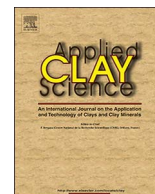




Contents lists available at ScienceDirect

## Applied Clay Science

journal homepage: [www.elsevier.com/locate/clay](http://www.elsevier.com/locate/clay)

## Research paper

## Effect of acid activation of palygorskite on their toluene adsorption behaviors

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## ARTICLE INFO

## Keywords:

Volatile organic compounds (VOC)  
Acid activation  
Palygorskite  
Adsorption  
Kinetics

## ABSTRACT

In this paper, acid-activated palygorskite (APalx) samples were prepared by a facile acid treatment method with different concentrations of HCl (0.5, 1, 3, 5 and 7 mol/L). The dynamic toluene adsorption performances of APalx were evaluated and the relevant adsorption mechanism was discussed. The prepared adsorbents were characterized using X-ray diffraction (XRD), elemental analysis, transmission electron microscopy (TEM), nitrogen adsorption-desorption isotherms and Fourier-transform infrared spectroscopy (FTIR). The results show that the palygorskite has a good resistant ability to acid attack, the structure still remains when the acid concentration is as high as 7 mol/L. Acid activation could significantly enhance the surface area (228, 250, 271, 273, 329 and 308 for Pal, APal0.5, APal1, APal3, APal5 and APal7, respectively) and porosity of palygorskite. APal5 has the best toluene adsorption capacity (90.4 mg/g) due to its highest  $S_{\text{BET}}$  (329  $\text{m}^2/\text{g}$ ) and  $V_{\text{micro}}$  (0.055  $\text{cm}^3/\text{g}$ ). The adsorption performance in terms of dynamic toluene adsorption capacities follows the order of Pal (44.6 mg/g) < APal0.5 (63.5 mg/g) < APal1 (71.3 mg/g) < APal7 (74.2 mg/g) < APal3 (75.1 mg/g) < APal5 (90.4 mg/g). APal5 can be readily regenerated by thermal desorption and has exhibited steady reproducibility after 6 cycles. These results have demonstrated that acid activation is a feasible and effective method for the structure and surface optimizing of palygorskite, enabling the APalx to become a promising candidate for the adsorption of volatile organic compounds in practical applications.

## 1. Introduction

Volatile organic compounds (VOC) such as benzene, toluene, xylene and formaldehyde are the most common air pollutants due to their widely distributed emission sources. These VOC are recognized not only harmful to the environment, causing the photochemical smog, destruction of ozone layer and global warming (Einaga et al., 2001; Weber et al., 2007) but also hazardous to human health, correlating with chronic asthma, respiratory disease and even cancer (Du et al., 2014; Mendell, 2010). Therefore, considering the above risks and, on the other hand, their economic values, necessary treatments should be employed to trap and recycle these VOC. Enormous efforts have been paid on the development of technologies to reduce the concentration of the VOC and minimize their harmful effect. Many technologies, such as

adsorption (Wang et al., 2016), thermal or catalytic oxidation (Liang et al., 2016; Liu et al., 2016; Peng et al., 2003), photocatalytic oxidation (Zhao and Yang, 2003), membrane separation (Ozturk et al., 2015), and biological treatment (Cheng et al., 2016) are widely reported. Among them, adsorption is one of the most advocated methods due to its inexpensive operation cost, low energy consumption and flexibility of the adsorption system (Wang et al., 2014; Yu et al., 2015).

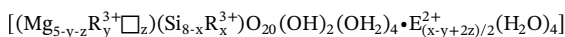
Activated carbon, as a versatile adsorbent, is the most commonly used material owing to its large surface area, highly developed porous structure, low cost and excellent adsorption property (Lillo-Ródenas et al., 2005). However, some disadvantages including flammability, pore clogging, hygroscopicity and hard to regeneration hinder its practical application (Zhao et al., 1998). Therefore, for the adsorption capacity, heat resistance, thermal recyclability, as well as the economic

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reasons, much attention has been paid on the application of naturally occurring and highly active materials. Currently, some raw clay minerals, such as montmorillonite, kaolinite and halloysite (Deng et al., 2017) have been recommended as alternative adsorbents because of their special structural characteristic, natural active groups as the potential adsorption sites on the surface (Si-OH, Al-OH etc.) (Hernández et al., 2004), and the feasibility for modification (Wang et al., 2016). In addition, the wide distribution and abundant reserves of clay minerals are also the merits that make them promising adsorbents for VOC treatment.

Palygorskite is a hydrated magnesium aluminum silicate with the chain-layer structure. Its universal chemical formula is



, where  $R^{3+}$  are  $Al^{3+}$  and  $Fe^{3+}$ ,  $\square$  represents octahedral vacancy and  $E^{2+}$  is exchangeable cation (Wu et al., 2011). Owing to its large surface area and ion-exchanging ability, palygorskite is considered as an excellent alternative adsorption material. Acid activation is usually employed in industrial application for modifying the surface properties of clay minerals (Komadel, 2016). For palygorskite, acid treatment can produce significant structural changes (surface area, porosity), eliminate mineral impurities, increase amounts of silanol groups (Si-OH), which would mainly affect its adsorptive properties (Galan, 1996; Myriam et al., 1998). Up to now, most applications of acid-activated palygorskite are focused on the adsorption of heavy metals ( $Cu^{2+}$ ,  $Pb^{2+}$ ,  $Cd^{2+}$ ,  $Hg^{2+}$ ) (Chen et al., 2007; Eloussaief and Benzina, 2010; Frini-Srasra and Srasra, 2010), removal of organic compounds (toxic dyes) (Zhang et al., 2016) and inorganic phosphate (Li et al., 2016) in aqueous solution, and its catalytic performance as a solid acid catalyst (Jiang et al., 2014). However, to the best of our knowledge, the VOC adsorption performance of acid-activated palygorskite and its adsorption mechanism integrated with the structural characteristics and surface properties have rarely been investigated.

In this study, acid-activated palygorskite was prepared by a facile acid treatment method with different concentrations of HCl. Although toluene is much less toxic than benzene, its presentation in indoor air at higher concentration might also cause serious harm to human health. Thus, toluene was taken into consideration in this work and used as a model pollutant. The VOC dynamic adsorption performance of acid-activated palygorskite was investigated by evaluating the adsorption capacity of toluene and the relevant adsorption mechanism. The objectives of this study are to investigate the effect of acid treatment on the structure and surface property of palygorskite and to explore the application of acid-activated palygorskite for VOC adsorption.

## 2. Experimental

### 2.1. Materials

The raw palygorskite (Raw-Pal) was obtained from Mingguang city, Guanshan, Anhui Province, China. The cation exchange capacity (CEC), measured by adsorption of  $[Co(NH_3)_6]^{3+}$ , is 20 meq/100 g. Hydrochloric acid (HCl) in a mass fraction of 36–38 wt% was purchased from Guangzhou Reagent Company and toluene was purchased from Aladdin Reagent Company. All chemicals are of analytical grade and used without purification.

The palygorskite was purified via sedimentation and weak acid treatment, and the obtained purified palygorskite was marked as Pal. Acid-activated palygorskite was prepared using different concentration of HCl. In a typical procedure, about 5 g Pal was suspended in 100 mL of  $x$  mol/L HCl solution ( $x = 0.5, 1, 3, 5$  and  $7$  respectively) and mixed evenly under vigorous stirring at  $40^\circ C$  for 4 h. After that the mixture was collected via centrifugation at 4000 rpm for 5 min, and washed by deionized water for several times until the supernatant was free of  $Cl^-$  (determined by  $AgNO_3$  solution). Finally, the samples were dried at

$80^\circ C$ , then crushed and sieved to  $< 0.075$  mm. The final products were labeled as APal $x$ ,  $x$  denotes the concentration of HCl in mole concentration.

### 2.2. Characterization methods

The Power X-ray diffraction (XRD) patterns were obtained using a Ni filter and Cu K $\alpha$  radiation ( $\lambda = 0.154$  nm) on a Bruker D8 Advance X-ray diffractometer. The patterns between  $5^\circ$  and  $50^\circ$  were recorded at 40 kV and 40 mA with a scanning speed of  $2^\circ/\text{min}$ .

Major element oxides of APal $x$  were analyzed using a Rigaku RIX 2000 X-ray fluorescence spectrometer (XRF) on fused glass beads. Calibration lines used in quantification were produced by bivariate regression of data from 36 reference materials encompassing a wide range of silicate composition, and analytical uncertainties are mostly between 1 and 5%.

Nitrogen adsorption-desorption isotherms were carried out on a Micromeritics ASAP 2020 specific surface area and porosity analyzer at  $-196^\circ C$ . Prior to tests, samples were degassed at  $120^\circ C$  for 12 h. The specific surface area (SSA) was evaluated by the Brunauer-Emmett-Teller (BET) equation, and the total pore volume was obtained from nitrogen adsorption at a relative pressure of 0.97. The micropore volume and microporous specific surface area were calculated by the t-plot method. The pore size distributions (PSD) analysis was determined by the non-local density functional theory (NLDFT) method due to the advantages of the independence of capillary condensation and applicability across the entire range of micropore-mesopore (Wang et al., 2015).

Fourier-transform infrared (FTIR) spectra were acquired on a Bruker Vertex-70 Fourier-transform infrared spectrometer. The specimens were prepared with a sample/KBr ratio of approximate 1:100, ground in an agate mortar for 10 min and then pressed into a pellet. The spectra were measured over  $400\text{--}4000\text{ cm}^{-1}$  with 64 scans at a resolution of  $4\text{ cm}^{-1}$  at room temperature.

### 2.3. Adsorption experiments

The adsorption performance of VOC was evaluated at atmospheric pressure in a laboratory-scale fixed-bed quartz column with an inner diameter of 10 mm. The Schematic overview of the setup was shown in Fig. 1. Before adsorption testing, the samples were heated at  $105^\circ C$  for 4 h to remove all adsorption water. At each run, 0.2 g of sample was sandwiched in the middle of the reactor. The stream of toluene was

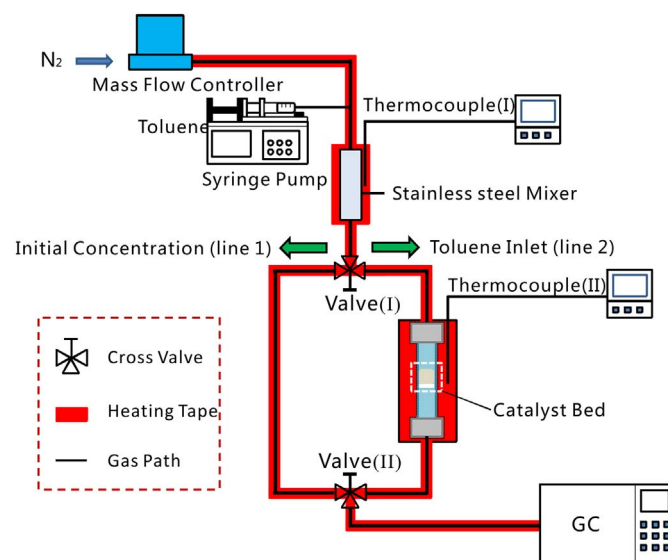


Fig. 1. Schematic diagram for the dynamic adsorption of toluene.

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