A New Liquid Membrane Diffusion Model for Characterizing the Adsorption Kinetics of Europium Using a Continuous Measurement Adsorption Platform

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Abstract

To explore the kinetic adsorption under continuous and nonequilibrium states, an integration of continuous measurement and adsorption platform kinetics method was proposed, which was initially called the ICM-AP kinetics method, and a corresponding kinetic adsorption experimental method was developed. Adsorption experiments of europium (Eu) on Ca-bentonite, Na-bentonite, and the D231 cation exchange resin were performed using the ICM-AP kinetics method and continuous measurements. Because the kinetic experimental results observed in this study were different from those of traditional batch adsorption data, pseudo-first-order or pseudo-second-order kinetic models were unsuitable for fitting the experimental data. Hence, a liquid membrane diffusion (LMD) model was developed based on the assumption of simultaneous adsorption/desorption to discuss the mechanism of kinetic adsorption. The kinetic adsorption mechanism was also studied by using XPS. The results indicated that the proposed adsorption model can fit the experimental data more suitably, and the adsorption/desorption behaviors of Eu on bentonite and the D231 resin were simultaneously observed, suggesting that the adsorption kinetics of Eu( ) was mainly dominated by hydrated Eu (III) ions on the liquid membrane.

Full Text

Preamble

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Abstract

To investigate adsorption kinetics under continuous and non-equilibrium conditions, this study proposes an integrated continuous measurement and adsorption platform kinetics method (ICM-AP kinetics method) and develops a corresponding kinetic adsorption experimental approach. Adsorption experiments of europium (Eu) on Ca-bentonite, Na-bentonite, and D231 cation exchange resin were conducted using the ICM-AP method with continuous measurements. Since the kinetic experimental results differed from traditional batch adsorption data, conventional pseudo-first-order or pseudo-second-order kinetic models were unsuitable for fitting the experimental data. Therefore, a liquid membrane diffusion (LMD) model was developed based on the assumption of simultaneous adsorption/desorption to elucidate the kinetic adsorption mechanism. X-ray photoelectron spectroscopy (XPS) was also employed to study the adsorption kinetics mechanism. The results demonstrated that the proposed adsorption model fits the experimental data more appropriately, with simultaneous observation of adsorption/desorption behaviors of Eu on bentonite and the D231 resin, suggesting that Eu(III) adsorption kinetics is primarily dominated by hydrated Eu(III) ions on the liquid membrane.

Keywords: ICM-AP method; LMD model; Adsorption Mechanism; Eu(III)

Introduction

Nuclear energy is receiving increasing attention worldwide as a clean and efficient energy source. France, as a long-standing nuclear power, has decided to restart large-scale nuclear power projects to maintain its status as a nuclear nation [1]. By 2021, China' s nuclear power generation accounted for 5.02% of total electricity generation for the first time, a proportion that continues to grow steadily [2]. However, the large-scale utilization of nuclear energy has led to the release of radioactive and highly toxic wastes into the environment, posing increased risks to human health and ecosystems.

Consequently, studies on radionuclide adsorption in ecological environments, including model development and experimental investigations, are critical for predicting the behavior of released radionuclides and assessing the safety of nuclear waste disposal [3]. According to the IAEA' s Status and Trends in Spent Fuel and Radioactive Waste Management [4], low-level radioactive waste accounts for approximately 95% of total radioactive waste, while high-level radioactive waste represents less than 1%. Reprocessing is widely considered an effective treatment for low-level radioactive waste, where the separation of radionuclides from waste streams is crucial [5-7].

Traditional adsorption is recognized as an effective and widely adopted method for removing radioactive pollutants from wastewater [8-10]. Research on radionuclide adsorption behavior primarily focuses on three aspects: nuclide species, adsorbent materials, and thermodynamic/kinetic models characterizing adsorption mechanisms. Nuclide species studied include uranium, thorium, transuranic elements (Np, Am, Cm, and Pu), fission products (Cs, Cr, and Pm), and lanthanides (Eu, Sc, and Ce) [11,12,13-16]. Adsorbent materials investigated encompass rock minerals (granite, attapulgite) [17,18], clay minerals (bentonite, red or yellow soil) [19,20], metal-organic frameworks (MOFs) [21], and organic polymeric materials [22,23], with uranium extraction from seawater receiving particular attention [24]. Studies on Eu adsorption onto clay minerals have practical significance; for instance, bentonite, due to its strong adsorption capacity and low hydraulic conductivity, is considered a major buffer and backfill material for geological disposal of high-level radioactive waste [25]. Numerous thermodynamic and kinetic models have been developed to characterize and predict adsorption behavior, including non-linear two-site Langmuir models for describing kinetic adsorption.

Previous studies [26,27] employed two-site Langmuir models to investigate the adsorption mechanisms of Cs and Se on mudrock. Non-linear heterogeneity-based isotherms have also been used to characterize anaerobic and aerobic adsorption of Se and Cs on various clay rocks.

In this study, europium (Eu) was selected among various cations for adsorption tests due to its stable speciation, primarily existing as Eu^{3+} cation at pH $<$ 9. Variations in pH affect H^{+} concentration, which significantly influences the adsorption capacity of Am(III) on Na-bentonite [28]. Theoretically, desorption fluctuation curves are more likely to be observed at relatively higher temperatures and initial Am(III) concentrations. Therefore, a series of tests varying pH values, temperatures, and initial concentrations were conducted to investigate the fluctuation mechanism.

Adsorption models are typically constructed based on the assumption of equilibrium attainment. Under this assumption, adsorption and desorption isotherms should be identical because thermodynamic equilibrium theory presumes complete chemical reversibility, yielding a unique (C, Q) pair [25]. However, adsorption mechanisms are driven by various controlled reactions or physical phenomena with reaction times varying from seconds to years [29]. This temporal variability primarily depends on activation energy (kJ/mol), representing the difference between adsorption activation energy $_1$ and desorption activation energy $_2$. For kinetic adsorption experiments, previous studies [30,31] focused solely on either adsorption or desorption kinetics. The time scales in these studies were relatively long, and measurement methods (ICP-OES or ICP-MS) for intermittent sampling had limitations, resulting in kinetic curves exhibiting only single adsorption or desorption states. In reality, adsorption and desorption kinetics should not be considered independently as they occur simultaneously, with one process dominating the overall mechanism. Therefore, these processes

should not be treated separately. This study proposes a novel kinetic experimental method incorporating continuous measurement to meet specific experimental requirements. An integrated continuous measurement and adsorption kinetics platform was designed, and an exponential kinetics model of liquid membrane diffusion was developed based on simultaneous adsorption/desorption assumptions to simulate the experimental kinetic data and calculate activation energy according to the Arrhenius law. The kinetic adsorption process was assumed to comprise two steps: (1) hydrated Eu(III) ions in solution diffuse to the adsorbent particle' s liquid membrane surface while desorption simultaneously occurs in this region, and (2) hydrated Eu(III) ions adsorbed on the liquid membrane further diffuse into solid internal pores [20].

2.1 A New Liquid Membrane Diffusion Model

A new exponential kinetics model of liquid membrane diffusion was proposed based on simultaneous adsorption/desorption assumptions to describe the complete non-equilibrium adsorption kinetics of Eu on Ca-bentonite, Na-bentonite, and D231 cation exchange resin. In this model, Eu adsorption on adsorbent particles occurs primarily in the outer liquid membrane layer and internal pores. The complete adsorption/desorption process was divided into two steps. First, hydrated Eu(III) ions diffuse into the liquid membrane at the outer layer of bentonite or resin particles, while hydrated Eu(III) ions in the liquid membrane are released back into solution. Second, hydrated Eu(III) ions attached to the liquid membrane further diffuse into solid internal pores, while simultaneously, hydrated Eu(III) ions are released from solid internal pores back into the liquid membrane (with physisorption primarily controlling the overall process). A schematic of this mechanism is shown in Figure 1 [Figure 1: see original paper].

In the first step, the reaction equation for solute diffusion into the liquid membrane can be expressed as follows:

$$\mathbf{N}(cid:3397)\mathbf{L} \Rightarrow \mathbf{NL} \quad (1)$$

Figure 1: Schematic diagram of the adsorption mechanism kinetics. The complete kinetic adsorption process was presumably divided into two steps: (1) Nuclides diffuse into the liquid membrane, expressed as (cid:3397) , and diffuse from the liquid membrane to solution, expressed as (cid:3397) . (2) Adsorption of nuclides from the liquid membrane onto solid internal pores occurs simultaneously with desorption, expressed as (cid:3397) and (cid:3397) , respectively.

In the aforementioned equations, N represents the nuclide solute, L is the liquid membrane, and NL is the compound of nuclides that have diffused into the liquid membrane. Since desorption occurs throughout the entire adsorption process, but the observed desorption fluctuation curves are random, irregular,

and difficult to quantify, only the empirical exponential rate of the adsorption reaction is given by Eq. (2):

$$\mathbf{dC1/C0}(cid:3404)\mathbf{k1e}(cid:2879)\boldsymbol{\gamma}\mathbf{1t} \quad (2)$$

where is the concentration of Eu in the liquid membrane (mg/L), is the initial concentration of the solution (mg/L), and t is the reaction time (s). and (1/T) are the coefficient and rate constant of the exponential equation, respectively.

In the second step, the adsorbate (Eu) located in the liquid membrane diffuses into the solid internal pores of bentonite and resin (with adsorption kinetic reactions driven by chemical surface complexation and cation exchange, respectively). The reaction equation can be expressed as:

$$\mathbf{NL}(cid:3397)\mathbf{S}(cid:3404)\mathbf{NS} \quad (3)$$

where S represents the solid internal pores and NS is the compound of nuclides adsorbed onto the solid internal pores. The reaction rate is given by Eq. (4):

$$\mathbf{dC2/C0}(cid:3404)\mathbf{k2e}(cid:2879)\boldsymbol{\gamma}\mathbf{2t} \quad (4)$$

where is the concentration of Eu in the solid internal pores (mg/L). Both and $_2$ represent initial concentrations of Eu in solution (C_0). Compared to the previous step, the non-equilibrium adsorption kinetics are relatively weaker. Considering the entire adsorption kinetics process, both steps occur simultaneously, but with different weight factors. If experimental conditions change, the weight factors of the two steps also change. Therefore, the total reaction rate can be expressed by Eq. (5):

$$\mathbf{dC1/C0}(cid:3397)\mathbf{dC2/C0} = \mathbf{a}(cid:3400)\mathbf{k1e}(cid:2879)\boldsymbol{\gamma}\mathbf{1t}(cid:3397)(cid:4666)\mathbf{1}(cid:3398)\mathbf{a}(cid:466$$

Eq. (5) can be rearranged to Eq. (6) as follows:

$$\Rightarrow d\left(\frac{C_t}{C_0}\right) = \left[a \cdot k_1 e^{-\gamma_1 t} + (1-a) \cdot k_2 e^{-\gamma_2 t}\right] dt \quad (6)$$

The indefinite integration of the total reaction rate in Eq. (6) yields Eq. (7):

$$\Rightarrow \int \frac{C_t}{C_0} = \int \left[a \cdot k_1 e^{-\gamma_1 t} + (1-a) \cdot k_2 e^{-\gamma_2 t}\right] dt \quad (7)$$

The indefinite integral result can be expressed by Eq. (8):

$$\Rightarrow C_t/C_0 = a \cdot \left(\frac{k_1}{\gamma_1}\right) e^{-\gamma_1 t} + (1-a) \cdot \left(\frac{k_2}{\gamma_2}\right) e^{-\gamma_2 t} \quad (8)$$

The parameter indicates the weight factor of the first step, while $(cid:4666)(cid:2879)\boldsymbol{\gamma 1}(cid:4667)$ and $((cid:2879)\boldsymbol{\gamma 2})$ are constants regarded as B and C. Rearranging this equation yields:

$$C_t/C_0 = a \cdot Be^{-\gamma_1 t} + (1-a) \cdot Ce^{-\gamma_2 t} \quad (9)$$

where is the concentration of Eu in solution at various reaction times (mg/L) and is the initial Eu concentration (mg/L). However, numerous unknown parameters significantly affect fitting accuracy. According to the indefinite integral derivation, parameters "B" and "C" in Equation (9) should be constants, both considered as "1" , with parameters "k_1" and "k_2" equal to r_1 and r_2, respectively. Since parameters "a" , "r_1" , and "r_2" were sufficient to accurately describe the experimental data, parameters B and C are not shown in Tables (1), (2), and (3).

Nevertheless, the random, irregular, and difficult-to-quantify desorption fluctuation curves observed for Ct/C_0 are shown in Figures 6, 7, and 8, respectively. The desorption rate equations for the two steps could not be determined in this study. The Arrhenius law provides the relationship between the kinetics constant and activation energy (kJ/mol) [31], which can be used to calculate the standard energy of the two steps proposed in the exponential kinetics model of liquid membrane diffusion:

$$\mathbf{k} = \mathbf{De}^{-E/RT} \quad (10)$$

where represents a dimensionless collision probability factor, is the molar gas constant (8.314 J/(K · mol)), and is the thermodynamic temperature (K). The "k" parameter in Equation (10) is based on the reaction constant. Using Equation (10), the activation energy E for steps 1 and 2 was calculated. The "k" parameter in Equation (10) was directly obtained from parameter "$_1$" shown in Equation (8) without mathematical deduction. The Δ calculated according to Equation (10) represents only a relative value providing reference for the two steps. The calculated parameter was considered as the weight factor , which can approximate the collision probability instead of parameter . The liquid membrane diffusion kinetics model proposed in this study is a non-linear equation; its parameters were directly fitted using MATLAB (version 2019b) rather than through linearization, followed by non-linear estimation.

2.2 Kinetics Adsorption Conditions

To meet the specific experimental requirements of the modified thermodynamic adsorption platform (relatively short kinetics adsorption time within a maxi-

mum of 60 min), a new kinetics adsorption method is proposed. The main difference from traditional batch tests is the simultaneous adsorption of Eu on bentonite and continuous monitoring of Eu concentration using ultraviolet spectrophotometry. The kinetics adsorption times in batch tests (generally occurring within 7 days) are significantly longer than those in the ICM-AP kinetics method.

Table 1 summarizes the various experimental conditions.

Table 2 details the experimental conditions for Eu adsorption on the D231 resin (Figure 8 [Figure 8: see original paper]).

2.3 Integration of Continuous Measurement and Adsorption Platform Kinetics Method

Each Ct/C_0 curve was obtained approximately 2-3 times because single measurements might show fluctuations caused by signal interference. For instance, if air entered the rubber tubing, the absorbance value would suddenly increase, affecting results. Key experimental conditions such as peristaltic pump rotation speed and mixed solution pH influence absorbance values, causing apparent errors in Ct/C_0. After extensive testing, the optimal rotation speeds for the magnetic rotor and inlet peristaltic pump were maintained at 1500 rpm and 20 rpm, respectively, with the mixed solution pH measured at 2.7. A schematic of the experimental setup is shown in Figure 2 [Figure 2: see original paper].

The kinetic adsorption devices used in this study differ from traditional batch or column methods. As shown in Figure 2, the adsorption reactor was filled with standard europium solution at concentrations of 1, 1.5, and 2 mg/L, and material powders of Ca-bentonite, Na-bentonite, and D231 cation exchange resin at a solid/liquid ratio of 30 g/L. Note that different solid/liquid ratios influence kinetic adsorption results, but under these specific conditions, the ratio remains essentially constant because the small particle size of material powders creates a homogeneous solution state, resulting in proportional reduction of solution and clay particles. To enable continuous measurements, traditional visible spectrophotometry was employed. When using traditional spectrophotometry to determine sample concentrations, specific conditions must be satisfied, including optimal sample pH and adequate time for color development stability. To meet these requirements, two electromagnetic heating stirrers (Figure 2) were used to adjust sample solution temperature and shorten color development time. The integrated kinetics experimental process comprises two major steps: the adsorption reaction and real-time online detection/recording. As shown in Figure 2, the mixed adsorption solution in beaker 1 contained either Ca-bentonite, Na-bentonite, or D231 cation exchange resin powders and standard europium solution. A magnetic rotor ensured complete reaction, and a 0.45 m filter membrane connected to the injection rubber pipe separated sorbent powders from the europium solution. The outlet rubber conduit connected to a three-way valve mixed the arsenazo solution (containing acetic acid-sodium acetate) with

the Eu sample solution. The mixed solution then flowed into a heating/cooling beaker before entering the modified cuvette for absorbance detection and recording via computer program, finally flowing into a waste liquid beaker. Key experimental conditions such as peristaltic pump rotation speed and mixed solution pH significantly influence absorbance values, causing apparent errors in Ct/C_0. After optimization, the magnetic rotor and inlet peristaltic pump speeds were maintained at 1500 rpm and 20 rpm, respectively, with mixed solution pH at 2.7. Appropriate rotation speeds ensured adequate adsorption reaction and color development. A peristaltic pump speed of 20 rpm provided sufficient adsorption reaction time. Initial Eu concentration was adjusted to maintain absorbance within the linear working range of the SP-721E spectrophotometer, generally not exceeding 2 mg/L, with arsenazo reagent pH maintained at 2.7.

3.1 Materials

All raw materials and reagents used were analytical grade without further purification, except for the D231 resin raw material, which had a particle size of approximately 0.45 m and was ground and passed through ~100 mesh sieves prior to use. The bentonite sample was obtained from Gaomiaozi and converted into Na-bentonite and Ca-bentonite according to a previous study [31]. The Eu solution was purchased from Guobiao (Beijing) Testing & Certification Co., Ltd. The acetic acid-sodium acetate pH buffer solution (pH 2.7) controlled by sodium hydroxide was purchased from Xilong Scientific Co., Ltd. The arsenazo reagent (1.0 g/L) was also purchased from Xilong Scientific Co., Ltd. An ultraviolet spectrophotometer (SP-721E), peristaltic pump (L100-1S-2), pH meter (PHS-3C), and X-ray photoelectron spectroscope were used for testing.

3.2 Preparation of the Integration of Continuous Measurement and Adsorption Kinetics Platform

Traditional adsorption kinetics research methods such as batch or column experiments have inherent limitations, including intermittent measurement of adsorption kinetics data. Since measurement and adsorption reactions were not simultaneous, many studies [20,32] suggested that fluctuations in adsorption capacity versus reaction time observed in kinetics curves resulted from measurement or artificial errors. Moreover, due to the lack of integrated adsorption and measurement equipment and corresponding test methods, irregular fluctuations in kinetics curves have not been thoroughly investigated. Traditional kinetic adsorption methods cannot explain irregular fluctuations observed in early-stage kinetic adsorption (within one hour), during which the majority of Eu adsorption on bentonite occurs, as indicated by frequent fluctuations in kinetics curves.

Therefore, to accurately understand adsorption kinetics, integration of continuous measurements and adsorption/desorption kinetics was proposed. The traditional SP-721E spectrophotometer (INESA Analytical Instrument Co., Ltd.) was retrofitted to achieve continuous injection and real-time online absorbance

display on a computer. The original cuvette bottom was pierced; a diagram of the physical device is shown in Figure 3 [Figure 3: see original paper].

For real-time online detection and recording, a visualization Chinese window program was developed, as shown in Figure 4 [Figure 4: see original paper]. This software collects experimental data from the aforementioned instruments, generating curves of adsorption capacity versus time (calculated from absorbance).

3.3 Kinetic Adsorption Tests and Modeling

The kinetic adsorption method used differs from traditional batch experiments. Three types of adsorbent materials were prepared, with operating concentrations designed using standard Eu solutions at 1, 1.5, and 2.0 mg/L. Experiments were conducted at varying temperatures (25°C, 35°C, and 45°C) and pH values (approximately 3.0, 4.0, 5.0, and 6.0) to investigate their influence on adsorption kinetics. Experimental data obtained using this specific kinetics method were simulated using a liquid-membrane diffusion exponential kinetic model to characterize adsorption kinetics. The trust region reflective algorithm and Levenberg-Marquardt option, essential for reliable analysis of experimental data from the new adsorption kinetics method, were employed. The residual root mean square error (RMSE) was used to determine goodness of fit, defined by:

$$RMSE = \sqrt{\frac{1}{m-v}\sum_{i=1}^{m}(Q_i - q_i)^2} \quad (11)$$

where is experimental data from the new kinetics adsorption method, is the corresponding fitting value, is the number of data points, and is the number of parameters in the liquid membrane diffusion exponent model.

4.1 XPS Study

XPS was used to study Eu(III) adsorption kinetics under different adsorption times. As shown in Figure 5 [Figure 5: see original paper], the main peak position of Eu $3d_5/_2$ varies at 15 and 30 minutes, indicating different binding energies of adsorbed Eu(III) at variable adsorption times. Since the adsorption reaction on the liquid membrane of Ca-bentonite particles dominated the initial adsorption process, the main Eu $3d_5/_2$ peak at 15 minutes may be attributed to Eu(III) hydration on the liquid membrane. As adsorption time increased, hydrated Eu(III) on the liquid membrane further diffused to the surface, with surface complexation occurring inside pore sites, increasing the Eu $3d_5/_2$ binding energy. The main peak positions for kinetic adsorption at 15 and 30 minutes were stable at 1130.8 eV and 1132.1 eV, respectively, indicating that Eu(III) adsorption on Ca-bentonite gradually stabilized. The binding energy of hydrated Eu(III) on the liquid membrane was lowest, and its binding was relatively unstable.

4.2 Analysis of the Ct/C_0 Curves for Eu Adsorption Kinetics on Na/Ca-Bentonite and D231 Resin

Prior to interpreting results, note that fluctuations in Ct/C_0 curves are not attributed to signal noise. First, if fluctuations were signal noise, they would be observed throughout entire Ct/C_0 curves and from the beginning. Second, as shown in Figure 6(b), Ct/C_0 curves for Eu(III) adsorption on Ca-bentonite at pH 5 and 6 were smooth without fluctuations, explained by the following states. A previous study [16] reported similar fluctuations in kinetic curves for Am(III) adsorption on Na-bentonite as a function of contact time.

Adsorption experiments were performed as functions of Ca-bentonite volume, pH, temperature, and initial Eu concentration, with each kinetic test lasting approximately one hour. As shown in Figure 6(a), increasing Ca-bentonite volume gradually improved adsorption rate while smaller irregular fluctuations appeared in the backend of Ct/C_0 curves. This phenomenon is attributed to physical desorption behavior of Eu(III) on the Ca-bentonite surface liquid membrane. Note that the entropy change of hydrated Eu(III) ions diffusing to bentonite surface is positive ($\Delta S > 0$). The dehydration step requires high energy provided by reaction temperature (25°C); thus, reaction rate apparently improves with increasing temperature. This represents step "1" of the liquid membrane diffusion model, where physical desorption nearly occurs as the rate-controlling step at the beginning (within 15 min), as indicated by Ct/C_0 curves. Based on liquid membrane diffusion model assumptions, the step 1 equation ((cid:3397)) shown in Figure 1 represents this physisorption kinetics behavior.

Ct/C_0 curves as functions of pH (4, 5, and 6) are shown in Figure 6(b). The descending behavior of Ct/C_0 curves at pH 5 and 6 was smooth, indicating that the entire reaction process was adsorption-dominated while physical desorption of Eu(III) on the Ca-bentonite surface liquid membrane was negligible. Two main interpretations explain this: decreased ionized H^+ concentration weakened competitive adsorption between Eu(III) and H^+ (bentonite surface charge is negative, and competitive adsorption influences step 2 ((cid:3397)) shown in Figure 1). However, the surface complexation chemical reaction process was dominant at these pH values, expressed by:

$$\equiv \mathbf{SOH} + \mathbf{Eu^{3+}} \Longleftrightarrow \equiv \mathbf{SOEu^{2+}} + \mathbf{H^+}$$

$$\equiv \mathbf{SOH} + \mathbf{Eu^{3+}} + \mathbf{H_2O} \Longleftrightarrow \equiv \mathbf{SOEuOH^+} + \mathbf{2H^+}$$

$$\equiv \mathbf{SOH} + \mathbf{Eu^{3+}} + \mathbf{2H_2O} \Longleftrightarrow \equiv \mathbf{SOEu(OH)_2} + \mathbf{3H^+}$$

The Eu adsorption process on bentonite does not alter bentonite's physical structure, only forming complex compounds $SOEu^{2+}$, $SOEuOH^+$, and $SOEu(OH)_2$. As indicated in these equations, reaction equilibrium shifts forward. These two factors ultimately led to steady decline in Ct/C_0 curves with pH.

When kinetic adsorption tests were performed at different temperatures (Figure 6(c)), curve discrimination was subtle, with few irregular fluctuations observed in the backend. This clearly indicates physical desorption of Eu(III) on the Ca-bentonite surface liquid membrane. As shown in Ct/C_0 curves in Figures 6(d), 6(b), and 6(c), hardly any fluctuations were observed, consistent with expectations for physical desorption of Eu(III) on the surface liquid membrane due to excessive Eu(III) in solution.

Comparing Eu adsorption curves on Ca-bentonite, Ct/C_0 curves for Eu on Na-bentonite were similar, as shown in Figures 7(a), (b), (c), and (d), with only slight differences in adsorption rates. The Eu adsorption process on D231 cation resin did not change the resin' s physical structure; instead, cation exchange occurred with the D231 resin functional group. Irregular fluctuations were also observed in the backend of Ct/C_0 curves, though their timing was difficult to determine precisely. These observations indicate desorption occurs during adsorption but do not confirm the exact timing. However, as shown in Figures 8(a), (b), and (c), irregular fluctuations in Ct/C_0 curves for Eu adsorption on D231 cation exchange resin are clearly observed, indicating that desorption was relatively stronger than on bentonite, with lower adsorption capacity. Kinetic adsorption of Eu on D231 was completely driven by cation exchange chemical mechanism with relatively lower selectivity. Its adsorption binding energy was also relatively weak, leading to easily reversible reactions. In contrast, fluctuations observed in Figures 6 and 7 were relatively weak because bentonite has higher adsorption capacity and selectivity for Eu, demonstrating weaker desorption phenomena.

4.3 Analysis of Parameters of the Exponential Kinetics Model of Liquid Membrane Diffusion

Table 3 presents parameters of the exponential kinetics model of liquid membrane diffusion for simulating experimental data of Eu adsorption on Ca-bentonite.

The RMSE values for simulation of the exponential model shown in Tables 3, 4, and 5 were considerably small, ranging from 1.45$×10^{-4}$ to 2.07$×10^{-5}$ (at least four to five orders of magnitude), indicating the proposed adsorption model is effective. Key parameters of the liquid membrane diffusion model and calculated activation energies are listed in Tables 3, 4, and 5. As shown in Table 3, increasing Ca-bentonite volume gradually increased parameter (weight factor for step 1) from 0.40 to 0.87, with rate constant $_1$ values larger than $_2$ (1.21×10^{-2}–6.89×10^{-3} > 1.26×10^{-4}–6.20×10^{-5}). *Moreover, step1activationenergy*(**E**_{1}$, for Eu adsorption on the liquid membrane) was lower than Δ_2 (for Eu adsorption on solid internal pores); lower activation energy resulted in faster, easier reaction rates. As Ca-bentonite volume increased, Δ_1 values hardly changed (9.89–10.6 kJ/mol), while Δ_2 values gradually decreased (22.7–15.8 kJ/mol). These results can be attributed to the non-equilibrium, unsaturated state of kinetic adsorption tests in this

study. The total liquid membrane volume of Ca-bentonite gradually increased, leading to more hydrated Eu(III) ions diffusing into the liquid membrane and consequently improving the weight factor ( ) value.

Meanwhile, increasing Ca-bentonite volume also rapidly increased surface complexation sites ( ), facilitating complexation reactions. Therefore, the activation energy Δ_2 calculated according to the Arrhenius law gradually decreased (22.7–15.8 kJ/mol). As mixed adsorption solution pH progressively increased, values increased and remained at approximately 0.7, indicating that hydrated Eu(III) ion diffusion into the liquid membrane (step 1) dominated the overall adsorption kinetics process. The rate constant $_1$ was larger than $_2$ (4.66×10^{-3} > 1.01×10^{-4}), and activation energy Δ_2 was larger than Δ_1 (14.7–20.2 > 9.89–12.7 kJ/mol), also indicating step 1 occurred more easily and rapidly than step 2. With temperature increase, parameters and Δ_1 first increased then decreased. Combined with Ct/C_0 curves at 35°C, step 1 for hydrated Eu(III) ion diffusion into the liquid membrane (= 0.8) dominated the kinetics process. As temperature increased, calculated Δ_2 values gradually decreased from 20.2 to 18 kJ/mol, facilitating step 2 occurrence. Adsorption tests under different initial Eu concentrations showed different trends for parameters , Δ_1, and Δ_2. As initial Eu concentration increased, total adsorbed Eu concentration (C_1+C_2) on liquid membrane and solid internal pores increased, while liquid membrane volume remained unchanged. However, the relative proportion concentration (C_1) decreased because step 2 for Eu adsorption on sites improved (C_2 increase was larger than C_1), causing reaction rate decrease (gradual Δ_2 increase from 20.2 to 25.4 kJ/mol).

Key parameters for Eu adsorption on Na-bentonite are also listed in **Table 4** , indicating similar adsorption kinetics processes based on the proposed model theory as Ca-bentonite. The calculated step 1 reaction rate ($_1$) was always larger (4.19×10^{-3} > 1.58×10^{-4})$than\gamma\_2$, indicating that front-end (rapidly decreasing) and rear-end (slowly decreasing) portions of curves correspond to Eu adsorption on the liquid membrane and solid internal pores, respectively.

Parameters for Eu adsorption onto D231 cation-exchange resin are listed in **Table 5** . For the pH series, parameters gradually increased (0.23–0.45) and D231 resin adsorption capacity improved according to Ct/C_0 curves in Figure 8. This occurs because Eu adsorption on D231 resin follows a cation exchange mechanism primarily dependent on solution pH. As pH increases, Eu(III) on the liquid membrane further supplies step 2 demand. Calculated step 1 reaction rates ($_1$) were always larger (5.13×10^{-3} > 1.50×10^{-4})$thanstep2rates(\gamma\_2$). The calculated weight factor and activation energies of both steps were hardly influenced by temperature. Comparing adsorption materials, bentonite parameters were larger than D231 resin parameters. Considering D231 resin parameters, the weight factor for Eu adsorption on bentonite was more strongly influenced by different experimental conditions.

However, according to calculated parameters in Table 5, Eu adsorption on D231 resin was primarily controlled by step 2 (chemical behavior: cation exchange).

5 Conclusions

In this study, desorption reactions were observed in Ct/C_0 curves during kinetic adsorption tests under various conditions. A new automated adsorption platform for continuous measurement and its corresponding kinetic adsorption experimental method were proposed to conduct kinetic adsorption experiments of Eu on Ca-bentonite, Na-bentonite, and D231 cation exchange resin. A new exponential kinetics model of liquid membrane diffusion simulated the experimental data to evaluate Eu adsorption kinetics characteristics. The model was consistent with experimental data. According to Ct/C_0 curves for Eu on Ca-bentonite, Na-bentonite, and D231 resin, irregular fluctuations in the backend of curves clearly indicated simultaneous adsorption and physical desorption. Eu desorption on D231 resin was more significant than on bentonite, attributed to lower selectivity of Eu on D231 resin functional groups. The values in Tables 3 and 4 were larger than those in Table 5, indicating that step 1 weight in Eu adsorption on bentonite was stronger than on D231, implying that bentonite' s negative surface charge improved Eu surface adhesion. Meanwhile, for D231 resin, resin particle surfaces were electrically neutral (step 1 weight factor lower than bentonite), and Eu adsorption on solid internal pores occurred through equal-charge cation exchange. The calculated step 1 reaction rate ($_1$) was always larger than $_2$, reflecting that front-end (rapid decrease) and rear-end (slow decrease) portions of curves indicate Eu adsorption on the liquid membrane and solid internal pores, respectively, consistent with Ct/C_0 curves and reflecting reaction activation energy Δ_2. XPS results demonstrated that Eu(III) adsorption on Ca-bentonite gradually stabilized. The binding energy of hydrated Eu(III) on the liquid membrane was lowest, and its binding was relatively unstable. A previous study [20] reported similar conclusions, supporting this study' s results.

Based on the above analysis, adsorption models proposed in this study can be integrated into chemical and physical adsorption models. The adsorption mechanism is shown in Figure 9 [Figure 9: see original paper], where kinetic curves observed in this study were not smooth but fluctuated, with curve (a) integrated with curves (b) and (c). Curve (b) represents chemical adsorption occurring on bentonite/D231 resin surfaces and internal pores, while curve (c) represents physical adsorption occurring in the liquid membrane. Curve (b) represents chemical adsorption types, indicating stable chemical bonds not immediately desorbed, whereas curve (c) represents hydrated Eu ion diffusion into the liquid membrane, which is relatively unstable. Therefore, fluctuation amplitudes in Ct/C_0 curves observed in this study were controlled by the weights of the two steps.

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7 Author Contributions

All authors contributed to study conception and design. Material preparation, data collection, and analysis were performed by Haoqi Yu, Tao Yu, and Jianhua Ye. The first draft was written by Haoqi Yu, and all authors commented on previous manuscript versions. All authors read and approved the final manuscript.

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Note: Figure translations are in progress. See original paper for figures.