



## Research paper

## Kinetics and thermodynamic analysis of the adsorption of hydroxy-Al cations by montmorillonite



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## ABSTRACT

Hydroxy-Al pillaring agent was prepared and used to modify montmorillonite (Mt), and the effects of temperature, initial  $\text{Al}^{3+}$  concentration and contact time were investigated by using a batch technique. The results showed that the uptake of  $\text{Al}_{13}$  by Mt increased with increasing temperature, initial  $\text{Al}^{3+}$  concentration and contact time. The adsorption equilibrium was achieved in 12 h as determined by kinetics. The adsorption kinetics demonstrated that the adsorption of  $\text{Al}_{13}$  by Mt followed the pseudo-second-order kinetic model. The adsorption isotherms at the temperatures of 40, 60, 80 and 90 °C were determined and simulated using Langmuir, Freundlich and Redlich–Peterson models. The three kinds of isotherms could represent the experimental data well. The specific surface areas and pillar density increased while the total porous volumes slightly decreased with increasing  $\text{Al}^{3+}$  concentrations. The XRD result showed that adsorbed  $\text{Al}_{13}$  ions were located in the Mt interlayer spaces through monolayer adsorption. Thermodynamic analysis of adsorption process showed that the adsorption of  $\text{Al}_{13}$  by Mt was spontaneous, endothermic with increasing disorder during the adsorption process and mainly physical in nature.

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## 1. Introduction

Montmorillonite (Mt) is a well-known naturally occurring 2:1 type layered clay mineral composed of two tetrahedral sheets sandwiching one octahedral sheet (Bergaya and Lagaly, 2006). The 2:1 type layers are negatively charged and stacked one on top of another along the c-axis. The negative charges on the layers are balanced by cations in the interlayer spaces (Bergaya and Lagaly, 2013). These inorganic cations are exchangeable and can be replaced by organic cations and metal hydroxy polymeric cations, and the resulting materials are denoted as organic and inorganic pillared Mt, respectively (Pinnavaia et al., 1985; Malla, 1990; He et al., 2006; Zhu et al., 2009; Komarneni et al., 2013). Pillared Mt is obtained after calcination around 400 °C, which has high permanent porosity, excellent thermal stability, large specific surface area and micro-/meso-porosity (Kloprogge, 1997; Ocelli et al., 2000;

Yuan et al., 2006). It is widely studied as a selective adsorbent for the removal of heavy metal ions (Bhattacharyya and Gupta, 2008) and the separation of inorganic gases (Pires et al., 2008), catalysts for petroleum refinery (González et al., 1999) and environmental restoration (Shimizu et al., 2002; Chen et al., 2009). Numerous cations such as  $[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$  and polycations of Ti(IV), Zr(IV), Cr(III), Fe(III) or Ga(III), have been used for preparation of pillared Mt (Rat'Ko et al., 2001; Duong et al., 2005; Bergaya et al., 2006; Li et al., 2013; Bahranowski et al., 2015). Alumina-pillared Mt (Al-PILM) are the most easily prepared pillared clays, mainly because the synthesis of the intercalating polycation  $[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$ , usually known as  $\text{Al}_{13}$  cation is simple to prepare reproducibly. Since pillaring of Mt with  $\text{Al}_{13}$  polycations ( $[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$ ) was first reported in the late 1970s (Singh and Miles, 1978), preparation and properties of pillared Mt have attracted a great deal of research interest and have been intensively investigated. Wu et al. (Wu et al., 1997), for example, used a variety of methods to prepare aluminum polyhydroxy cations (Keggin ions) and found the most suitable pH value was about 4.5 for preparing the stable Keggin ions. They prepared a pillaring agent using this pH and used it for making an Al-pillared Mt with a c-axis (001) spacing of 2.4–2.5 nm. Mokaya (Mokaya et al., 1993) studied the effect of reaction temperature on the c-axis (001) spacing, specific surface area and pore

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volume of the Mt during the process of the preparation of Al-pillared Mt. The results showed that when the reaction temperature was 80 °C, the c-axis (001) spacing and the specific surface area of Al-pillared Mt were larger than those prepared at room temperature. Al-Zr pillared Mt was shown by Matthes et al. (Matthes et al., 1999), to adsorb heavy metal ions like Cu, Zn, Pb and Cd in aqueous solution. Their study also found that the above pillared Mt had high affinity for  $Zn^{2+}$  and its adsorption was not affected by ionic strength of the solution.

However, most of these studies did not investigate the detailed pillaring mechanism between hydroxy-Al pillaring reagent and Mt. In addition, the adsorption behavior of hydroxy-Al polycation onto Mt was not clear from the previous studies. Therefore, in this study, pillaring mechanism between hydroxy-Al pillaring reagent and Mt was investigated in detail using hydroxy aluminum as the pillaring agent to intercalate Mt as a function of temperature, initial  $Al^{3+}$  concentration and contact time. The kinetics and thermodynamics of adsorption of polyhydroxy Al cations onto Mt were also investigated.

## 2. Experimental

### 2.1. Materials and characterization methods

The raw montmorillonite (Mt) used in this study was from Weifang bentonite deposit in Shandong province of China. The raw sample was mainly a  $Ca^{2+}$  containing Mt (referred to hereafter as Ca-Mt) mineral. The raw bentonite material was purified by sedimentation and  $Na^+$  exchanged using  $Na_2CO_3$ , and the  $Na^+$  exchanged samples were used as starting materials for the preparation of Al-pillared Mt. The cation exchange capacity, methylene blue adsorption, colloidal index and the swelling volume of  $Na^+$ -Mt were 90.0 mmol/100 g, 39.5 g/100 g, 158.0 mL/g and 74.0 mL/g, respectively.

All the chemicals used in this study were of analytical grade and procured from different suppliers as follows:  $AlCl_3 \cdot 6H_2O$  (Tianjin BASF Chemical Company, China),  $Na_2CO_3$  (Tianjin Reagent Chemical Company, China), ferron (Beijing Hengye Zhongyuan Chemical Reagent Co., Ltd.),  $CH_3COONa$  (Tianjin Kaidi Chemical Reagent Co., Ltd.), HCl (Laiyang Shuangshuang Chemical industries Ltd.). Distilled water was used for the preparation of all solutions.

Powder XRD patterns were recorded using a Rigaku D/max-rB diffractometer with Cu  $K\alpha$  radiation at 40 kV and 100 mA. A  $2\theta$  range of  $0.8^\circ$  to  $15^\circ$  was used for the Mt samples at a scanning rate of  $4^\circ \text{ min}^{-1}$ . Thermogravimetric (TG) and differential thermal analysis (DTA) were carried out with a TG/SDTA851e thermal analyzer from Mettler Toledo Company of Switzerland. The samples were heated at the rate of  $20^\circ \text{ C/min}$  under a flow of high purity nitrogen from 30 to

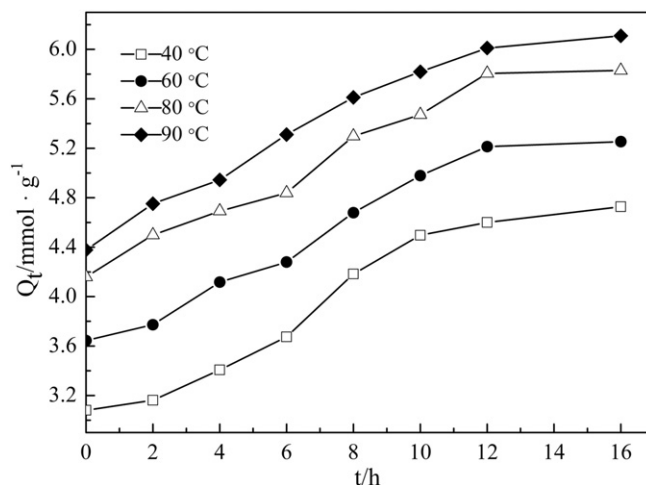


Fig. 2. Effect of temperature on the adsorption amount of  $Al_{13}$  onto Mt.

1000 °C. The BET specific surface area ( $S_{BET}$ ) and the total pore volume were measured on a SSA-4300 equipment at liquid nitrogen temperature (77 K).

### 2.2. Preparation of hydroxy-Al pillared reagent

A solution of  $0.4 \text{ mol} \cdot \text{L}^{-1}$   $Na_2CO_3$  was added at the rate of  $1 \text{ mL} \cdot \text{min}^{-1}$  to a solution of  $0.2 \text{ mol} \cdot \text{L}^{-1}$   $AlCl_3 \cdot 6H_2O$  under vigorous stirring at a temperature of 80 °C. The final  $OH^-/Al^{3+}$  mole ratio of Al pillaring solution was equal to 2.4. The hydrolyzed solution was allowed to continuously stir for 2 h at 80 °C, and then aged for 24 h at room temperature. The final pH of the solution was 4.9.

### 2.3. Determination of hydroxy-Al cation concentration

The first step was preparation of ferron colorimetric solution (Feng et al., 2006). The ferron colorimetric solution was obtained by mixing 0.2% (m/V) ferron solution, 20% (m/V)  $CH_3COONa$  (NaAc) solution and  $1.2 \text{ mol} \cdot \text{L}^{-1}$  HCl solution at a ratio of 2.5:2:1. The latter two solutions were mixed prior to the addition of ferron. Each individual reagent mentioned above was filtered through pre-washed  $0.45 \mu\text{m}$  membranes. The pH value of the resulting solution was about 5.2 and was stored in refrigerator for later use.

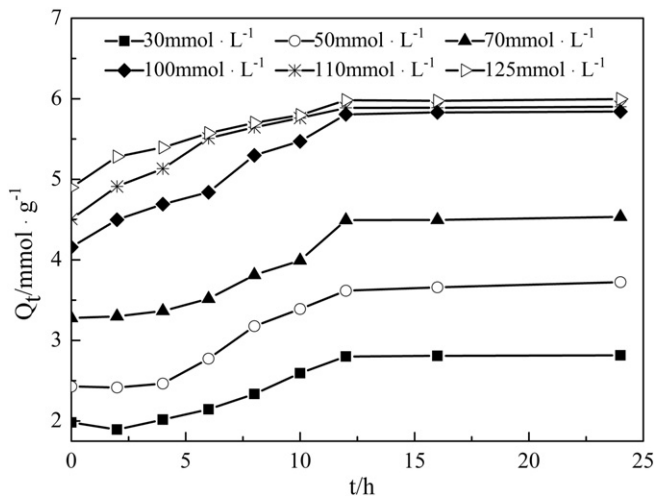


Fig. 1. Effect of initial  $Al^{3+}$  concentration on the adsorption amount of  $Al_{13}$  onto Mt.

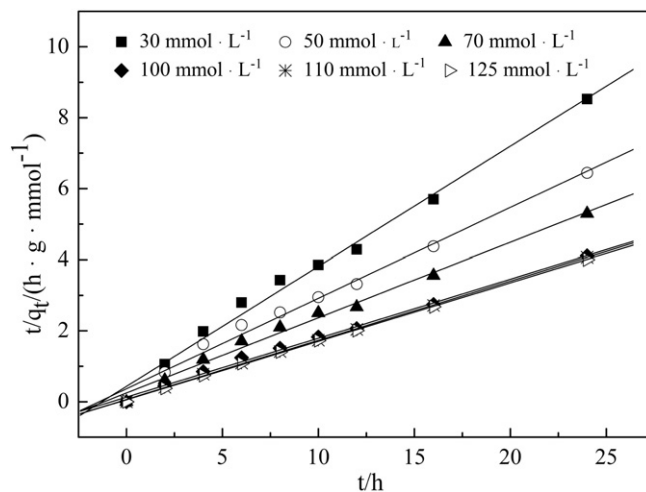


Fig. 3. Pseudo-second-order plots of  $Al_{13}$  onto Mt at different initial  $Al^{3+}$  concentrations.

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