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The kinetics and mechanism of using cationic surfactants to reduce the dissolution of clay minerals

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ABSTRUCT The dissolution kinetics occurring on the clay minerals are influenced by various factors, including pH, temperature, mineral lattice structure. However, the influence of the surfactant is rarely studied. In the present work, cationic surfactants were investigated in the dissolution of clay minerals in acidic environment. Kaolinite was selected as the representative of clay minerals. The cationic surfactant could inhibit the dissolution of clay minerals because it limited the attack of H^+ on the kaolinite surface and then inhibited the dissolution of kaolinite by modifying the hydrophilicity of the kaolinite surface to hydrophobicity. The inhibition ability of surfactant may be related to its molecular structure and the type of acid used in the dissolution experiment.

Key words: cationic surfactants; surface control; modification; dissolution kinetics; kaolinite.

INTRODUCTION

The study of dissolution kinetics of clay minerals is a multidisciplinary field with wide-ranging implications for geology, environmental science, and engineering. It provides fundamental insights into the interactions between minerals and their environments in various conditions, helping to address both practical and theoretical challenges in geochemical modeling, paleoclimate reconstruction, carbon sequestration, soil and sediment formation, nutrient cycling, geothermal energy extraction, petroleum geology, etc.

The kinetics and mechanism of clay minerals' dissolution in various conditions had been studied and discussed for decades. (Nagy & Lasaga, 1992; Jiwchar et al., 1995; Belver et al., 2002; KOHLER et al., 2003; Golubev et al., 2006; Yang & Steefel, 2008; Rozalen et al., 2009; KHAWMEE et al., 2013; Bibi et al., 2014). In 2015, Jordi Cama and Jiwchar Ganor provided a comprehensive overview of clay mineral dissolution kinetics in a chapter titled "Dissolution Kinetics of Clay Minerals". This chapter reviewed the kinetics of clay dissolution, grounded in the kinetic theory developed to describe and quantify mineral dissolution, especially of silicate minerals. It explored various clay dissolution rate laws and interpretations of dissolution mechanisms proposed over the past four decades, thereby enhancing our understanding of the kinetic theory of mineral dissolution. The dissolution rate and dissolution mechanism of clay minerals are related to the dissolution behavior of mineral surface in different environments. The clay minerals discussed in that paper fall into two categories 1:1 clay minerals, such as kaolinite, and 2:1 clay minerals, which include dioctahedral smectites (montmorillonite, beidellite, and nontronite), trioctahedral smectites (hectorite and saponite), dioctahedral micas (illite and muscovite), trioctahedral micas (biotite and phlogopite), vermiculite, and chlorite (Bergaya et al., 2011). It addressed such environmental variables as pH, temperature, catalysts/inhibitors, solution saturation state, and ionic strength influence on the dissolution kinetics of clay minerals.

The adsorption of surfactants into the surface of clay minerals has been studied widely (Kalam et al., 2021), however the studies that focus on the consequences of adsorption on the dissolution are less common. There is a lack of studies on the effect of surfactants, especially cationic surfactants on the dissolution of clay minerals under acidic conditions.

In this study, the effect of cationic surfactant on the dissolution of clay minerals was discussed. Kaolinite was chosen as an example to study the kinetics of clay mineral dissolution with cationic surfactants under acidic conditions. Kaolinite is a 1:1 clay mineral with the smallest specific surface area, and its surface negative charge is also the smallest in neutral conditions. If cationic surfactants can adsorb on the surface of kaolinite and inhibit its dissolution, then, under the same conditions, clays with more surface negative charge should theoretically adsorb more cationic surfactants and be inhibited from dissolving. Hydrochloric acid, nitric acid, and acetic acid were used for the dissolution of kaolinite over a 12-hour period. The molecular formula of kaolinite is $Al_2Si_2O_5(OH)_4$. Compared with other clay minerals, the composition of kaolinite is more favorable to indicate the dissolution rate. Wieland & Stumm (1992) had studied about indicating the dissolution rate of clay through the release of Al^{3+}, and researching the acid dissolution kinetics of kaolinite. The dissolution reaction mechanism of silicaluminate can be divided into proton promotion (acidic environment), water promotion (near neutral environment) and hydroxyl promotion (alkaline environment) according to the different acid and alkaline environment. Since this paper studies the dissolution kinetics of clay minerals under acidic environment, considering the actual implementation of the element detection method, Al^{3+} is selected to indicate the dissolution of clay minerals.

Four cationic surfactants with different structures were selected to compare their inhibitory effects, and the surfactant with the strongest inhibitory effect was selected to study the dissolution kinetics of modified minerals. The concentration of aluminum in the acidic solution was measured at various time points to investigate the dissolution kinetics of kaolinite under different acidic conditions. The inhibition ability of kaolinite dissolution by cationic surfactants was discovered and mechanism of the inhibition was discussed. By studying the effect of cationic surfactants on the dissolution of clay minerals under acidic conditions, a new way of controlling the dissolution of clay minerals by surface regulation was provided.

EXPERIMENTAL

Materials

The kaolinite samples used in this paper were purchased from Chengdu Kelong Chemicals Co., LTD. (Chengdu, China) The purity is greater than 99.5%.

Four cationic surfactants used in this paper: cetane trimethyl ammonium bromide (CTAB), n-tetrabutylammonium bromide (TBAB), benzyl trimethyl ammonium bromide (BTAC) and

Glycidyl trimethyl ammonium chloride (GTA). All of them are analytically pure grade. The surfactants were purchased from Chengdu Kelong Chemical Co., Ltd. (Chengdu, China). The abbreviations in parentheses refer to the corresponding cationic surfactants.

Method of measuring the dissolved Al^{3+}

The general equation of kaolinite dissolution under acidic conditions can be expressed as:

$$Al_2Si_2O_5(OH)_4+H^+ \rightarrow Al^{3+}+H_2SiO_4+H_2O$$

The Al^{3+} content in the solution was determined by UV spectrophotometry (UV5000 UV spectrophotometer, AOYI INSTRUMENTS SHANGHAI Co., LTD., Shanghai, China). 1 mL pipette was used to accurately transfer a quantitative amount of leaching solution into a 10 mL colorimetric tube. Then acid solution was added acidizing water (0.8 mL dilute nitric acid solution into 200 mL of water), and shaken well. 0.40 mL mixed reagent, 0.40 mL catechol purple solution and 2.00 mL hexamethylenetetramine buffer solution were added to the colorimetric tube with a pipette, and each reagent was fully shaken. After the reagent was placed for color development for 15 min, the absorbance of the reagent was measured with 1 cm colorimetric dishes at the wavelength of 580 nm within 60 min.

The content of Al^{3+} in solution was calculated by standard curve. Standard solution of Al^{3+} (1000 μg/L) was used to configure gradient solution, and the standard curve of Al^{3+} concentration between 0 and 500 μg/L was drawn. The standard curve of Al^{3+} concentration was shown in Fig.1. The absorbance is linearly correlated with the concentration, the linear equation fitting result is $y = 0.0018x + 0.0188$, $R^2=0.9996$ (Fig.1).

Fig.1 The standard curve of Al^{3+}

The dissolved amount of Al^{3+} is used to indicate the inhibition rate of the surfactant to inhibit the dissolution of clay using following equation:

$$A=\frac{a-b}{a}\times 100\% \tag{1}$$

In this equation:

A: inhibition rate: a rate of the difference of Al^{3+} dissolution of kaolinite before and after modification to the Al^{3+} dissolution of unmodified kaolinite;

a: Al^{3+} content dissolved from primitive clay, μg/L;

b: Al^{3+} content dissolved by surfactant modified clay, μg/L.

Modification of kaolinite and dissolution experiments

A series of four cationic surfactant solutions with a mass concentration of 0~30g/L were prepared in the experiment, and the inhibition of different cationic surfactants on the dissolution of kaolinite was investigated under the condition of mixing 3% KCl and 2%(volume fraction) acetic acid (pH=2.49) solution and dissolving 0.5h. Four different surfactants were used to modify the kaolinite. The precision balance was used to weigh 3.00g kaolinite. Cationic surfactants were added to 100ml ultrapure water for preparing solution with concentration between 0 and 30g/L. Kaolinite were stirred for 20h at room temperature with stirring speed of 500rpm (6.24g) in the solution.

After stirring, washing and centrifugation were performed, and drying for 5h at 60℃. 0.2g modified kaolinite was taken and dissolved by 25ml acid solution (adding 3% bulking agent KCl) at room temperature for 0.5h under shock. The supernatant was taken and the content of Al^{3+} was measured. Eq.1 was used to calculate the dissolution inhibition rate of clay. Surfactant with the best inhibitory effect was selected for computer molecular simulation and studying the influence of other acid dissolution conditions.

Temperature. The leaching temperature (30℃~80℃) was changed to explore the influence of temperature on the dissolution amount and inhibition rate of Al^{3+} when the modified kaolinite was dissolved in 2% acetic acid solution mixed with 3% KCl for 0.5h. The reaction temperature was controlled by using water bath. During the measurement of dissolution, the CTAB concentration was 25g/L and the concentration of acetic acid was 2%(volume fraction). Under the conditions of 25g/L CTAB concentration and 0.5h dissolution time, the leaching temperature was changed to explore the influence of temperature on the dissolution amount and inhibition rate of Al^{3+} when CTAB-kaolinite was dissolved in 2%(volume fraction) acetic acid (pH=2.49) solution mixed with 3% KCl.

Acid solution kinetics. Three acid solutions containing 3% KCl were prepared respectively, namely 2%HCl, 2%HNO_3 and 2%CH_3COOH, to explore the influence of different acids on the dissolution amount and inhibition rate of Al^{3+} in kaolinite and modified kaolinite. The dry kaolinite sample of 0.2g adsorbed by CTAB was placed in a 50mL beaker and 35mL acid solution containing 3%KCl was added. The supernatant was removed at 0.3h, 0.8h, 1.5h, 2.5h, 3h, 4.5h, 6.5h and 12h, respectively, and centrifuged at 10,000 RPM to determine the content of Al^{3+}. CTAB-kaolinite was placed in 2% (volume fraction) acetic acid, nitric acid and hydrochloric acid with 3%KCl added, and dissolved in oscillations for 12h. The concentration of Al^{3+} in the solution at different time points was determined, and the change of Al^{3+} concentration over time was plotted, and the kinetic equation was fitted.

In theory, the dissolution of kaolinite is a diffusion process of ionic solid phase and liquid phase, which accords with the kinetic characteristics (Bibi et al, 2014). The following three equations were used to conduct a kinetic analysis of the dissolution data of Al^{3+} from the modified kaolinite under the action of 3% KCl acid:

$$C_t = a + bt^{1/2} \tag{2}$$

$$C_t = a + b \cdot ln(t) \tag{3}$$

$$C_t = a[1 - exp(-kt)] \tag{4}$$

In these equations:

C_t: the dissolution amount of Al^{3+} at t(h) time, μg/L;

t: dissolution time, h;

a: initial concentration, μg/L;

b: reaction rate constant;

k: reaction rate constant.

Equation 2 is parabolic equation (diffusion equation). The physical significance of parabolic rate dynamics has been explained in terms of changing the diffusion transfer of the surface layer through the solid phase, and it is often used to represent the reaction controlled by the diffusion step. The parabolic equation is not suitable for the whole solution range of the closed system. Equation 3 is empirical equation (Elovich equation) which can represent the analytical process of adsorption in chemistry. This equation is suitable to represent the reaction in which the activation energy changes greatly, as well as the complex reaction mechanism in the slow reaction process, such as solute diffusion at the solution phase or interface, surface activation and deactivation, and surface reaction. Equation 4 is one-order kinetic equation, which can represent the ion exchange adsorption and chemical reaction process at the mineral reaction site.

Quantum chemistry and molecular dynamics calculations. To study the relationship between the molecular structure of cationic surfactants and their inhibitory effect, quantum chemistry and molecular dynamics calculations were carried out, and density functional method and molecular dynamics theoretical calculation and simulation methods were adopted. The adsorption configuration of surfactant molecules on the (001) surface of kaolinite was studied by quantum chemistry and molecular dynamics simulation, and the adsorption force between cationic surfactant and kaolinite was explained by mechanism.

Software “Forcite” was used to conduct Geometry Optimization simulation on the adsorption configuration calculated by CASTEP, and the initial adsorption configuration of surfactant was obtained. The specific simulation conditions are: COMPASSII force field is used, Ewald mode is used for electrostatic force, Atom based force is used for van der Waals force, and cut-off energy is set to 10 A. Based on the obtained initial configuration, the regular ensemble (NVT) was selected at 298 K temperature, the time step was 1 fs, and the non-bonding interaction (electrostatic force and van der Waals force) was calculated by vdw&Coulomb. The total simulation time was 100 ps to simulate the adsorption kinetics.

Crystal structure properties of kaolinite. Kaolinite crystal chemical formula is $2SiO_2 \cdot Al_2O_3 \cdot 2H_2O$, and kaolinite minerals belong to the 1:1 type of phyllosilicate. The crystal is mainly composed of silico-oxygen tetrahedron and aluminum hydroxide octahedron, which silico-oxygen tetrahedron in the way of sharing the top angle along the two-dimensional direction to form a hexagonal arrangement of grid layer, each silico-oxygen tetrahedron not common apex oxygen are toward one side. The unit layer of 1:1 is composed of the silico-oxygen tetrahedral layer and the aluminon-oxygen octahedral layer, which share the apex oxygen of the silico-oxygen tetrahedral layer. Belonging to Cc space group, crystal cell parameters respectively are a=b=5.226Å, c=14.590Å, α=β=86.801°, ɤ=120.135°, and main cleavage plane is plane (001).

Interaction energy. CTAB molecules are geometrically optimized and adsorbed on the surface of kaolinite. The optimized adsorption complex model, adsorbent model and adsorbed surface model are used to explore the interaction energy between surfactant functional groups and surface atoms. The energy is calculated by the following formula. The positive and negative values of the interaction energy (ΔE) indicate the stability of the adsorption system. The more negative the ΔE is, the more stable the adsorption system is and the more likely the adsorption will occur. When ΔE is 0 or positive, the adsorption is more difficult to occur (Yin et al., 2021).

$$\Delta E = E_A - (E_B + E_C) \quad (5)$$

In this equation:

E_A: Energy of optimized adsorption system model, kcal/mol;

E_B: Energy of CTAB model, kcal/mol;

E_C: Energy of kaolinite model, kcal/mol;

ΔE: Energy of interaction between CTAB and kaolinite, kcal/mol.

Determination Methods of Modified Kaolinite

X-ray diffraction (XRD) patterns. XRD tests were performed on a DX2700 type X-ray diffractometer (Fangyuan Instrument Co., LTD., Dandong, China). The kaolinite and CTAB-kaolinite samples were fully ground in an agate mortar to make its particle size refined to around 200 mesh. An appropriate amount of the sample was then evenly spread in the groove of the sample holder, compacted with proper pressure and scraped to make the surface flat, ensuring its close fit and smoothness. Subsequently, the sample holder was accurately placed at the testing position of the X-ray diffractometer. Regarding the setting of instrument parameters, the accelerating voltage of the X-ray tube was set to 35 kV, and the tube current was set to 35 mA. The 2θ scanning range was set from 5° to 70°, the scanning rate was set at 4° per minute, and the step size was precisely set to 0.05°. After the testing process was completed, the obtained XRD in-situ data were processed and analyzed.

Fourier Transform infrared spectrometry (FT-IR) patterns. FT-IR tests were carried out on the FT-IR 650S Fourier Infrared spectrometer (Thermo Fisher Scientific, USA). Accurately weigh 0.002g of CTAB, kaolinite, and CTAB-kaolinite. And then grind each sample with 200mg of dried potassium bromide powder. After pressing the mixture into a pellet, place it in the sample cell of the infrared scanner. Within the wavenumber range from 4000 cm^{-1} to 400cm^{-1} and under the parameter condition with the resolution set at 1cm^{-1}, subtract the background and then conduct 50 reciprocal scans on the sample.

Zeta potential analysis. Zeta potential tests are performed on the Nano Brook Zeta Potential analyzer (Brookhaven Instruments, USA). 0.1 g kaolinite soaked with different concentrations of CTAB was weighed and dispersed in 10 ml deionized water. Under the condition of pH = 6.8, the Zeta potential of each sample was determined, and the relationship between the concentration of CTAB and the Zeta potential of kaolinite was studied. The measurement parameters are set as Cycles: 3, Runs: 3, Inter Cycle Delay: 5s, Temperature: 20° C, and Liquid: water.

RESULTS and DISSCUSION

Inhibitory effect of cationic surfactants

Among the four cationic surfactants, the dissolution amount of Al^{3+} decreased with the increase of the concentration of cationic surfactants of the immersion agent, and eventually tends to equilibrium. CTAB maintained a better inhibition rate at different concentrations (Fig.2), so CTAB was selected as the cationic surfactant to be studied later.

Fig.2 Effect of different cationic surfactants and their concentrations on the dissolution inhibition rate of Al^{3+} in kaolinite

Characterization of kaolinite and CTAB-kaolinite

Fig.3 XRD of kaolinite and CTAB-kaolinite

XRD results of samples showed that the XRD pattern of kaolinite was clear and the characteristic peaks clearly indicated that the used kaolin had good crystallinity (Fig.3). CTAB-kaolinite did not generate new characteristic peaks, and the peak value of characteristic peaks almost did not change, which indicates that the crystal structure of kaolinite did not change after soaked with CTAB. In addition, by calculating the layer spacing of the samples before and after soaking, it was found that the characteristic peaks of d_{001} before and after soaking were 12.257 and 12.257, and the layer spacing was 0.721 nm and 0.721 nm, respectively. The 2θ of characteristic peak did not have a large shift, and the layer spacing did not change greatly, indicating that CTAB did not enter the kaolin interlayer, just adsorbed on the surface, mainly because kaolinite is a non-expansive mineral with a small cation exchange capacity, and CTAB molecules are not easy to enter its interlayer structure.

Fig.4 Infrared spectra of CTAB, kaolinite and CTAB-kaolinite

As can be seen from Fig.4, the absorption peaks of Si-O stretching vibration peaks appear at 979 cm^{-1} and 977 cm^{-1}, and the absorption peaks of 815 cm^{-1} and 823 cm^{-1} are Si-O, Si-O-Si and Si-O-Al vibration absorption peaks. The absorption peaks of Si-O bending vibration appear at 653 cm^{-1} and 665 cm^{-1}, and the absorption peaks of 1623 cm^{-1} and 1625 cm^{-1} are the offset vibration peaks of H_2O.

By comparing the three infrared absorption lines, there are two strong absorption peaks of CTAB-kaolinite at 2919 cm^{-1} and 2850 cm^{-1}. The absorption peak at 2919 cm^{-1} is the C-H asymmetric stretching vibration of $-CH_3$, and the absorption peak at 2850 cm^{-1} is the C-H symmetric stretching vibration absorption peak of $-CH_2-$. The results show that CTAB has been successfully adsorbed on the surface of kaolin (Zhao et al., 2007).

Fig.5 Change of interaction energy between CTAB and kaolinite with simulation time

During the interaction between CTAB and kaolinite, the electrostatic interaction energy between

CTAB and kaolinite at 10 ps is -30.47 kcal/mol, the van der Waals interaction energy is -54.90 kcal/mol, and the total interaction energy is -85.36 kcal/mol. With the passage of time, the absolute value of the three shows an increasing trend. At 40 ps, the electrostatic interaction energy of CTAB with kaolinite is -116.79 kcal/mol, the van der Waals interaction energy is -113.23 kcal/mol, and the total interaction energy is -230.03 kcal/mol. Since then, they remain in a relatively stable state, and the electrostatic energy and van der Waals action energy is not much different (Fig.5). At 100 ps, the electrostatic and van der Waals interaction energies account for 48.36% and 51.64% of the total adsorption energies respectively, in the distribution of interaction energies between CTAB and kaolinite (Table 1).

Table 1 Interaction energy between CTAB and kaolinite at 100 ps

Results show that as the contact time between CTAB and kaolinite surface becomes longer, the absolute value of the interaction energy between CTAB and kaolinite surface increases, the interaction is enhanced, and the adsorption ability of CTAB and kaolinite surface becomes stronger. After 40 ps simulation time, the interaction between CTAB and kaolinite surface can be relatively stable and no drastic changes will occur. Among them, the distribution of Van der Waals force and electrostatic force in the interaction energy is basically 1:1, and their contribution to the interaction energy is basically similar. This indicates that the interaction between CTAB and kaolinite surface is influenced by both Van der Waals and electrostatic force. In combination with Fig.8, it is found that the inhibition effect of CTAB on Al^{3+} dissolution will be reduced to some extent with the increase of temperature, which may be related to the decrease of the orientation force (electrostatic force) between CTAB and kaolinite surface.

Fig.6 Effect of CTAB concentration on Zeta potential of kaolinite surface

Zeta potential analysis after the interaction of kaolinite with cationic surfactants. According to the test results of Zeta potential, the type of charge carried by the mineral itself can be obtained, and the change of the surface charge of the mineral before and after the action of CTAB on the mineral can be understood. The surface electrical property of kaolinite increased rapidly after CTAB immersion, and the surface negative charge was continuously neutralized due to the adsorption of CTAB. After the increase rate reached a certain degree, the increase rate slowed down. Finally, with the increase of CTAB concentration, the surface potential of kaolinite basically remained unchanged, indicating that the adsorption capacity of kaolinite was limited. When the adsorption saturation is reached, the charge of kaolinite remains unchanged, although the concentration of CTAB increases (Fig.6).

In general, the Zeta potential on the surface of kaolinite changed from -25.97 mV to 0.41 mV. The results show that the addition of CTAB neutralizes the negative charge on the surface of kaolinite, and the surface property changes from hydrophilic to hydrophobic, which makes the hydrophilic H^+ not easy to contact with the clay surface, reduces the surface reaction rate, and thus inhibits the dissolution of kaolinite.

Inhibitory effect of temperature

The dissolution amount of Al^{3+} in kaolinite increased sharply with the rise of dissolution temperature. The temperature has little influence on the dissolution of kaolinite after adsorption in CTAB, while the dissolution amount of Al^{3+} in CTAB-kaolinite only slightly increases with the rise of dissolution temperature (Fig.7). At the same time, the adsorption stability of CTAB on kaolinite surface is good at the temperature range of 30~80℃, and it is not easy to fall off. CTAB can prevent H^+ from contacting with kaolinite surface.

Fig.7 Influence of temperature on the dissolution amount and inhibition rate of Al^{3+} in kaolinite

Moreover, it can be seen from the black broken line in the figure that, with the increase of temperature, the inhibition rate decreases from 91% to 74% (Fig.7). Two possible reasons cause this phenomenon. First, the forward reaction is gradually thorough. Second, CTAB adsorbed on the surface of kaolinite tends to have higher vibratory activity at higher temperature. As the temperature increases, the structure formed by CTAB and kaolinite becomes slightly unstable. It indicates that low temperature helps CTAB to inhibit the dissolution of kaolinite.

Acid solubility kinetics of CTAB- kaolinite

Fig.8 Inhibition rates of CTAB-kaolinite under different acid types

The type of acid affected the stability of surfactant adsorption on clay surface. Studies have found that changes in pH and salt solution concentration can affect the stability of surfactant adsorbed on clay surface (Hue et al., 2019). Under different acid dissolution conditions, cationic surfactants have different ability about inhibiting kaolinite dissolution: acetic acid > Nitric acid > Hydrochloric acid (Fig.8). As can be seen from the change curve of the inhibition rate over time, the inhibition rate gradually decreases with the increase of time, which is related to the adsorption stability of cationic surfactants in kaolinite. With the increase of time, the cationic surfactants may begin to desorption phenomenon and fall off from the clay surface. This causes increase of the contact area between H^+ and kaolinite, thus accelerating the dissolution of kaolin. And the inhibition rate was reduced.

Fig.9(a) Fitting curve for the dissolution of CATB-kaolinite in acetic acid (diffusion equation)

Fig.9(b) Fitting curve for the dissolution of CATB-kaolinite in nitric acid (diffusion equation)

Fig.9(c) Fitting curve for the dissolution of CATB-kaolinite in hydrochloric acid (diffusion equation)

Fig.10(a) Fitting curve for the dissolution of CATB-kaolinite in acetic acid (Elovich equation)

Fig.10(b) Fitting curve for the dissolution of CATB-kaolinite in nitric acid (Elovich equation)

Fig.10(c) Fitting curve for the dissolution of CATB-kaolinite in hydrochloric acid (Elovich equation)

Fig.11(a) Fitting curve for the dissolution of CATB-kaolinite in acetic acid (first-order kinetic equation)

Fig.11(b) Fitting curve for the dissolution of CATB-kaolinite in nitric acid (first-order kinetic equation)

Fig.11(c) Fitting curve for the dissolution of CATB-kaolinite in hydrochloric acid (first-order kinetic equation)

After fitting the dissolution data of Al^{3+} in acetic, hydrochloric and nitric acid with diffusion equation, Elovich equation and one-order kinetic equation, the dissolution of CTAB-kaolinite can be well described by diffusion equation ($R^2>0.917$, Fig.9a,9b,9c) and Elovich equation ($R^2>0.974$, Fig.10a, 10b, 10c). The correlation coefficient after fitting the first-order kinetic equation was lower ($R^2<0.870$, Fig.11a, 11b, 11c), indicating that in the dissolution process of acetic acid, hydrochloric acid and nitric acid, the diffusion equation and Elovich equation could better represent the dissolution process of Al^{3+} under the action of acid than the first-order kinetic equation (Table 2). In addition, it can be found that the dissolution rate of Al^{3+} in kaolinite under different acid solutions is as follows: hydrochloric acid > nitric acid > acetic acid. The results indicated that hydrochloric acid and nitric acid were easier to dissolve CTAB-kaolinite than acetic acid, which was related to the ionization degree of acid in deionized water.

Dissolution kinetics of CTAB-kaolinite. A basic concept of chemical dynamics is that reactions consist of a series of distinct physical and chemical processes that can be broken down into different steps. Berner (1978) pointed out that clay minerals are relatively insoluble minerals and the reaction rate is controlled by the surface. For kaolinite dissolution, the dissolution reaction steps usually include at least:

(a)The reactants (atoms, molecules or complexes) are diffused through the solution to the surface of the clay minerals;

(b)Adsorption of reactants on the surface of clay minerals;

(c)Chemical reactions between adsorbed reactants and clays that may involve several intermediate steps, such as bond breaking and formation, ionic hydration, etc.;

(d)The product diffuses from the clay surface to the solution.

One of the core concepts of reaction kinetics is that one of these steps is the slowest, and the rate of dissolution is determined by the slowest steps. Step (a) and Step (b) describe the diffusion of reactants and products through solution to and from the surface. When these processes are slowest, the reaction is considered diffusion-controlled. Steps (b) ~ (d) occur on a solid surface, and when one of them is a rate control step, the reaction is called surface control (Morse et al., 2002).

Upon comparing the equation fitting parameters of kaolinite and CTAB-kaolinite under experimental conditions, it is observed that following the modification of kaolinite using CTAB, there is a significant decrease in R^2 value for the first-order kinetic equation of CTAB-kaolinite, while minimal changes are noted in R^2 values for the diffusion equation and Elovich equation (Table.3). The diffusion equation and Elovich equation are more appropriate than the first-order kinetic equation for describing the dissolution of Al^{3+} in CTAB-kaolinite under the influence of different acids.

Furthermore, notable variations are observed in the parameters within each equation. When combined with mineral characterization results before and after CTAB modification, it becomes evident that CTAB undergoes electrostatic adsorption on clay mineral surfaces, thereby reducing contact between acid solution and mineral surface to inhibit clay mineral dissolution without altering crystal lattice structure. The modeling results showed that the acidity constants of the surface hydroxyl groups varied greatly depending on their structural positions and the presence of isomorphic substitution at tetrahedral or octahedral sites. It is generally accepted that the rate-limiting step for the dissolution of aluminum silicate is the hydrolysis of Si-O-Si and Si-O-Al bonds (Rs et al., 2021). The inhibitory effect of CTAB on kaolinite dissolution is achieved through regulation of kaolinite's dissolution kinetics. Both the dissolution of kaolinite and the adsorption of cationic surfactants occur on the surface of minerals and the surface diffusion of H^+ controls the dissolution rate, which theoretically verifies the feasibility of controlling the dissolution of minerals by modifying the surface of minerals.

Effect of CTAB on the dissolution of clay

The inhibition abilities of the four cationic surfactants were different: CTAB>TBAB>BTAC>GTA, and the inhibition effect of CTAB was the best. The inhibition efficiency of surfactants may be attributed to the following reasons: (1) Higher electron density on the functional group leads to easier bond formation and adsorption, thus having higher inhibition effect; (2) The increased length of hydrocarbon chains in surfactant molecules means larger molecules, which can shield the surface from attack (Migahed et al., 2005). In addition, it is generally believed that the ability of cationic surfactants for wetting modification of minerals is related to the length of carbon chain, and the longer the length of carbon chain, the better the effect of wetting modification. Researches show that the surfactants with shorter carbon chains are mainly adsorbed on the clay surface in the vertical form, and the surfactants with longer carbon chains are adsorbed on the clay surface in the inclined or flat form. This makes clay have a better hydrophobicity, which can better prevent H^+ in the solution from reaching the surface of kaolinite, thus inhibiting the dissolution of kaolinite (Li et al., 2021).

The concentration of cationic surfactant has a certain effect on the adsorption of surfactant: when the concentration is too low, the adsorption of surfactant and kaolinite in the solution is not enough, and the modification of kaolinite is not enough. When the concentration is too high, because of the adsorption capacity of kaolinite is limited, even if the concentration of cationic surfactant is increased, the dissolution of kaolinite will not be further affected. Besides, due to the increase of cationic surfactants adsorbed on kaolinite surface, the active sites on kaolinite surface are reduced, and the driving force of mass transfer is decreased. The cationic surfactants distributed on kaolinite surface and the free cationic surfactants in solution are prevented from further adsorption due to electrostatic repulsion. Under the combined action of these two reasons, the inhibition trend slows down, and it can be considered that the dissolution of Al^{3+} has reached equilibrium. Secondly, studies have found that surfactants can aggregate on various surfaces to form micelles, semi-micelles and rod-like aggregates at high concentrations, which weaken the ability of cationic surfactants to ionize cations, thus unfavorable to adsorption modification (Kim et al., 2021).

Temperature has little effect on the dissolution of kaolinite after CTAB adsorption. In the temperature range of 30~80℃, CTAB has good adsorption stability on the surface of kaolinite and is not easy to fall off. It can well prevent H^+ from contacting the surface of kaolinite. With the increase of temperature, the inhibition rate decreased. On the one hand, it may be due to the thorough reaction forward; on the other hand, it may be since CTAB adsorbed on the surface of kaolinite tends to have higher vibrational activity at higher temperatures, which results in the slight instability of the structure formed by CTAB and kaolinite with the increase of temperature, indicating that lower temperature helps CTAB to inhibit the dissolution of kaolinite.

In addition, acid properties also affect the stability of surfactant adsorption on the clay surface. A study has found that changes in pH and salt solution concentration can affect the stability of surfactant adsorbed on clay surface (Hue et al., 2019). As can be seen from the change curve of the inhibition rate over time, the inhibition rate gradually decreases with the increase of time, which is related to the adsorption stability of cationic surfactants in kaolinite. With the increase of time, the cationic surfactants may begin to desorption phenomenon and fall off from the clay surface. This increases the contact area between H^+ and kaolinite, thus accelerating the dissolution of kaolinite. The inhibition rate was reduced.

As mentioned above, under the action of acetic acid, nitric acid and hydrochloric acid, the diffusion equation and Elovich equation (R^2>0.900) can better describe the dissolution process of Al^{3+} in CTAB-kaolinite under the action of acid than the one-order kinetic equation. Under the action of three kinds of acids, the dissolution rate of Al^{3+} in CTAB-kaolinite is as follows: hydrochloric acid > nitric acid > acetic acid. Hydrochloric acid and nitric acid dissolve Al^{3+} more easily than acetic acid. This shows that among the three acids, the dissolution of acetic acid is relatively mild. And it conforms to the diffusion equation and Elovich equation, same as the dissolution of nitric acid and hydrochloric acid. The kinetic dissolution mechanism and law of the three acids are consistent, and the difference among acids is in acidity strength, which leads to changes in the surface diffusion dissolution rate of H^+, and slows down the dissolution rate of kaolinite minerals.

CONCLUSION

In this study, cationic surfactants were used to modify clay minerals to inhibit the dissolution of clay under acidic conditions. The characterization, adsorption simulation and kinetic equation of modified clay (CTAB-kaolinite) were studied, and the following conclusions were obtained:

Cationic surfactants adsorb to the mineral surface through electrostatic interaction with the head group and charged positions. The adsorption efficiency of cationic surfactants is influenced by their molecular structure. As the concentration of surfactant in the solution increases, the amount adsorbed onto the mineral surface also increases. This leads to a transition of the mineral's hydrophilic surface to a hydrophobic one, resulting in a stable cationic surfactant-modified mineral structure that inhibits kaolinite dissolution in solution. Furthermore, temperature exerts an influence on surfactant adsorption. Dissolution kinetics studies using acetic acid, nitric acid, and hydrochloric acid reveal that modified kaolinite behaves more consistently with diffusion equation and Elovich equation when exposed to these acids. In conclusion, selecting long-chain cationic surfactants (e.g., CTAB), weak acids, low temperatures, among other conditions are beneficial for inhibiting mineral modification and dissolution by surfactants.

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Figures and Tables

Figures

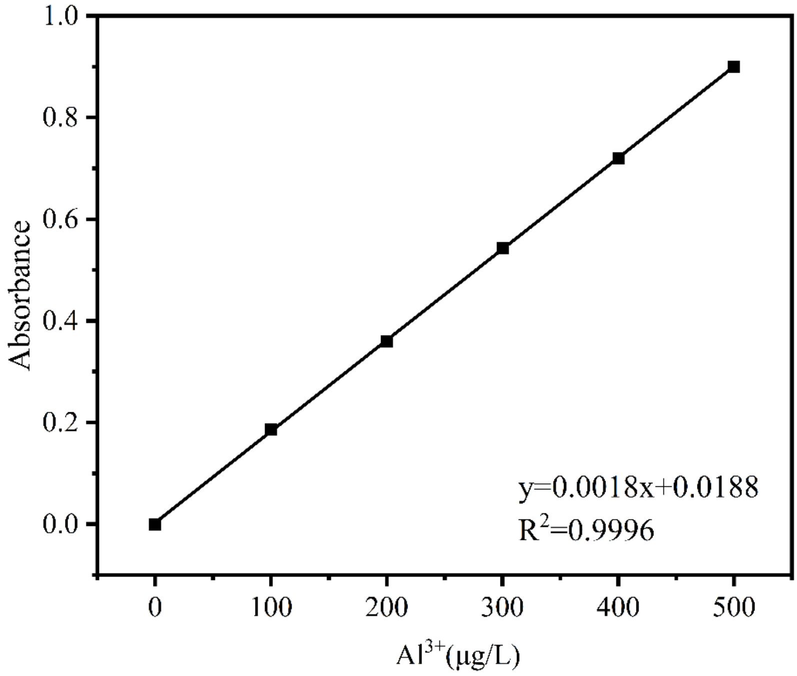

Fig.1 The standard curve of Al^{3+}

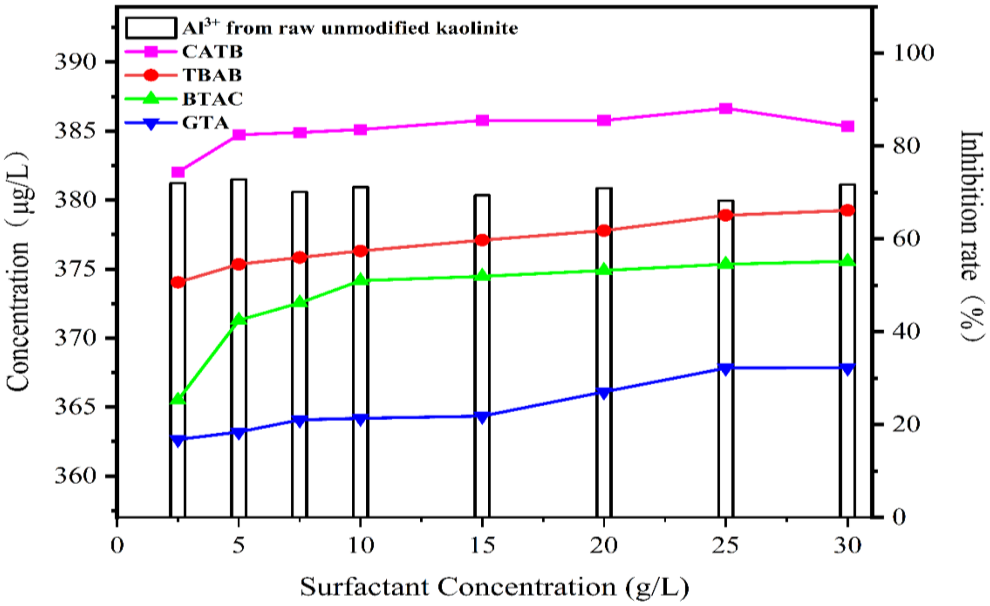

Fig.2 Effect of different cationic surfactants and their concentrations on the dissolution inhibition rate of Al^{3+} in kaolinite

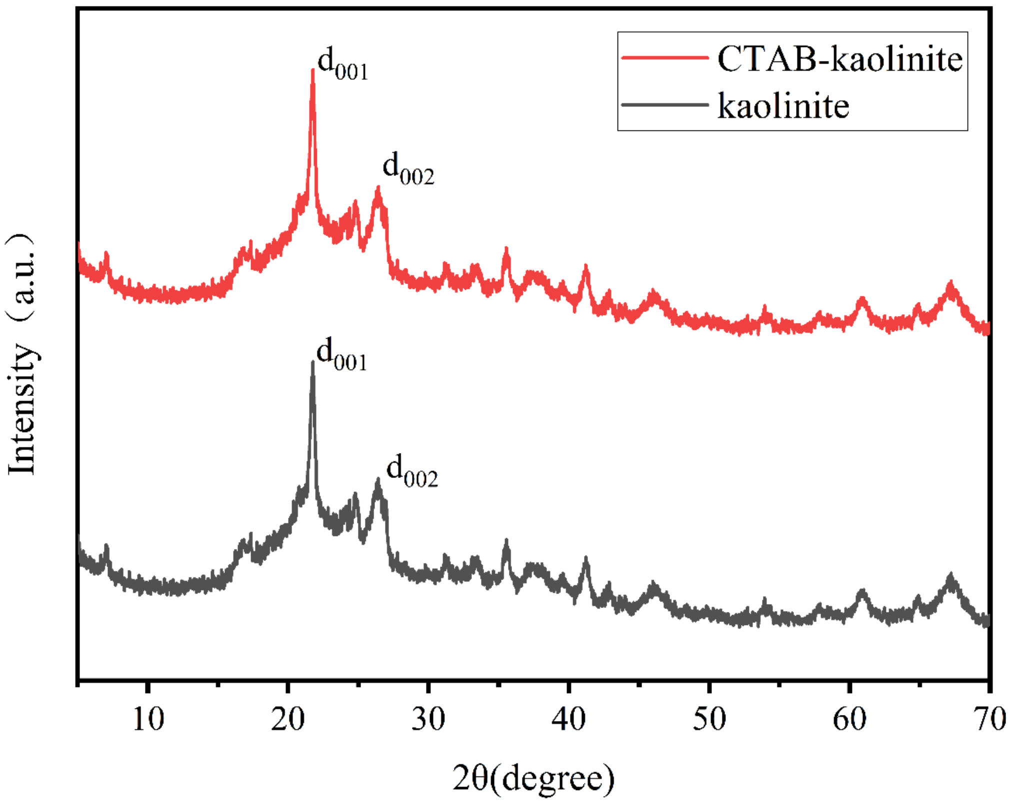

Fig.3 XRD of kaolinite and CTAB-kaolinite

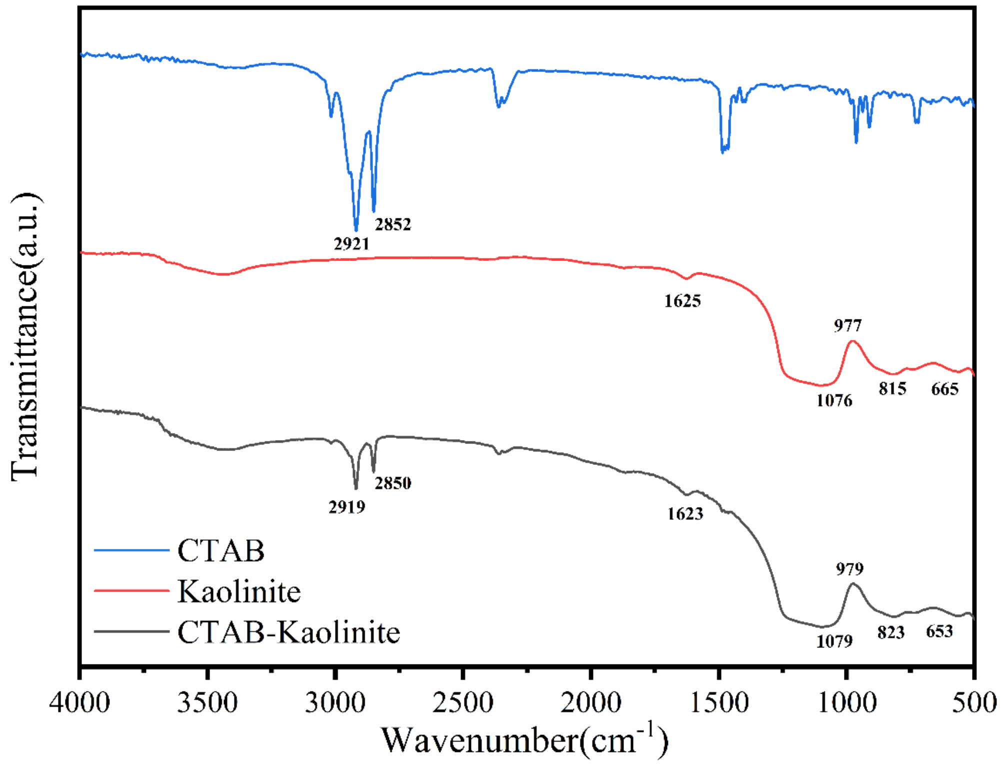

Fig.4 Infrared spectra of CTAB, kaolinite and CTAB-kaolinite

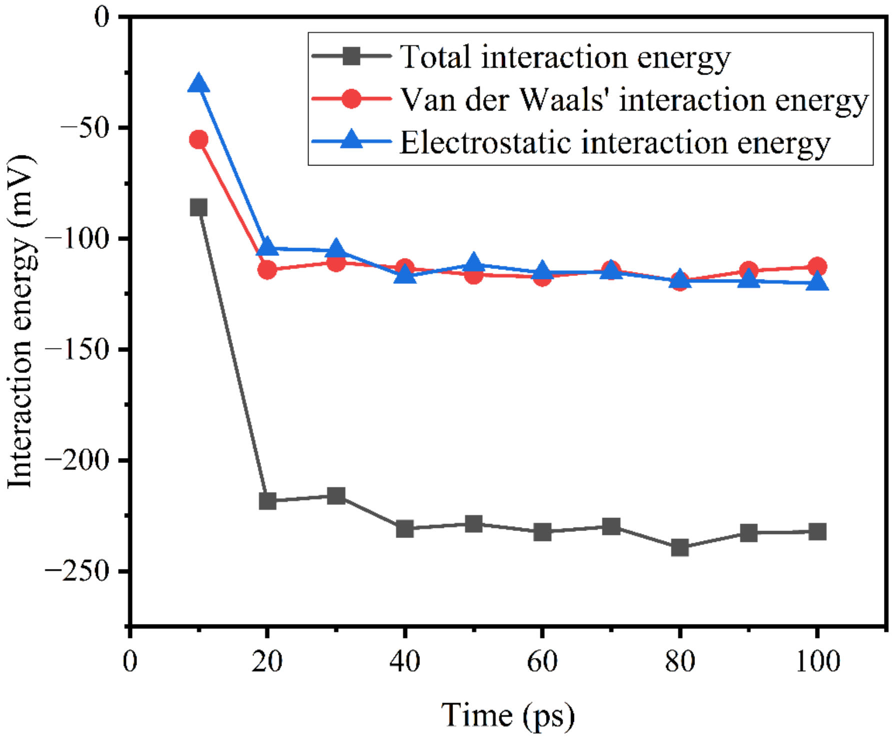

Fig.5 Change of interaction energy between CTAB and kaolinite with simulation time

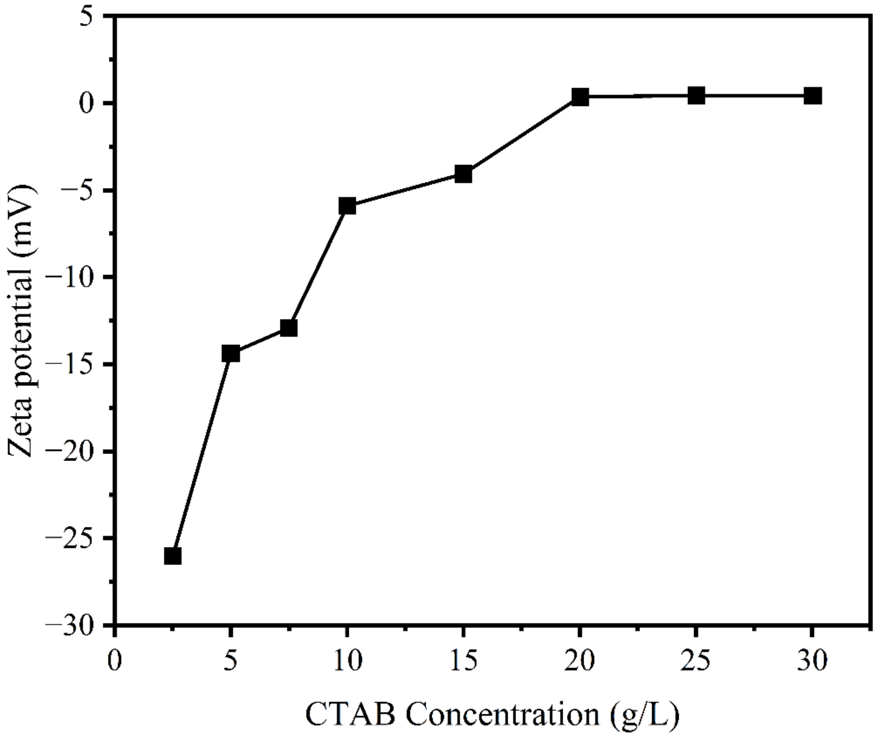

Fig.6 Effect of CTAB concentration on Zeta potential of kaolinite surface

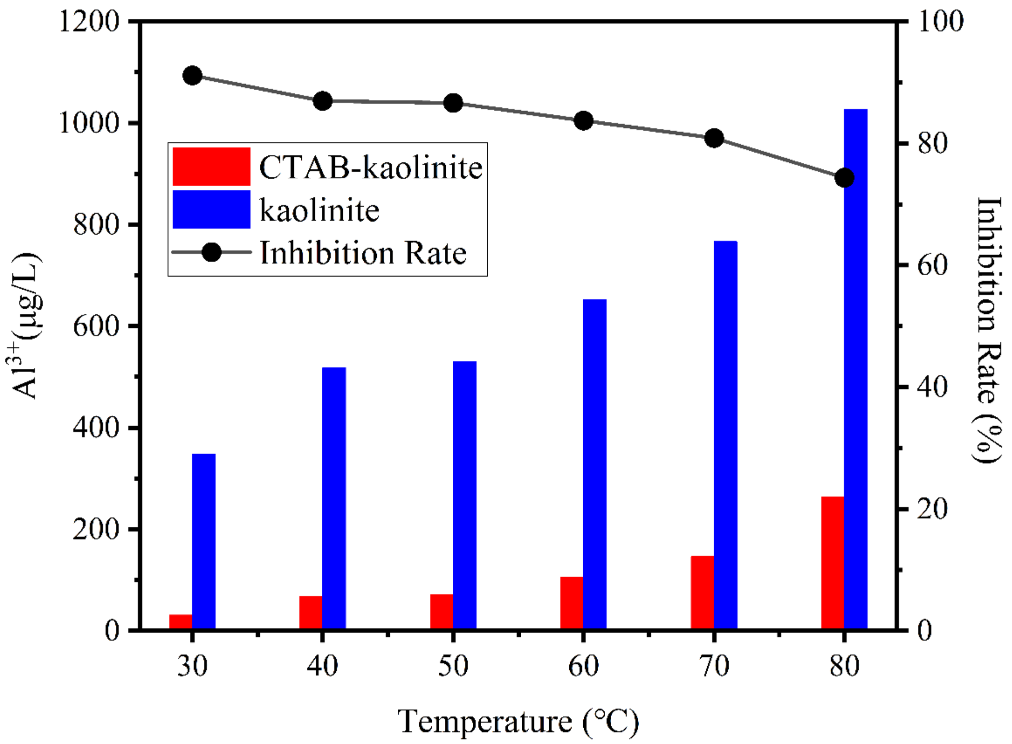

Fig.7 Influence of temperature on the dissolution amount and inhibition rate of Al^{3+} in kaolinite

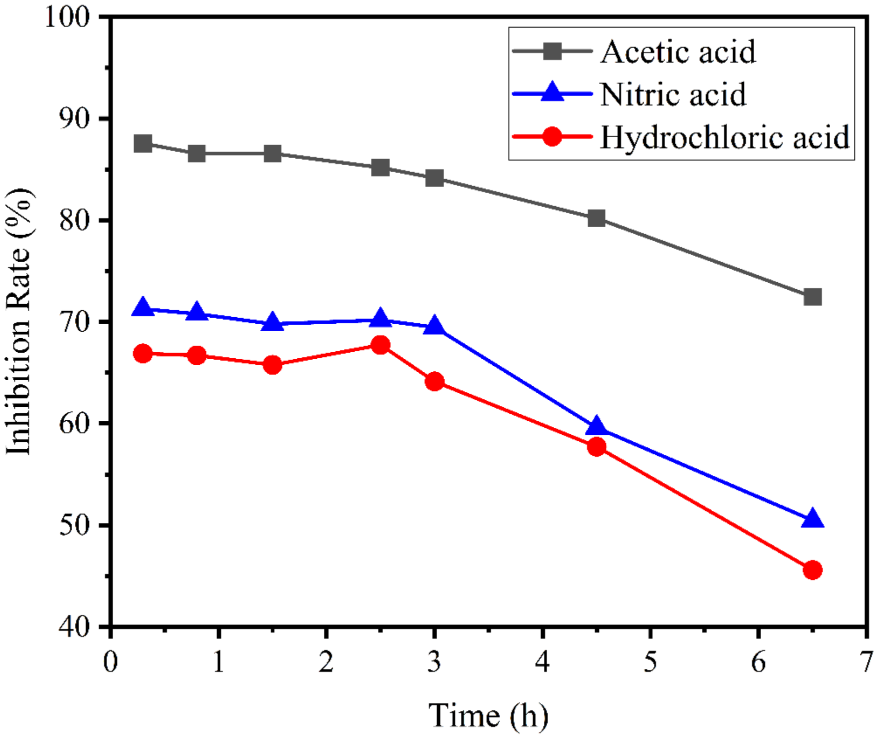

Fig.8 Inhibition rates of CTAB-kaolinite under different acid types

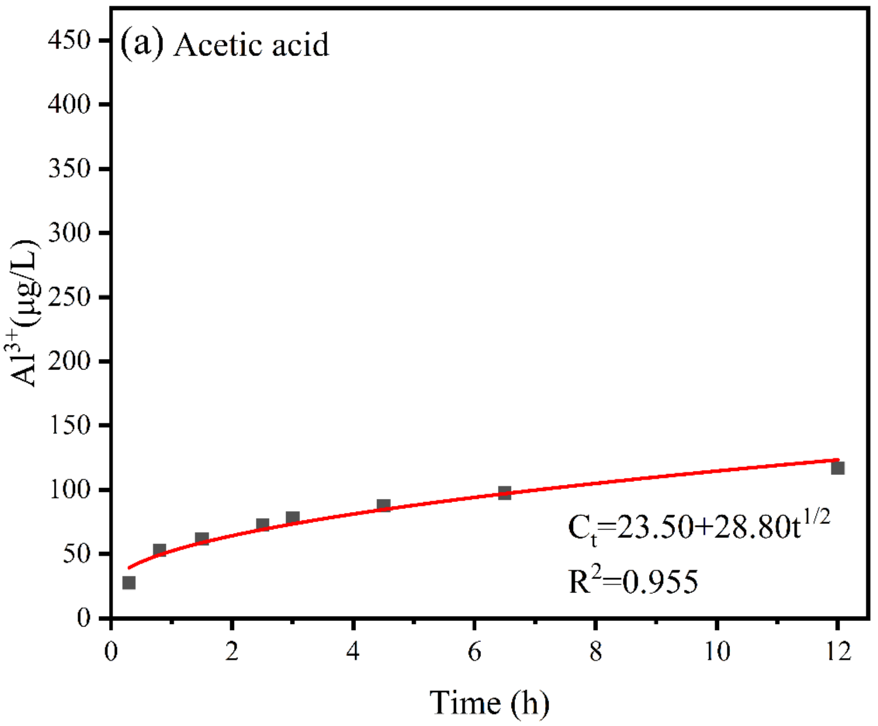

Fig.9(a) Fitting curve for the dissolution of CATB-kaolinite in acetic acid (diffusion equation)

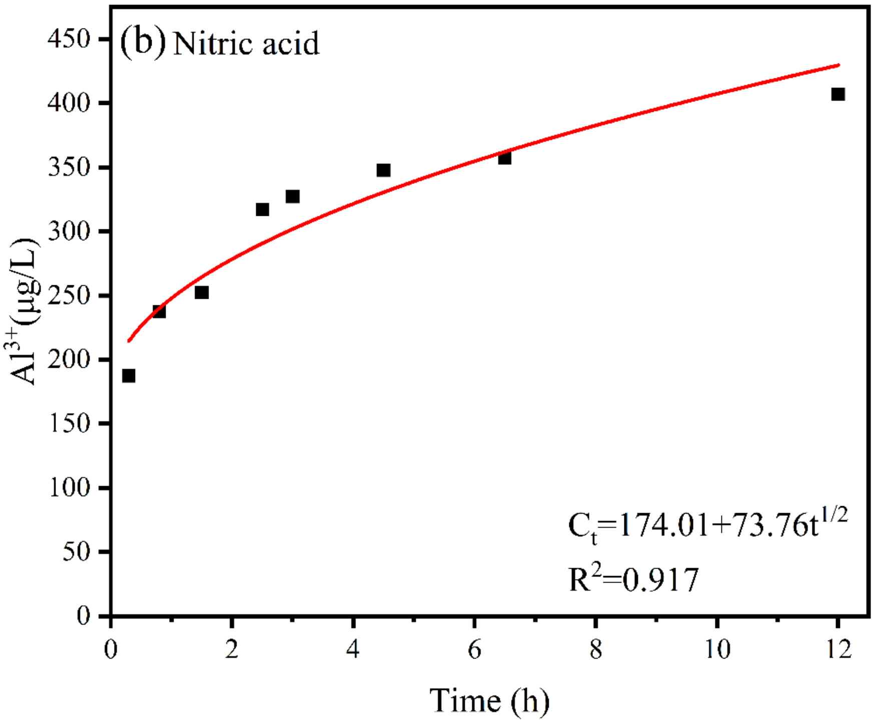

Fig.9(b) Fitting curve for the dissolution of CATB-kaolinite in nitric acid (diffusion equation)

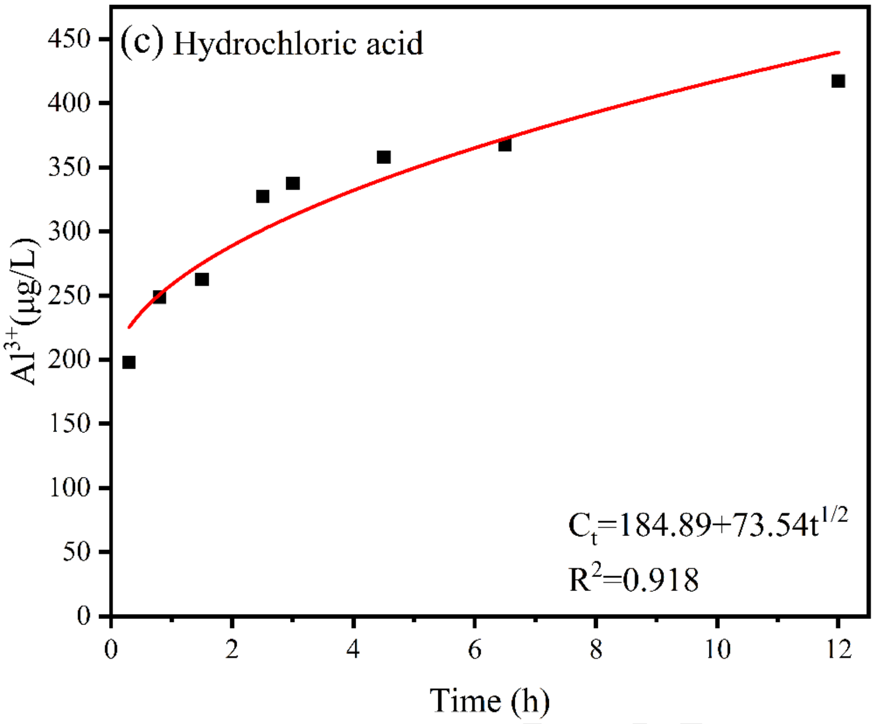

Fig.9(c) Fitting curve for the dissolution of CATB-kaolinite in hydrochloric acid (diffusion equation)

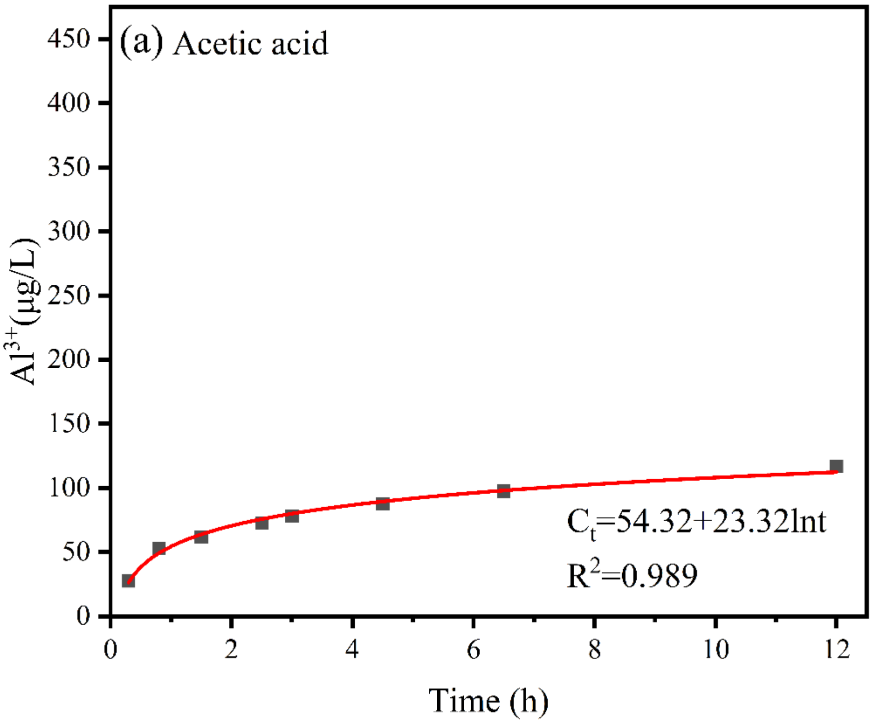

Fig.10(a) Fitting curve for the dissolution of CATB-kaolinite in acetic acid (Elovich equation)

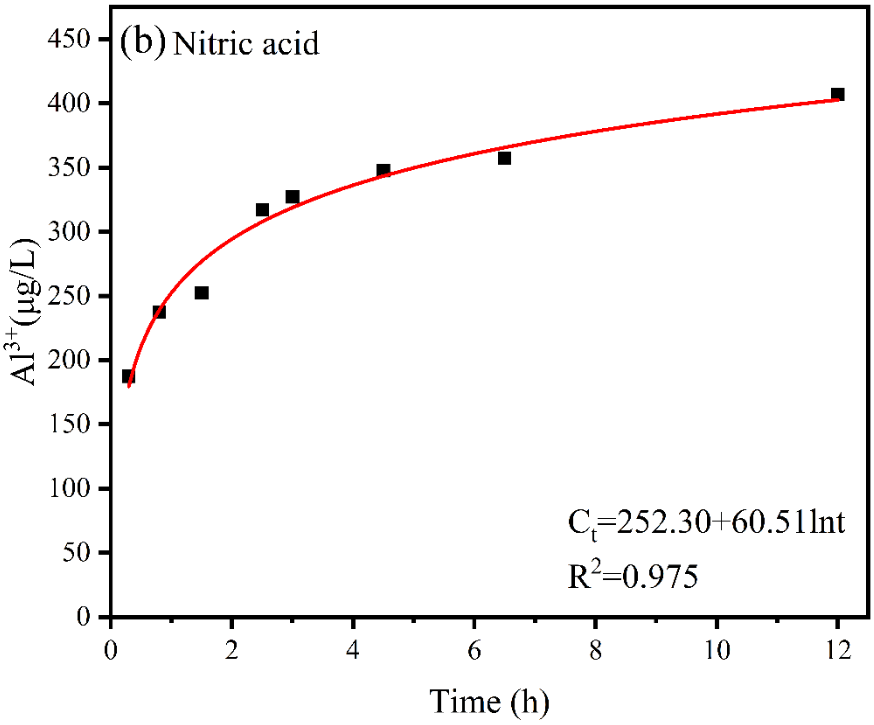

Fig.10(b) Fitting curve for the dissolution of CATB-kaolinite in nitric acid (Elovich equation)

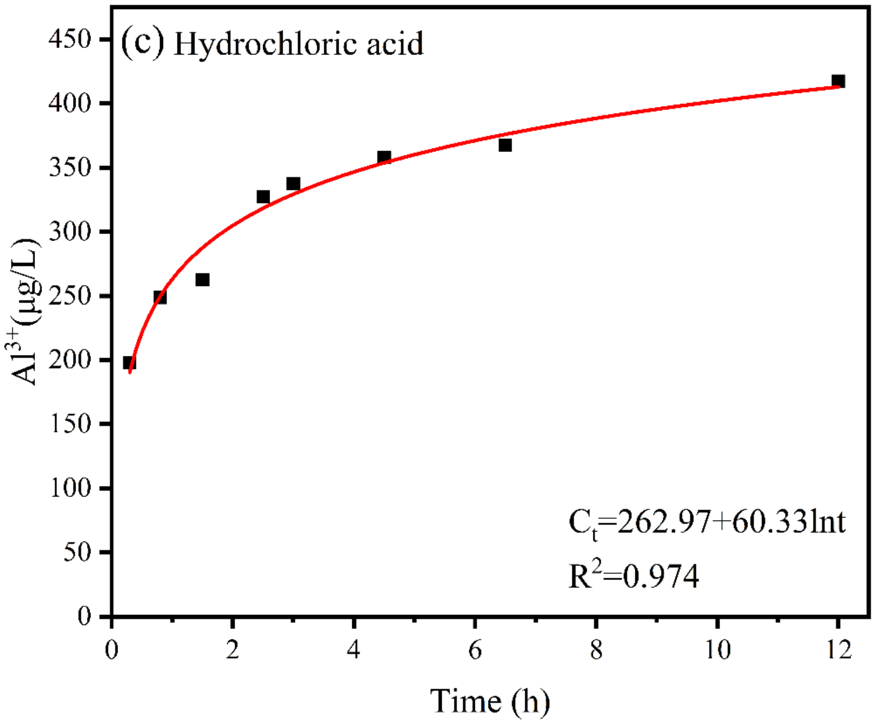

Fig.10(c) Fitting curve for the dissolution of CATB-kaolinite in hydrochloric acid (Elovich equation)

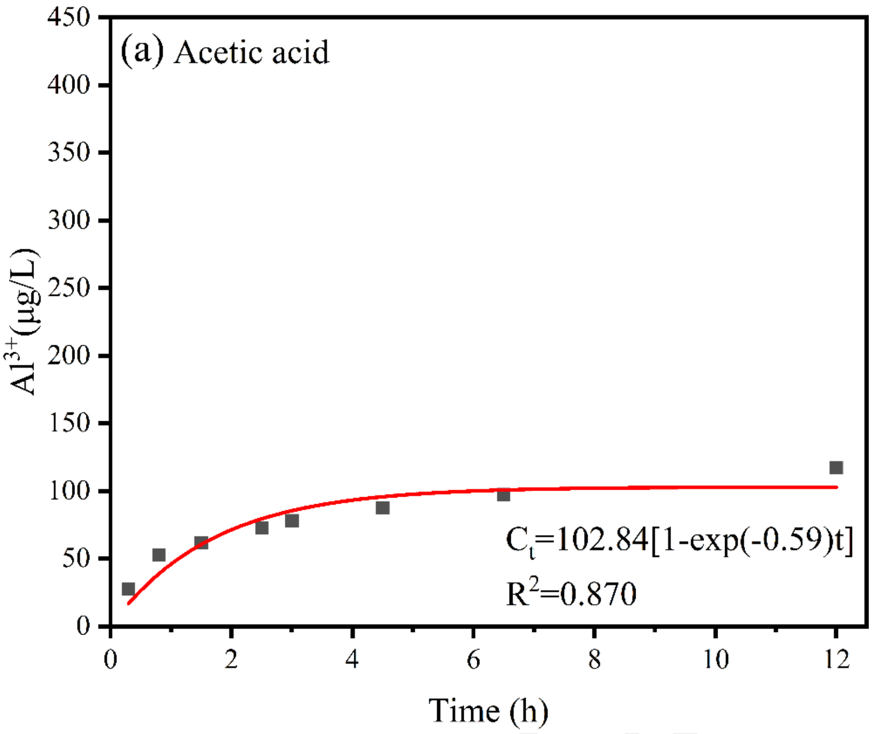

Fig.11(a) Fitting curve for the dissolution of CATB-kaolinite in acetic acid (first-order kinetic equation)

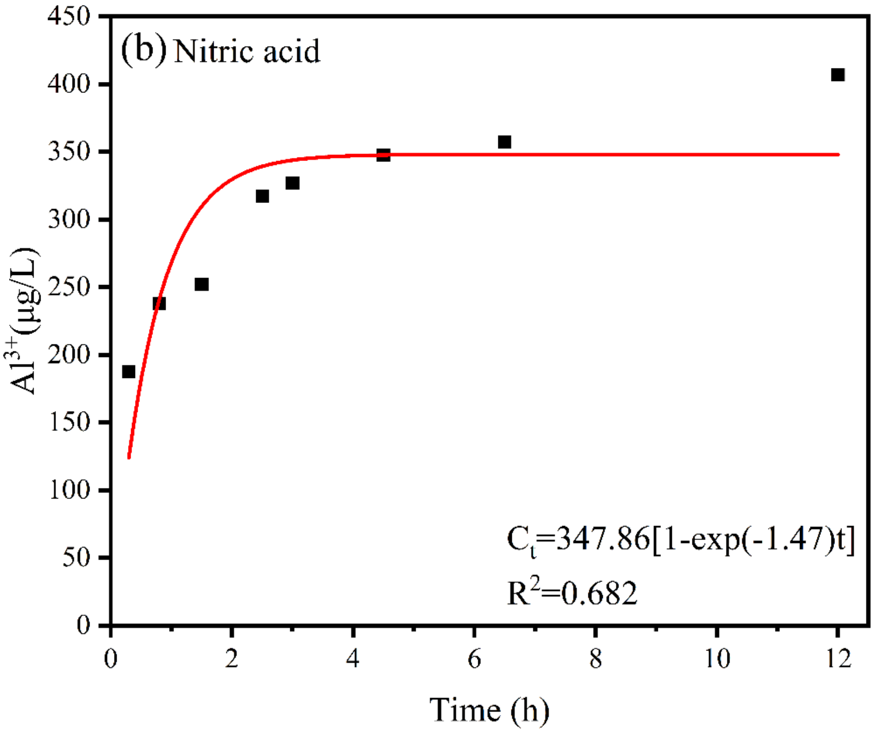

Fig.11(b) Fitting curve for the dissolution of CATB-kaolinite in nitric acid (first-order kinetic equation)

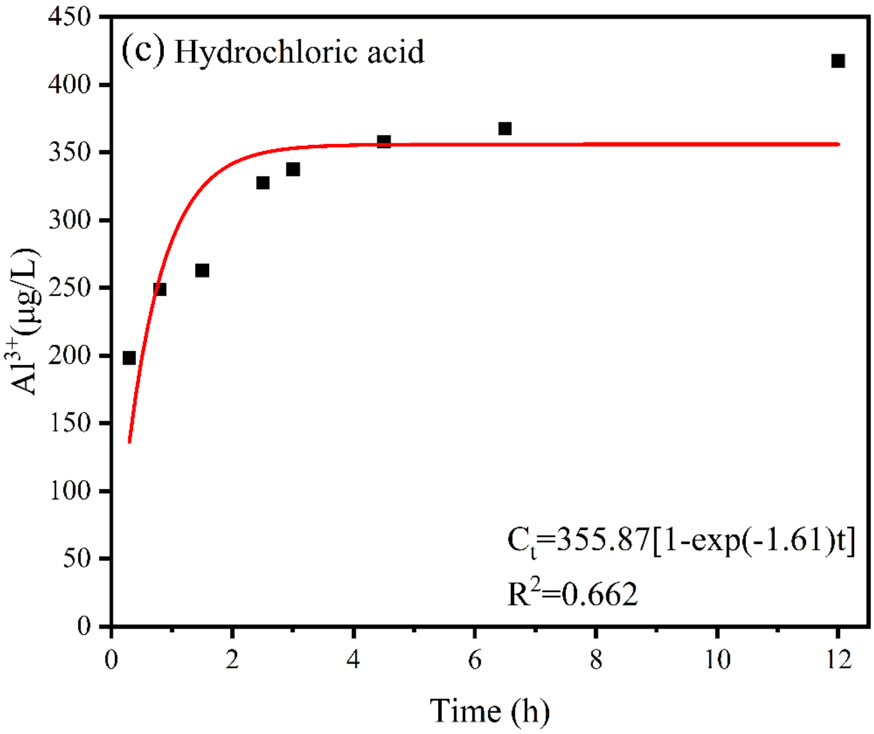

Fig.11(c) Fitting curve for the dissolution of CATB-kaolinite in hydrochloric acid (first-order kinetic equation)

Tables

Table 1 Interaction energy between CTAB and kaolinite at 100 ps

	Interaction energy (kcal/mol)	Percentage (%)
Total interaction energy	-231.21	100
Van der Waals interaction energy	-119.43	51.64
Electrostatic interaction energy	-111.79	48.36

Table 2 Kinetic parameters of Al^{3+} dissolution curve about CTAB-kaolinite under different acids

Acid	**volume fraction & pH**	$\mathbf{C_t = a + bt^{1/2}}$		$\mathbf{C_t = a + b \cdot \ln(t)}$		$\mathbf{C_t = a\,[1 - \exp(- kt)]}$	
		b	R^2	b	R^2	k	R^2
Acetic acid	2%, pH=2.49	28.80	0.955	23.32	0.989	0.59	0.870
Nitric acid	2%, pH=0.84	73.76	0.917	60.51	0.975	1.47	0.682
Hydrochloric acid	2%, pH=0.56	73.54	0.918	60.33	0.974	1.61	0.662

Table.3 Kinetics parameters of Al^{3+} dissolution curve under different systems

Systems	$C_t = a+bt^{1/2}$		$C_t = a+b\cdot\ln(t)$		$C_t = a(1-\exp(-kt))$	
	b	R^2	**b**	R^2	**k**	R^2
Acetic acid - Kaolinite	46.025	0.9708	41.575	0.9951	0.318	0.987
Acetic acid -CTAB- Kaolinite	28.80	0.955	23.32	0.989	0.59	0.870
Nitric acid - Kaolinite	182.49	0.9984	159.78	0.9614	0.418	0.837
Nitric acid -CTAB- Kaolinite	73.76	0.917	60.51	0.975	1.47	0.682
Hydrochloric acid - Kaolinite	295.67	0.9458	211.65	0.9381	0.401	0.847
Hydrochloric acid -CTAB- Kaolinite	73.54	0.918	60.33	0.974	1.61	0.662