



Research paper

Hydrothermal carbonization synthesis of Al-pillared montmorillonite@carbon composites as high performing toluene adsorbents

Changchi Liu^{a,b}, Weiquan Cai^{b,c,*}, Licheng Liu^{a,*}

^a CAS Key Laboratory of Bio-based Materials, Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao 266101, Shandong, China

^b School of Chemistry, Chemical Engineering & Life Sciences, Wuhan University of Technology, Luoshi Road 205#, Wuhan 430070, China

^c School of Chemistry and Chemical Engineering, Guangzhou University, Guangzhou 510006, China



ARTICLE INFO

Keywords:

Montmorillonite
Nanocomposite
Toluene
Adsorption

ABSTRACT

Clay-based composites coated with carbon are highly promising for volatile organic compounds (VOC) removal because of their unique and adjustable layered structures and good stability in high temperature regeneration. To develop such kind of cost-effective clay-based adsorbents, we synthesized a series of Al-pillared Montmorillonite@Carbon (Al-Mt@C) composites by a hydrothermal carbonization method on laboratory scale. The mass ratio of Al-pillared Montmorillonite (Al-Mt) to carbon precursor glucose was varied from 3/3, 3/5 to 3/7. The samples were extensively characterized by XRD, SEM, FTIR, N₂ adsorption/desorption and TG techniques. The adsorption/desorption performance for toluene, one of the typical VOC, was investigated by measuring the breakthrough curve under a dynamic condition. There were two forms of carbon formed in the Al-Mt@C composites: carbon microspheres and smaller carbon clusters. Both micropores and mesopores were formed by accumulation of the carbon clusters in the Mt. layers, which contributes to the enhanced adsorption capacity toward toluene in general. Among the Al-Mt@C samples, Al-Mt@C(3/5) showed the best adsorption and regeneration performance. The highest toluene adsorption capacity reached 39.9 mg/g. This research extends the possible use of the Al-Mt@C composites to the field of air pollutant control.

1. Introduction

Montmorillonite (Mt), one of the common clay minerals, is naturally abundant and has good thermal stability (Kadoura et al. 2016). It has been widely used as adsorbent for removal of various contaminants (Catalano and Brown Jr 2005; Ramos et al. 2015; Hu et al. 2017a; Deng et al. 2017). In order to further improve the removal efficiency of Mt., pillared Mt. and organic-inorganic nanocomposites have been developed. Pillared clays (PILC) with large specific surface area and basal spacing are usually synthesized by the cation exchange method, which has become a general modification method for clays (Bergaya and Lagaly 2013; Liu et al. 2015). A recent development is the synthesis of Montmorillonite@carbon (Mt@C) composite adsorbents which exhibited excellent adsorption performance (Ai and Li 2013; Li et al. 2014; Zhang et al. 2015). According to Wu et al. (2016), the carbon formed in the Mt.@C composites is actually hydrochar, which is also known as hydrothermal carbon, or a solid carbon-rich material often derived from the hydrothermal carbonization of biomass. Up to now, Mt. and its derivatives are mostly used as adsorbents to treat wastewater in aqueous mediums, but not often used for gas pollutant

adsorption, particularly for volatile organic compounds (VOC) adsorption and removal (Ding et al. 2015; Deng et al. 2017).

VOC are an important class of air pollutants, which refer to organic compounds having boiling points within the range of 50–260 °C (Atkinson and Arey 2003; Le Cloirec 2012; Dai et al. 2012). They are mostly discharged from industrial processes including petrochemical, pharmaceutical, textile industries, and so on (Nunes et al. 2008; Huang et al. 2017). To address the severe environmental pollution issues, VOC emission and abatement has become a hot research topic, because most of VOC are toxic and even carcinogenic, such as toluene, benzene, and formaldehyde, and brings many detrimental effects to the environment and human health (Mishra et al. 2015; Khanchi et al. 2015). Techniques for VOC abatement include thermal incineration (Cooper et al. 1991), catalytic combustion (Li et al. 2009; Scirè and Liotta 2012; Kamal et al. 2016), absorption (Lalanne et al. 2008), condensation (Belaissaoui et al. 2016), and adsorption (Gironi and Piemonte 2011). Among them, the adsorption technology is widely used, and development of adsorbents with high performance is essential to the process (Wang et al. 2014).

Activated carbon is a common choice as adsorbent in adsorption technology owing to its large specific surface area, abundant

* Corresponding authors.

E-mail addresses: caiwq@whut.edu.cn (W. Cai), liulc@qibebt.ac.cn (L. Liu).

microporosity and abundant functional groups, and wide range of raw material sources. However, its application is limited by its sensitivity to high temperature, the difficulty in regeneration, pore clogging and hygroscopicity (Zhao et al. 1998). Synthetic zeolites (X- and Y-type, ZSM-5) and natural zeolites are another important class of adsorbents for VOC adsorption and elimination (Kim and Ahn 2012). Mesoporous silica (MCM-41, SBA-15) and alumina also have similar properties to zeolite adsorbents. But most of these adsorbents suffer from either high-cost or low capacity problems. Therefore, new adsorbents with both high resistance to high temperature regeneration, especially under oxygen or air, and large adsorption capacities, should be developed. Mt. and its derived composites exhibit great potential to be applied as VOC adsorbents, because they are not combustible and have unique and adjustable layered structures.

In the last few years some clay-based composites have been developed to adsorb VOC. The novel composite AlCr-pillared clays (AlCr-PILC) were prepared with specific surface area, pore volume, and maximum basal spacing of 266–362 m²/g, 0.16–0.22 cm³/g, and 2.06 nm, respectively, and its adsorption capacity toward benzene reached 48.3 μmol/g (Ding et al. 2015). Surface-functionalized porous clay heterostructures (PCH) have been synthesized and used as VOCs adsorbent (Qu et al. 2009; Wang et al. 2016). However, the use of large amount of organic template and tetraethyl orthosilicate may limit its large-scale preparation and industrial application.

In order to solve these problems and test the feasibility of Mt.@Carbon composite for VOC adsorption, Al-pillared Mt. composites coated with amorphous carbon (Al-Mt@C) were fabricated by a well-established hydrothermal carbonization process (Wu et al. 2016), which was followed with calcination at 500 °C under N₂ flow to make the composites more stable when used as adsorbents. For VOC adsorption test, toluene was selected as it is a typical VOC pollutant in indoor air and industry waste gas (Luengas et al. 2015; Hu et al. 2017b; Kim et al. 2018). As demonstrated, Al-Mt@C samples showed much improved adsorption capacity compared with Mt.

2. Experimental

2.1. Materials and chemicals

The Mt. used (> 99%, ~48 μm) in this study was obtained from Inner Mongolia, China. Its composition (mass%) is Na₂O:MgO:Al₂O₃:SiO₂:CaO:Fe₂O₃ = 3.75:3.01:19.37:68.08:3.63:1.52 and cation exchange capacity (CEC) is 0.55 mmol/g. Glucose, Aluminum chloride (AlCl₃), NaOH and toluene were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were of commercially available with analytical grade.

2.2. Preparation of Al–Mt and Al-Mt@C composite

The sample of Al pillared Mt. (Al–Mt) was prepared as follows: 6.674 g AlCl₃ was dissolved in 200 ml distilled water under stirring at room temperature, then 0.65 M NaOH solution was titrated into the AlCl₃ solution to form a pillaring solution with a molar ratio of OH⁻/Al³⁺ = 2.6. After that, 10.0 g of Mt. was added into the pillaring solution. The resulting dispersion was stirred for 24 h at room temperature. It was filtered and washed repeatedly with distilled water until no chloride ions was detected. The obtained solid was dried at 120 °C, ground and stored before use.

The sample of Al-Mt@C was prepared as follows: glucose with desired amount (3.0, 5.0 or 7.0 g) was dissolved in 70 ml distilled water under stirring at room temperature. 3.0 g of Al–Mt was then added to above solution and stirred for 30 min to form a homogeneous dispersion. The mixed solution was transferred into a Teflon-lined stainless-steel autoclave with a volume capacity of 100 ml and heated at 160 °C for 24 h. When the hydrothermal reaction was finished, the as-synthesized products were filtered and washed repeatedly with distilled water

several times, and dried at 80 °C for 4 h. Then calcination under nitrogen gas flow was carried out at 500 °C for 4 h in a tube furnace. Composite Al-Mt@C synthesized under different Al-Mt/glucose mass ratio, were labeled as Al-Mt@C(3/3), Al-Mt@C(3/5), Al-Mt@C(3/7), respectively.

2.3. Characterization

The XRD patterns were recorded by using a Bruker D8 Advanced Diffractometer equipped with Ni-filtered Cu Kα radiation (λ = 0.154 nm) operating at 40 kV and 40 mA with a fixed slit width of 0.3 mm. The scan rate was 1.0°(2θ)/min with a step size of 0.02 and the scanning range was from 3.5° to 70° (2θ). The samples were ground to fine powder and sieved to no < 320 mesh, before they were pressed into a very flat surface.

Surface morphologies of the samples were observed by using a scanning electron microscope (SEM Hitachi S-4800). In each experiment, a very small amount of the powder sample was put on a stub and then coated with gold prior to recording the micrographs. The acceleration voltage was set at 10 kV. The Energy Dispersive X-Ray Spectroscopy was collected at the same machine.

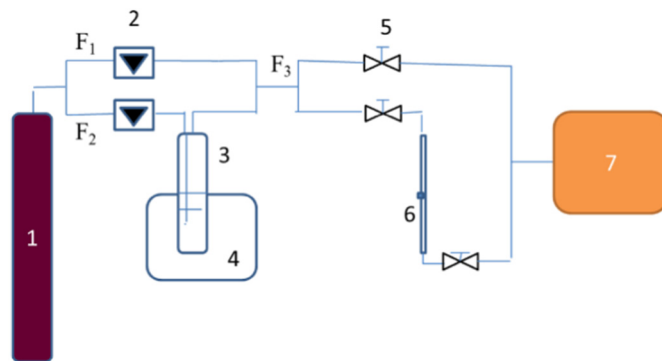
FTIR spectra were obtained using a ThermoFisher iS50 Fourier transform infrared spectrometer. The KBr pellets were prepared by pressing the mixtures of 0.9 mg powder and 80 mg KBr. All spectra were collected at room temperature in the range 450–4000 cm⁻¹ with a resolution of 4 cm⁻¹ and 64 scans.

N₂ adsorption-desorption isotherms were measured on a Micromeritics ASAP 2020 M instrument at -196 °C. The vacuum pressure applied during the outgassing (200 °C for 4 h) employed prior to the measurement. Calculation of the specific surface area (Brunauer-Emmett Teller (BET)), pore volume, and average pore size (Barrett Joyner-Halenda method) was performed with the software of the apparatus. The pore size is referred to pore diameter all through this article.

Thermogravimetry Analysis (TGA) were performed on a Setaram Simultaneous TG/DTA instrument under air flows with a heating rate of 5 °C/min from room temperature to 800 °C.

2.4. Toluene adsorption and desorption tests

The adsorption of toluene was evaluated by measuring the breakthrough curve at 25 °C in a fixed-bed quartz tube (7.0 mm i.d., 44.0 cm long) with a home-made apparatus (Scheme 1). As shown in Scheme 1, the total flow rate F₃ = F₁ + F₂ = 100 ml/min. The flow rates of F₁ and F₂ were regulated by the two mass flow controllers (2). The toluene vapor concentration in F₃ was adjusted by F₁/F₂ ratio. When fixing the F₁/F₂ flow rates, the toluene concentration was obtained by weighing and calculating the mass loss of toluene bubbler after flowing for 24 h,



Scheme 1. the construction device for breakthrough curve measurement. (1) N₂ gas cylinder; (2) mass flow controller; (3) toluene bubbler; (4) icewater bath; (5) globe valve; (6) tube with adsorbent; (7) gas chromatography.

Download English Version:

<https://daneshyari.com/en/article/8045648>

Download Persian Version:

<https://daneshyari.com/article/8045648>

[Daneshyari.com](https://daneshyari.com)