

Article

Preparation of Modified Montmorillonite and Its Application to Rare Earth Adsorption

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Abstract: Montmorillonite, the major clay mineral in the tailings of weathered crust elution-deposited rare earth ores, was modified as an excellent adsorbent to enrich rare earth ions from solutions. It was demonstrated that 5% H₂SO₄ could be used as a modifier to effectively enhance the adsorption capacity of montmorillonite after modifying for 3 h with a liquid:solid ratio of 40:1 at 90 °C. A superior modified montmorillonite over montmorillonite on adsorption performance was analyzed by the XRD, FT-IR, SEM, and BET (Specific Surface Area and Pore Diameter Analysis). The adsorption behaviors of La³⁺ and Y³⁺ on modified montmorillonite were fitted well with the Langmuir isotherm model and their saturated adsorption capacities were 0.178 mmol/g to La³⁺ and 0.182 mmol/g to Y³⁺, respectively. Furthermore, (NH₄)₂SO₄ as a common leaching agent in weathered crust elution-deposited rare earth ores, were successfully used as the eluent to recover the adsorbed rare earth ions.

Keywords: rare earth; montmorillonite; adsorption; elution

1. Introduction

As an important clay mineral, montmorillonite (Mt) is also the main component of weathered crust elution-deposited rare earth ores, which is a typical ion adsorption ore providing the major resource of mid-heavy rare earth elements in the world [1,2]. In the mineralization of weathered crust elution-deposited rare earth ores, the original rocks containing rare earth (RE) are weathered and converted to clay minerals through a series of chemical, physical and biological effects in a warm and humid climate. Meanwhile, the hydrated or hydroxyl hydrated rare earth ions are adsorbed onto clay minerals during the weathering and infiltration process [3–5]. The RE in this ore can neither be dissolved nor hydrolyzed in water, but it can be leached out by an electrolyte solution through the ion-exchange method [6,7]. Therefore, numerous tailings made up of clay minerals are stacked in the heap leaching field. These clay minerals can be used as a natural scavenger of pollutants by taking up cations and anions either through ion exchange or adsorption or both, and are good adsorbents because of the existence of several types of active sites on their surfaces, including Bronsted and Lewis acid sites, and ion exchange sites [8]. The edge hydroxyl groups have been particularly active for various types of interactions. Further, clay minerals are cheap and thus can be used as low-cost and excellent adsorbents due to their unique properties as well as no toxic effects on the ecosystem [9,10]. Although the performance of clay minerals is mostly determined by intrinsic properties such as surface area, porosity, pH, and surface modifications, their final adsorption capacity changes with the type of substance adsorbed.

The adsorption capacity of clay minerals to RE ions is as follows: Mt > halloysite > illite > kaolinite [11]. Among them, Mt has a net negative charge of 0.8 unit per unit cell. In other words, Mt contains abundant adsorption sites available within its interlayer space as well as on the outer surface

and edges and this is responsible for giving superior activity to Mt as an adsorbent [12]. Mt is formed by negatively charged silicate layers (about 1 nm) connected by electrostatic interaction. It belongs to the 2:1 clay minerals, the basic structure unit of which is composed of two silica tetrahedrons with an interlayer of aluminum oxygen octahedron. The atoms in this interlayer, which are common to both sheets, become oxygen instead of hydroxyl [13]. The isomorph substitution of Al^{3+} by Si^{4+} in the tetrahedral sheet and by Mg^{2+} or Zn^{2+} in the octahedral sheet results in a net negative charge on the clay surface, which makes it gain the ability to absorb certain cations. Moreover, Mt invariably contains exchangeable cations and anions held to the surface. The prominent cations and anions found between the sheets are K^+ , Na^+ , Mg^{2+} , Cl^- etc., and these ions are easily exchanged by other lower valence ions, which mainly carries out between the crystal layers and shows no effect on the Mt structure [14]. Adsorption of cations onto Mt involves two distinct mechanisms: (1) an ion exchange reaction at permanent charge sites, and (2) formation of complexes with the surface hydroxyl groups [15]. However, the industrial application of Mt is limited due to the crystal structure and negative charge of natural clays and interlayer impurity defects [16]. Single modifications of Mt through acid activation, inorganic salts, and cationic surfactant or polymer activation have attracted considerable interest and the adsorption capability of clay minerals can be successfully improved through modification [17].

In industry, the RE concentration of leachate from weathered crust elution-deposited RE ores is approximately 0.2–2.0 g/L [11]. Although the precipitation and extraction are used to recycle RE, there is still some residual RE in the liquor with the concentration approximately below 0.15 g/L. To some extent, a large amount of RE resources is wasted. Therefore, the reuse of dumped tailings to enrich and recover RE in low-concentration solution is getting more and more attention. At present, some scholars have conducted a lot of researches to enrich RE using chemisorbent, ion exchange resin and so on [18–20]. As the major component of weathered crust elution-deposited rare earth ores, the clay minerals are considered superior to other adsorbents such as activated carbon, which can contribute to the removal of heavy metals [21–23], organic pigments [24] and dyes [25,26] owing to their higher surface area, pore volume. The above studies mainly focus on the adsorption process by the untreated clay minerals. Mt as the major component of weathered crust elution-deposited rare earth ores, is abundant in the RE ores processing field, which can be modified to recycle low concentration RE from the mineral processing wastewater. In order to find a new and efficient technology to recover RE from liquid through ore tailings, modified Mt was prepared and applied to recover RE in this study.

2. Experimental

2.1. Materials and Apparatus

Mt with a cation exchange capacity (CEC) of 70 mmol/100 g, Lanthanum nitrate, Yttrium nitrate, hexadecyl trimethyl ammonium bromide (HDTMA), Sodium diethyl dithiocarbamate (DDTC), zinc oxide, sulfuric acid, ascorbic acid, sulfosalicylic acid, xylene orange, hexamethylenetetramine, hydrochloric acid, and ammonium hydroxide were purchased from Sinopharm Chemical Reagent Co, Ltd., China with analytical grade. Standard solution of zinc was purchased from National Center of Analysis and Testing for Nonferrous Metal and Electronic Materials.

Mechanical thermostatic water bath vibrator (MMS-1) and electronic analytical balance (AL-104) by mettler Toledo instrument were used in the study.

2.2. Preparation of Modified Mt

We placed 2 g Mt in a three-necked flask with an acid mixture, which was made up of 40 mL HCl solution at the volume ratio of 1:1 and 40 mL H_2SO_4 solution at the volume ratio of 1:4. The mixture was stirred for 4 h at 90 °C, and then filtrated and washed with deionized water until the filtrate became neutral. The modified Mt, G1, was obtained after drying at 60 °C for 24 h prior to being ground. The acid modified Mt, G3, was prepared through H_2SO_4 (80 mL) modification under the same condition.

Similarly, 20 mL HCl solution at the volume ratio of 1:1 and 1:10 were mixed with 2 g Mt, respectively. The mixtures were stirred for 2 h at room temperature, and then filtrated and washed with deionized water until neutral. After drying and grinding, the acid modified Mt, G2 and G4, were obtained.

We dissolved 0.413 g mixture of HDTMA and DDTC (the mole ratio is 1:1) equal to the cation exchange capacity (CEC) of Mt in 100 mL deionized water to form an organic composite modifier. 2 g Mt was dispersed in 100 mL of deionized water and kept standing for 24 h prior to addition of the organic composite modifier. After stirring at 70 °C for 2 h, the mixture continued to be stirred at room temperature for 24 h. The sample was filtered and washed repeatedly with deionized water until without Br⁻ checked by AgNO₃ (0.1 mol/L) solution. After drying and grinding, the organo-modified Mt, G5, was obtained.

We dispersed 2 g Mt in 100 mL of deionized water containing 0.510 g HDTMA equal to CEC of Mt and stirred at 70 °C for 2 h. After filtration, the sample was washed by deionized water until supernatant without Br⁻ checked by AgNO₃ solution and then dried at 60 °C for 24 h prior to being ground. The organo-modified Mt, G6, was obtained.

As shown in Table 1, the G0 is the raw Mt and the acid modified Mt (G1–G4) and organo-modified Mt (G5–G6) are described as follows:

Table 1. Preparation of different modified Mt.

Modified Mt	Modifier	Volume (mL)/Mass (g)	Temperature (°C)	Time (h)
G0	-	-	-	-
Acid-Mt	G1 HCl (1:1) + H ₂ O ₄ (1:4)	40 mL + 40 mL	90	4
	G2 HCl (1:1)	20 mL	room temperature	2
	G3 H ₂ SO ₄ (1:4)	80 mL	90	4
	G4 HCl (1:10)	20 mL	room temperature	2
Organo-Mt	G5 HDTMA + DDTC (mole ratio is 1:1)	0.413 g	70	2
	G6 HDTMA	0.510 g	room temperature	24
			70	2

Note: “-” means untreated.

2.3. Analysis and Characterization Methods

The concentration of RE before and after adsorption was determined by ethylene diamine tetraacetic acid (EDTA) titration using xylenol orange as indicator and hexamethylenetetramine as buffer. Solution pH was adjusted with NH₃·H₂O and HCl to keep pH values ranging from 5.0 to 5.5. The detailed description of this method also can be found in the literature [27].

An X-ray diffractometer (XRD, D8-ADVANCE, Bruker, Karlsruhe, Germany) was used to analyze the crystal structure of clay powders. The samples were tested in dry state, so the powder wafer method and Cu target radiation were adopted. Powder X-ray diffraction (XRD) experiments were performed between 2° and 80° (2θ) with a step size of 0.02° and a measuring time of 0.8 s per step.

A Fourier transform infrared spectrometer (FT-IR, Nicolet 6700, Thermo Fisher Scientific, New York, NY, USA) was used to estimate changes in chemical bonds of clay minerals. FT-IR spectra were carried out at room temperature. The specimens were prepared by mixing sample and KBr with the ratio of 1:100 (mass ratio) followed by pressing the mixture into pellets. A pure KBr was measured as background. All spectra were collected over 64 scans at a resolution of 4 cm⁻¹ in the wavenumbers range from 4000 to 400 cm⁻¹.

A scanning electron microscope (SEM, JSM-5510LV, Japan Electron Optics Laboratory, Tokyo, Japan) was used to estimate the thickness and observe the morphology and microtopography of Mt. The samples were initially placed in a vacuum chamber to coat with a thin layer (few nanometers) of gold (Au). The secondary electron resolution was 3.5 nm (30 KV, WD = 6 MM). All the experiments were conducted at room temperature of 25 °C.

A surface area and porosity analyzer (BET, ASAP 2020 HD88, Micromeritics, Atlanta, GA, USA) was used to analyze the specific surface area, pore volume and pore size of Mt. The specific surface area of the Mt was determined by N₂ adsorption method.

2.4. Adsorption and Elution Experiment

2.4.1. Adsorption Experiment

We placed 0.5 g modified Mt into a centrifuge tube containing 25 mL RE ions solution to take an adsorption in the constant temperature oscillator with the volatile rate of 165 r/min for 14 h. Then the mixture underwent a solid/liquid separation process by filtration. The RE concentration was analyzed to calculate the equilibrium adsorption capacity (Q_e) according to the following equation [28,29]:

$$Q_e = \frac{(C_0 - C_{e1})}{m} \times \frac{V}{M_{RE^{3+}}}, \quad (1)$$

where the C_0 and C_{e1} are initial and adsorption equilibrium concentration of RE, mmol/L. V is the volume of solution, cm³ and m is the weight of adsorbent, g. $M_{RE^{3+}}$ is the molar mass of rare earth ion.

2.4.2. Isothermal Adsorption

Modified Mt (0.5 g) was mixed with 25 mL RE solution with different concentrations and filtrated after shaking for 14 h. The RE concentration of filtrate was measured and the equilibrium adsorption capacity was calculated. Adsorption isotherms are important for describing how molecules or ions interact with adsorbent surface sites. The Langmuir isotherm model and the Freundlich isotherm model were applied to fit the adsorption data and they are expressed by the following Equations (2) and (3) [30,31].

$$Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \quad (2)$$

$$Q_e = K_F C_e^{\frac{1}{n}}, \quad (3)$$

where K_L is the Langmuir equilibrium constant, which used to measure the affinity between adsorbate and adsorbent; Q_e is the equilibrium adsorption amount; Q_m is the saturated adsorption capacity; C_e is the equilibrium concentration of RE remained in solution; K_F is the Freundlich equilibrium constant, representing the adsorption ability; and n is a constant, representing the adsorption intensity [32].

The linear form of Langmuir adsorption isotherm is expressed as:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{K_L Q_m} \quad (4)$$

The linear fitting equation of Freundlich adsorption isotherm is as follows:

$$\log Q_e = \frac{1}{n} \cdot (\log C_e) + \log K_F \quad (5)$$

2.4.3. Elution Experiment

We used 0.1 mol/L (NH₄)₂SO₄, 0.1 mol/L HCl and deionized water as leaching agent to conduct a static stirring elution experiment in this study. The solid/liquid ratio is 2 g/25 mL, and the elution time is 5 h. The elution efficiency (E) is calculated as follows [33]:

$$E = \frac{V \times C_{e2}}{m \times Q_e}, \quad (6)$$

where C_{e2} is the elution equilibrium concentration of RE remained in solution, mmol/L. Q_e is the equilibrium adsorption capacity of RE on adsorbent, mmol/g. V is the volume of solution, cm^3 and m is the weight of adsorbent, g.

3. Results and Discussion

3.1. Selection of Modifier

In order to select the suitable modifier to prepare the Mt with an excellent adsorption capacity to RE, different modifiers were applied to the modification of Mt and the modified Mt was prepared for adsorption of Y^{3+} . The results are shown in Figure 1. As illustrated in Figure 1, the adsorption capacity of Y^{3+} on Mt was higher than raw Mt (G0). The modification of Mt by organic surfactant mainly had two functions: (1) the Mt surface changed from hydrophilic to hydrophobic, and showed a better swelling property. At the same time, the interface polarity and chemical microenvironment of Mt was improved to form adsorbents with excellent adsorption properties on organic macromolecules or groups [34]; (2) Organic macromolecules with long carbon chains entered the Mt interlayer and interlaminar organic molecules were arranged in multiple molecular layers, expanding the interlayer structure of Mt thus allowing greater ion-exchange to occur [35,36]. Thus, its adsorption capacity to rare earth ions increased to a certain extent. Among them, the composite of HDTMA and DDTC presented a greater modification than single HDTMA. However, the adsorption capacity of Y^{3+} on acid-modified Mt was higher than that of organo-Mt. That may be explained by the ion-exchange of Na^+ , K^+ , Al^{3+} (octahedral cations) by H^+ , which has lower atomic radius and the interlayer ions are converted into soluble salts and dissolved. This acid modifying process would significantly increase the basal spacing and specific surface area of Mt, along with the elimination of several mineral impurities and partial dissolution of the external layers, which improves its adsorption capacity [37]. Since modification by the composite acid of HCl and H_2SO_4 only showed a little difference from that of single HCl and H_2SO_4 . In industrial applications, HCl shows a volatile properties and difficult transportation. Thus, H_2SO_4 was chosen as a modifier in this study.

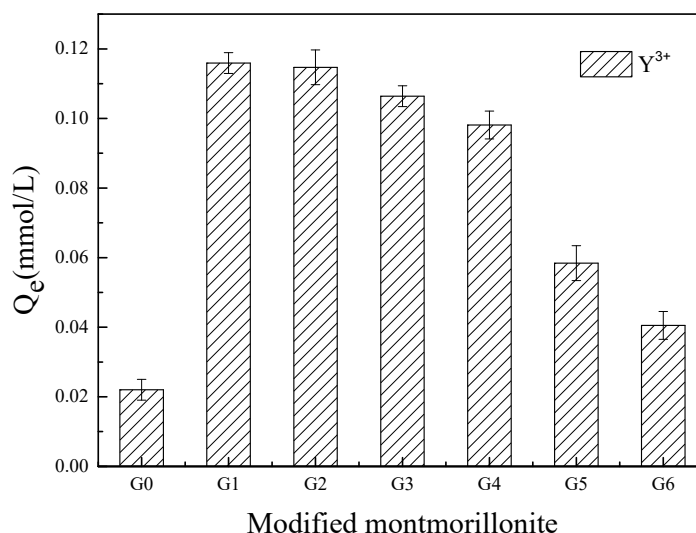


Figure 1. Effects of modifiers on adsorption of Y^{3+} .

3.2. Effect of Reaction Conditions on the Preparation of Modified Mt

In order to optimize the modification conditions of montmorillonite, effects of H_2SO_4 concentration, liquid:solid ratio, modification time, and temperature on adsorption capacity of Y^{3+} were evaluated as shown in Figure 2. With the increasing of H_2SO_4 concentration, the adsorption capacity of Y^{3+} on modified Mt increased gradually to a balance, followed by a slight decrease. At the low acidity,

the H^+ reacting to the exchangeable cations in the Mt layer was lesser than that under high acidity. Additionally, the high acidity would dissolve Al in the octahedral aluminum oxide of Mt skeleton and separate layers of Mt to form a loose and porous structure [38]. Thus, the adsorption capacity of modified Mt significantly was improved by the increasing of surface area and loose channels due to the removal of amorphous Al or silica components, formation of cracks and voids in the surface. However, the absorbability of acid-modified Mt would decrease with the further increasing of acid concentration attributed to the destroyed and collapsed crystal structure of Mt at over-high acid concentration. Therefore, according to Figure 2a, it can be seen that when the concentration of H^+ was 1.878 mol/L, 5% (volume ratio) of H_2SO_4 , a modified Mt with a better adsorption capacity could be obtained.

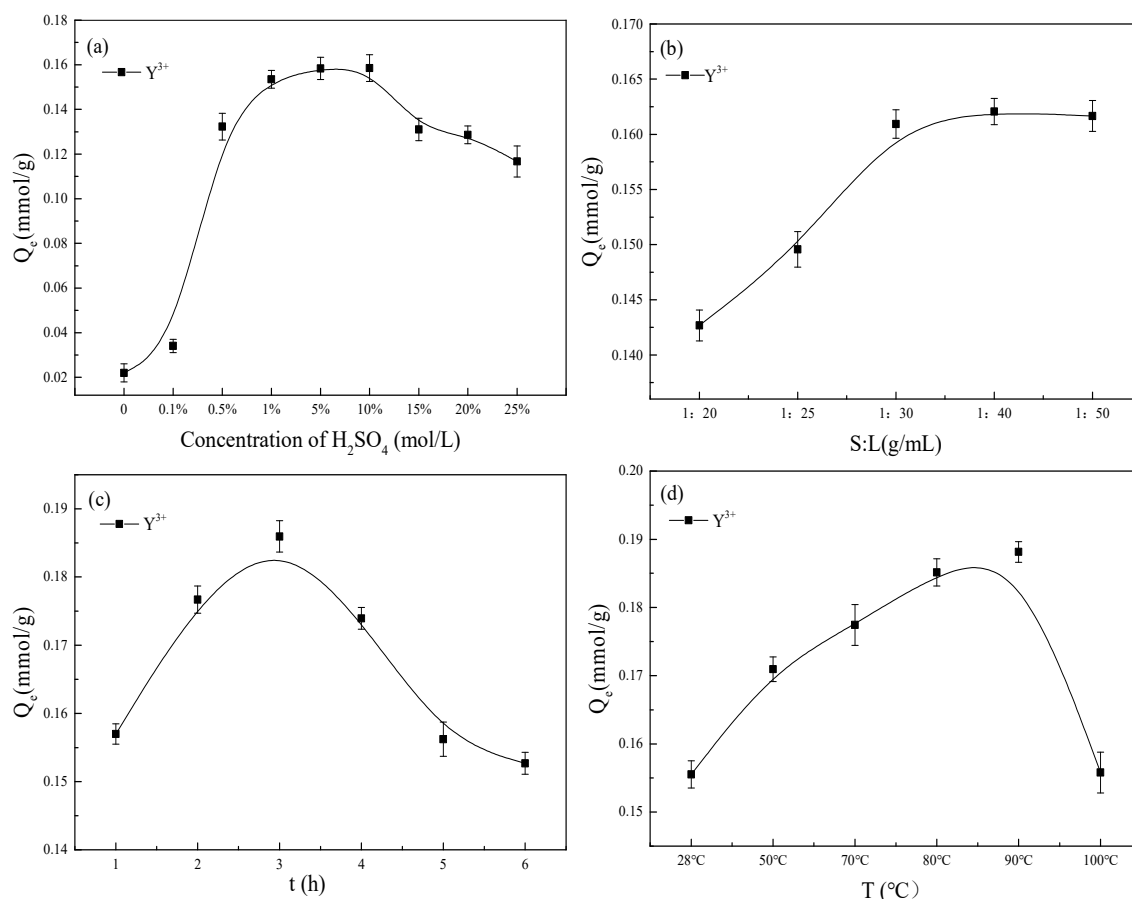


Figure 2. Effects of (a) H_2SO_4 concentration; (b) solid:liquid ratio; (c) modification time; (d) modification temperature on adsorption of Y^{3+} .

The liquid:solid ratio improved the adsorption capacity of Y^{3+} on modified Mt, but it tended to be equilibrium when the liquid:solid ratio is above 40:1. At a low liquid:solid ratio, fewer amounts of H^+ exist in the solution, which results in the presence of mass transfer resistance between solution and adsorbent. The exchangeable cations in Mt layers cannot be exchanged adequately with H^+ so as to no more adsorption spacing and specific surface area of Mt. However, H^+ ion-exchanges with the metal ions between the Mt layers increase with the increasing of liquid:solid ratio, which is conducive to the formation of surface pores or interlamellar spaces on Mt. Considering economic cost and actual situation, in this study, the optimum condition of liquid:solid ratio is determined as 1:40.

Figure 2c,d discuss the effect of modification time and temperature. Figure 2c showed that too short or too long modification time was unfavorable. In the process of acid modification, H^+ would ion-exchange with the metal ions and dissolve the oxides in the Mt layers so as to produce a large number of loose pores to adsorb Y^{3+} . The ion exchange reaction between H^+ and metal ions did not

react adequately at the short modification time. With the increasing of modification time, the interlayer space of Mt increased and the active surface could be enhanced accompanied by the Al^{3+} dissolved gradually [39]. The loose and porous structures was formed and the Mt surface charge potential became more negative. Thus, the adsorption capacity of Y^{3+} on acid modified Mt was significantly improved. However, over 3 h, the reduction of Y^{3+} adsorption capacity might be due to the destroyed crystal structure of Mt by excessive H^+ . In this study, 3 h was applied as the optimum modification time. The results of modified Mt under different modification temperature, 28 °C, 50 °C, 70 °C, 80 °C, 90 °C, and 100 °C, are showed in Figure 2d, where the adsorption capacity of Y^{3+} on modified Mt increased gradually with the increasing of modified temperature. However, when the temperature was above 90 °C, the adsorption capacity showed a trend of decline. It was due to the interlayer structure collapse of Mt caused by the over-high temperature. Thus, adsorption active sites on the surface of modified Mt were destroyed resulting from plugging the pores and reducing the specific surface area and pore volume at the same time, which greatly increased the barriers of adsorption of RE ions to a great extent [40]. Therefore, the optimum condition of modification temperature is applied as 90 °C in this study.

3.3. Characterization of Mt, Modified Mt, Modified Mt Adsorbed Y^{3+}

3.3.1. X-Ray Diffraction Analysis (XRD)

The results of XRD patterns of Mt, modified Mt and modified Mt adsorbed Y^{3+} were summarized in Figure 3, where (001) crystal surface belonged to the characteristic peak of Mt. The crystallographic spacing (d) of Mt is calculated by the Bragg's equation.

$$2d \sin \theta = n\lambda \quad (7)$$

where λ is the wavelength of the X-ray radiation used, d is the spacing between diffraction lattice planes, θ is the measured diffraction angle, and $n = 1, 2$.

The most pronounced modification occurred in the Mt $d(001)$ peak showed the interlayer space of modified Mt increased from $d(001) = 1.482 \text{ nm}$ to $d(001) = 1.587 \text{ nm}$. Comparing to the unmodified Mt, the $d(001)$ peak of modified Mt shifts from 5.905° to 5.647° , which is in accordance with the reported result [41]. This observation indicates that the acid could exchange the metal cations such as Na^+ , K^+ et al. and consequently weaken the binding force of Mt layers. Meanwhile, the acid can make Mt form the active acid site which is beneficial to absorbing RE ions. $d(100)$ peaks of three different Mt in Figure 3b reveal no major differences, indicating that the modified Mt and the modified Mt adsorbed Y^{3+} will not destroy the original crystal structure of Mt.

3.3.2. Fourier Transform Infrared Spectrometer (FT-IR)

The infrared spectra of Mt (a), modified Mt (b), modified Mt adsorbed Y^{3+} (c) are shown in Figure 4. Compared with the infrared spectra of Mt, the adsorption band at 3442 cm^{-1} , corresponding to $-\text{OH}$ stretching vibration of H_2O of Mt, weakens and shifts to the lower wave number 3426 cm^{-1} in Figure 4b and 3425 cm^{-1} in Figure 4c [42]. The adsorption band at 3635 cm^{-1} in Figure 4a is the stretching vibration of structural OH groups of Mt. The band at 629 cm^{-1} is the Al–O and Si–O out-of-plane vibrations. A complex band at 1038 cm^{-1} is related to the stretching vibration of Si–O groups, while the bands at 527 and 470 cm^{-1} in Figure 4a are due to Al–O–Si and Si–O–Si bending vibrations, respectively. The bands at 843 and 795 cm^{-1} are due to (Al,Mg)–OH vibration modes.

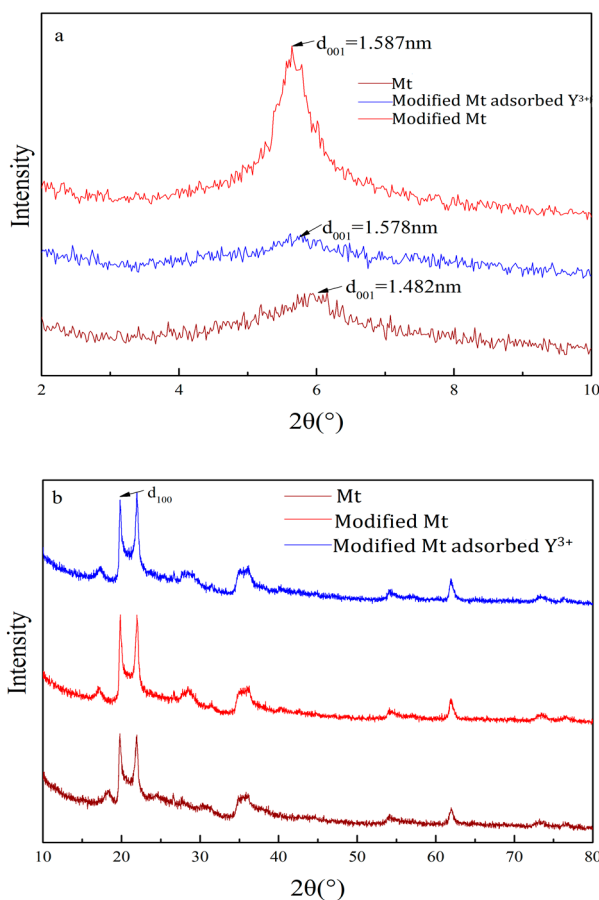


Figure 3. XRD pattern: (a) is the enlarged view on the small diffraction angle part of (b).

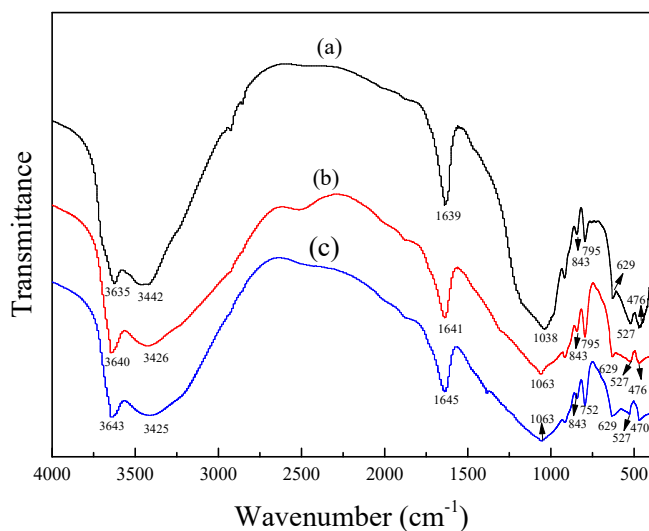


Figure 4. IR spectra of Mt (a), modified Mt (b), modified Mt adsorbed Y³ (c).

The changes in the Si environment after H₂SO₄ modification are reflected in both the position and the shape of Si–O stretching band near 1038 cm⁻¹. A slight shift of this band to higher frequencies indicates the alternation of structure. The IR spectrum of the modified Mt in Figure 4b shows a slight shift of tetrahedra Si–O band to from 1038 cm⁻¹ to 1063 cm⁻¹, which was due to the Si–O vibrations of amorphous silica with a three-dimensional framework [37]. The spectrum of modified Mt had the adsorption band characteristics of amorphous silica (476 cm⁻¹) which confirms a high degree of

structural decomposition. The FT–IR analysis results suggest the success of modified Mt by H_2SO_4 and the chemical activation and chemisorption of modified Mt to Y^{3+} .

3.3.3. Scanning Electron Microscopy (SEM)

The morphologies of Mt, modified Mt, modified Mt adsorbed Y^{3+} are shown in Figure 5. The typical characteristic morphology of Mt showed a schistose structure and contains pores, which provides channels and higher surface area for RE ions adsorption in Figure 5a. In aqueous medium, the Y^{3+} were easily adsorbed as the water permeation on account of the layered, folded and richly wrinkled morphology of Mt [43]. However, the introduction of H_2SO_4 in Figure 5b led to the irregular schistose structure of modified Mt with numerous cavities, which was convenient for Y^{3+} adsorption into the pore spaces and resulted in an increase in the adsorption capacity of Y^{3+} . That accounts for that the acidification process makes the structure fluffy. This is in accordance with the results indicated by the XRD pattern. The modified Mt adsorbed Y^{3+} in Figure 5c shows no significant difference compared with the modified Mt.

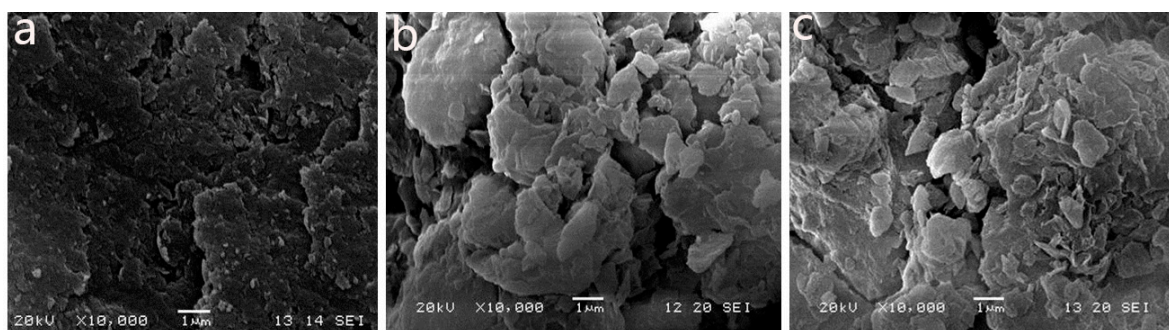


Figure 5. SEM image of (a) Mt (b) Modified Mt and (c) Modified Mt adsorbed Y^{3+} .

3.3.4. Specific Surface Area and Pore Diameter Analysis (BET)

BET characterization of Mt, modified Mt, and modified Mt adsorbed Y^{3+} were performed shown in Table 2. The specific surface area of modified Mt increased from $37.198 \text{ m}^2/\text{g}$ to $107.074 \text{ m}^2/\text{g}$ (Mt), and the pore volume also increased from $0.109 \text{ cm}^3/\text{g}$ to $0.227 \text{ cm}^3/\text{g}$, which demonstrates the improved adsorption capacity. In the modifying process, H^+ removed impurities in the Mt, resulting in the tinier pores and improving its pore structure. The pore size of modified Mt is thus smaller than that of Mt, suggesting the formation of micropore in the modified Mt and thus a better adsorption performance.

Table 2. BET characterization results of the Mt, modified Mt, and Modified Mt adsorbed Y^{3+} .

Samples	Specific Surface Area (m^2/g)	Pore Volume (cm^3/g)	Pore Size (nm)
Mt	37.198	0.109	11.689
Modified Mt	107.074	0.227	8.479
Modified Mt adsorbed Y^{3+}	82.947	0.223	10.764

3.4. Application of Modified Mt to Recover Rare Earth from Solutions

3.4.1. Isothermal Adsorption

Figure 6 shows the plot of adsorption isotherm, adsorption capacity versus the equilibrium REs concentration for the adsorption of La^{3+} and Y^{3+} on modified Mt. It can be seen that at lower adsorption equilibrium RE concentration, adsorption capacity rose sharply and thereafter the increase was gradual with an increase of equilibrium RE concentration. The results suggested that the initial RE ions concentration could increase the mass transfer driving force of RE ions between the aqueous solution and adsorbent phase, which led to an increase in RE adsorption capacity. Langmuir model

and Freundlich model were used to fit the adsorption isotherm data shown in Figure 7 and the model parameters were calculated and were listed in Table 3. The Q_m and constant K_L of Langmuir isotherm model were evaluated from slope and intercept of the linear plots of C_e/Q_e versus C_e , respectively and the K_F and $1/n$ of Freundlich isotherm model were determined from the intercept and slope of linear plot of $\log Q_e$ versus $\log C_e$, respectively. As shown in Table 3, the saturated adsorption capacity (Q_m) for Y^{3+} and La^{3+} are 0.182 mmol/g and 0.178 mmol/g, respectively, which are greatly increased compared to the results reported by Zhou et al. [5]. Furthermore, Yu et al. [29] investigated that the maximum adsorption capacity of Mt to RE ions is 0.00352 mmol/g and Xiao et al. [44] also found that the saturated adsorption capacity of RE ions by clay minerals is only 0.012 mmol/g.

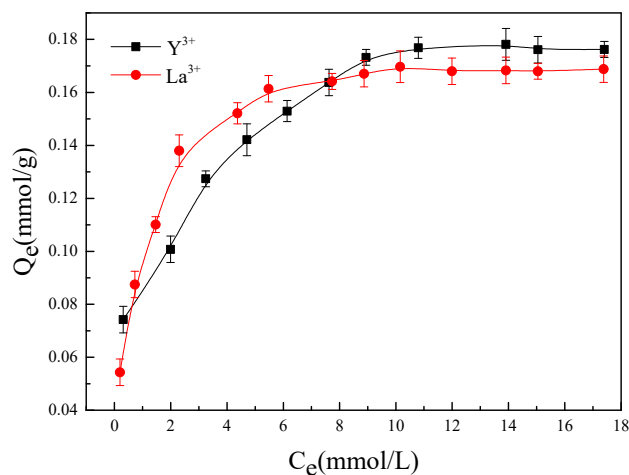


Figure 6. Adsorption isotherms of La^{3+} and Y^{3+} on modified Mt.

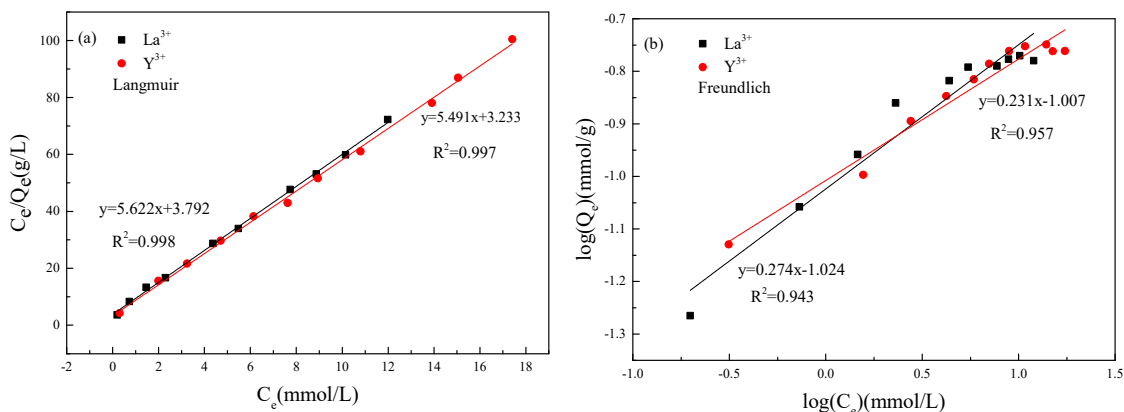


Figure 7. Linear fitting of isothermal adsorption model. (a) The Langmuir adsorption isotherm of La^{3+} and Y^{3+} onto modified Mt. (b) The Freundlich adsorption isotherm of La^{3+} and Y^{3+} onto modified Mt.

Table 3. Model parameters for the adsorption of Y^{3+} and La^{3+} on modified Mt.

Rare Earth Iron	Langmuir Model Parameters			Freundlich Model Parameters		
	Q_{max} (mmol/g)	K_L (L/mol)	R^2	$1/n$	K_F (L/mol)	R^2
Y^{3+}	0.182	1.718	0.997	0.231	0.098	0.957
La^{3+}	0.178	1.482	0.998	0.274	0.095	0.943

In Figure 7, the correlative coefficients R^2 of Y^{3+} and La^{3+} in Langmuir model are 0.997 and 0.998, respectively, which are closer to 1 than the R^2 value of Freundlich, 0.957 and 0.943 respectively. Hence, the adsorption data of RE fit Langmuir isotherm better than Freundlich isotherm. The fact that K_L are

greater than zero indicates that it was a favorable adsorption. The empirical constant $1/n$ of Freundlich model was used to measure the degree of heterogeneity of adsorption material and was between 0 and 1 indicating that the adsorption was favorable at studied conditions and the adsorption process fit a monolayer adsorption, which is consistent with the typical Langmuir model [45]. Thus, the adsorption of RE on modified Mt was superficial monolayer adsorption, and the adsorption capacity depended on the number of active sites on the Mt.

3.4.2. Elution Experiment

In order to prove that modified Mt could be used to recycle RE effectively, the elution experiment was also investigated shown in Figure 8. Elution experiments were carried out under the condition of adsorption equilibrium concentration of RE ions, where La^{3+} and Y^{3+} were 12.277 mmol/L and 15.943 mmol/L, respectively. It is indicated that $(\text{NH}_4)_2\text{SO}_4$ elution efficiencies of La^{3+} and Y^{3+} , 94.0%, 91.5% were higher than that of HCl (30.3%, 27.5%) and distilled water (0.06%, 0.08%). The results confirm RE ions adsorbed on the modified Mt and reveal this adsorption was mainly chemical adsorption. Therefore, $(\text{NH}_4)_2\text{SO}_4$ was selected as an eluent to study the enrichment of RE in low concentration. When the RE concentration was 0.1 g/L, the adsorption efficiency and the elution efficiency of Y^{3+} and La^{3+} reached 91.5%, 93.0% and 95.3%, 94.0%, respectively. When the RE concentration was 0.6 g/L, the adsorption efficiency and the elution efficiency of Y^{3+} and La^{3+} reached 53.8%, 94.0% and 59.4%, 95.0%, respectively. The results suggest that the modified Mt can be considered as a suitable adsorbent to enrich RE and then recover it by $(\text{NH}_4)_2\text{SO}_4$ solution. As the most widely used leaching agent in weathered crust elution-deposited RE ores, $(\text{NH}_4)_2\text{SO}_4$ used as the eluent for the modified Mt after adsorbing RE realizes the green efficient recovery of RE ions without increasing the variety of reagents and the mining cost.

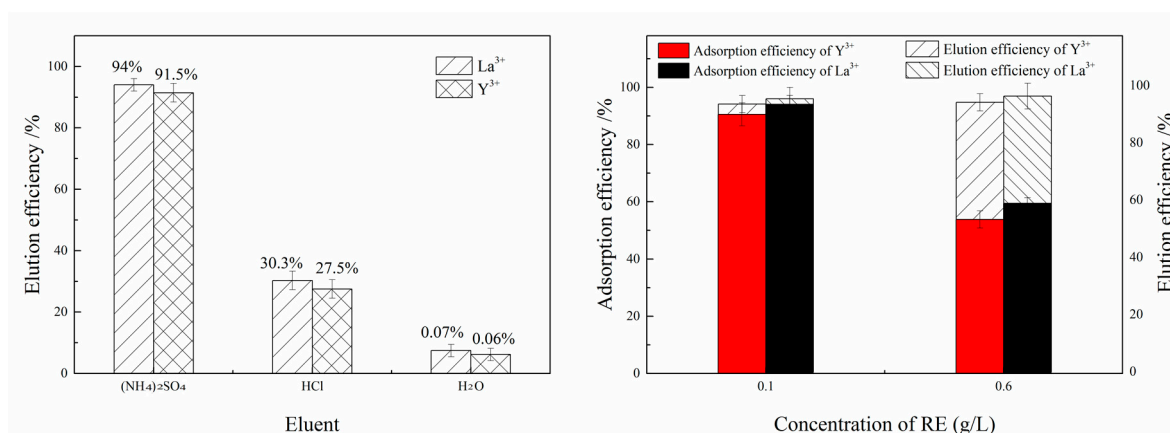


Figure 8. Elution results of different eluents and the adsorption efficiency of Y^{3+} and La^{3+} with low concentration and the elution efficiency of $(\text{NH}_4)_2\text{SO}_4$.

4. Conclusions

Mt, the major clay mineral in the tailings of weathered crust elution-deposited rare earth ores was modified as an excellent adsorbent to enrich and recycle RE ions from the low concentration solution in this study, which would provide useful information and new insight into the reuse of tailings to recover RE from the mineral processing wastewater. According to the comparison among different modifiers, it was found that H_2SO_4 could be used as a better modifier to effectively enhance the adsorption capacity of Mt. The modified Mt was prepared using 5% H_2SO_4 to modify 3 h with a liquid:solid ratio of 40:1 at 90 °C. The isothermal adsorption results suggest that the adsorption behaviors of Y^{3+} and La^{3+} on modified Mt were fitted well to the Langmuir model and the saturated adsorption capacities were 0.183 mmol/g (Y^{3+}) and 0.178 mmol/g (La^{3+}). The results of characterization, XRD, FT-IR, BET and SEM reveal that the interlayer space, the specific surface area and the pore volume of modified Mt were

significantly increased and thus greatly improved the adsorption capacity of Mt. The $(\text{NH}_4)_2\text{SO}_4$ as a good eluent to recover RE ions adsorbed on the modified Mt was demonstrated with the adsorption efficiency and the elution efficiency of La^{3+} and Y^{3+} more than 90%, which confirms the successful application of modified Mt to recycle RE resource.

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