^{-5} \text{ M}$, $m/V = 0.33 \text{ g/L}$, $T = 298\text{K}$, $\text{pH} = 5$ and $V = 30 \text{ mL}$).

financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.net.2020.06.009>.

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