Applied Clay Science 95 (2014) 60–66

Contents lists available at ScienceDirect

Applied Clay Science

journal homepage: www.elsevier.com/locate/clay

Research paper

# Synthesis of clay/carbon adsorbent through hydrothermal carbonization of cellulose on palygorskite

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ARTICLE INFO

*Article history:*
Received 26 February 2013
Received in revised form 6 August 2013
Accepted 19 March 2014
Available online 21 April 2014

*Keywords:*
Clay/carbon
Adsorbent
Palygorskite
Cellulose

ABSTRACT

Organophilic palygorskite/carbon composites were prepared through a green hydrothermal carbonization process using palygorskite clay and cheap cellulose as raw materials. The effects of reaction temperature (210 °C to 250 °C) and time (2 h to 48 h) on the product structures were investigated, and a potential reaction mechanism was proposed. Nanocarbon particles (10 nm in diameter) were loaded onto the palygorskite surface (220–250 °C, 12 h or 210 °C, 24–48 h). Results from the Fourier transform infrared and X-ray photoelectron spectroscopy showed that the resultant palygorskite/carbon composites contained organic groups, including $-CH-$, $CH_2-$, $CH{=}CH$ and $C{=}O$. The coating mechanisms of palygorskite and nanocarbon were also discussed. The contribution of organic carbon to organophilic improvement was further confirmed by the static adsorption of phenol. The removal rate of phenol from aqueous solution increased with hydrothermal time and temperature, indicating that the loading of nanocarbon particles with organic groups made an important contribution for the organic modification of palygorskite. The palygorskite/carbon obtained at 250 °C in 48 h exhibited the highest adsorption (92 wt.%) of phenol, which was slightly higher than that of commercial active carbon (90 wt.%) and significantly higher than that of unmodified palygorskite (18 wt.%).

## 1. Introduction

Carbon materials are widely used in several applications as catalyst support, gas storage, electrode, absorbent, fuel battery, etc. (Kubo et al., 2010). Thus, the preparation of carbonaceous materials has received increasing attention especially materials from low-cost biomass through a hydrothermal carbonization process (Cui et al., 2006; Falco et al., 2011, 2012; Hu et al., 2008; Qian et al., 2006; Sevilla and Fuertes, 2009a, 2009b; Shin et al., 2008; Sun and Li, 2005a, 2005b; Wang et al., 2001, 2005; Xiao et al., 2012; Yu et al., 2012; Zheng et al., 2010). The morphology and size of the prepared carbon can be easily controlled by varying the hydrothermal conditions, including temperature, template, and carbon source. More importantly, some organic groups, such as $-CH_2$ and $-CH_3$, co-exist with the carbon materials obtained from hydrothermal carbonization, indicating that the resultant carbon does not require further organic modification for use in the organic field. Glucose, saccharides, and starch are frequently used as carbon sources in the preparation of nanocarbons and microcarbons with organic groups. Additionally, some nanosized templates, such as silver nanoparticles, copper nanofibers, and tellurium nanofibers, have been introduced into hydrothermal carbonization to guide the growth of carbon (Luo et al., 2006; Qian et al., 2006; Sun and Li, 2005a, 2005b; Wang et al., 2001, 2005).

In our previous study we reported the coating of nanocarbon with palygorskite from glucose using palygorskite as a hard template at a mild hydrothermal temperature (Wu et al., 2011). Palygorskite is a hydrated magnesium aluminum silicate naturally present as a nanofibrous clay mineral with 30 nm to 50 nm diameter as described in our previous paper. The structure of palygorskite can be described as $[(Mg_{5-y-z}Ry^{3+}{}_{\triangle z})\,(Si_{8-x}R_x^{3+})\,O_{20}(OH)_2(OH_2)_4 \cdot E^{2+}{}_{(x-y+2z)}/2(H_2O)_4]$, where $R^{3+}$ represents $Al^{3+}$ and $Fe^{3+}$, $\triangle$ is the octahedral vacancy, and $E^{2+}$ is an exchangeable cation (Bradley, 1940). The natural nanofibrous structure of palygorskite is a good candidate source of templates used to induce carbon growth during the hydrothermal processes (Qian et al., 2006; Shi et al., 2009; Wu et al., 2008). In addition, palygorskite is an excellent alternative sorbent material because of its large surface area and ion-exchange ability. However, the removal efficiency of organic contaminants from palygorskite is very low because of the water-filled channel in palygorskite (Sanchez-Martin et al., 2008; Ye et al., 2006). Therefore, we presented a novel organic modification of palygorskite by depositing nanocarbons onto the palygorskite surface through the hydrothermal carbonization of glucose using palygorskite as a hard template (Wu et al., 2011). Nanocarbons with organic groups were loaded onto the palygorskite surface when a suspension of palygorskite and glucose was hydrothermally treated from 160 °C to 200 °C. Hence, palygorskite may have an important role as a template

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http://dx.doi.org/10.1016/j.clay.2014.03.010
0169-1317/

for nanocarbon growth. The obtained modified palygorskite showed a significant increase in the adsorption of phenol contaminant. Compared with the normal organic modification of palygorskite, such as octodecyl trimethyl ammonium chloride modification, the hydrothermal deposition of carbon is more environmentally friendly.

In the present study, another palygorskite/carbon composite was prepared by hydrothermal carbonization using cellulose as a carbon source. Among all saccharides, cellulose is the carbon source with the highest potential because it is the cheapest and most abundant of all natural renewable biomass (Bartosz et al., 2010; Sevilla and Fuertes, 2010). After carbonization, cellulose dehydrates and decomposes into shell-core structured carbon (Sevilla and Fuertes, 2010; Wang et al., 2001). Moreover, synthesized templates are often used as hard templates in hydrothermal carbonization processes, whereas natural mineral templates are rarely used.

## 2. Experimental

### 2.1. Starting materials

Natural palygorskite acquired from Jiashan, China was sieved through a 200 mesh (75 μm). The chemical composition and texture properties were determined by chemical analysis and X-ray diffraction. The chemical composition of the clay was 65.52% $SiO_2$, 5.36% $Al_2O_3$, 13.93% MgO, 3.19% $Fe_2O_3$, 0.42% FeO, and 11.58% others. The specific area was 229 $m^2/g$, the pore volume was 0.41 $cm^3/g$, and the maximum pore diameter was 2.8 nm. Analytical-grade reagents, including cellulose, phenol, and ammonium iron sulfate hexahydrate [$FeSO_4(NH_4)_2SO_4\cdot 6H_2O$], were bought from Shanghai Chemical Reagent Factory and used as received without further purification. Active carbon was obtained from the Institute of Coal Chemistry, Chinese Academy of Sciences. The Brunauer–—mmett–—eller (BET) surface area was 927 $m^2/g$.

### 2.2. Preparation of palygorskite/carbon

In a typical procedure, cellulose (5.0 g) and $FeSO_4$ $(NH_4)_2SO_4\cdot 6H_2O$ (2.97 g) were mixed in 72 mL distilled water. Palygorskite (2.5 g) was then introduced, followed by stirring for 2 h at room temperature. The final mixture was transferred to a Teflon-lined stainless steel autoclave (100 mL in total inner volume), sealed and then maintained at 210 °C for 12 h. The obtained black product was centrifuged at 8000 rev/min, washed thrice with double-distilled water and ethanol, and then dried in an oven at 60 °C for 5 h.

### 2.3. Characterization methods

Scanning electron microscopy (SEM) images were obtained with a JEOL JSM-6700 field-emission scanning electron microscope. Fourier-transform infrared (FTIR) absorption spectra of the material powders were obtained using a Nexus 470 FTIR spectrophotometer. Elemental analysis was conducted on a Germany Vario EL cube. The pH value of the solution was measured using a China PHS-25 detector. UV analysis was conducted using UV-401PC. X-ray photoelectron spectroscopy (XPS) was performed with an ESCALAB250 spectrometer using Mg $K_\alpha$ (1253.6 eV) radiation from a double anode at 50 W.

### 2.4. Adsorption properties

Adsorption experiments were conducted in batch equilibrium mode. Approximately 0.25 g of adsorbent was added into a 250 mL conical flask filled with 25 mL of 5 mg/L phenol solution. Adsorption experiments were conducted in a water bath with a mechanical shaker. The conical flasks were kept in the water bath at 25 °C with a shaking frequency of 200 rev/min for 12 h to achieve equilibrium. The aqueous phase was separated by centrifugation at 12,000 rev/min for 10 min. The phenol concentration analysis of the filtrate solution was measured with a spectrophotometer (722E, Shanghai Spectrum Co., Ltd., PR China) at a wavelength of 510 nm. The percentage of phenol removal was calculated.

## 3. Results and discussion

### 3.1. Effect of reaction time and coating mechanism of palygorskite and carbon

The changes in element and pH with reaction time were shown in Table 1. The carbon and hydrogen contents in unmodified palygorskite were 1.48 wt.% and 2.61 wt.%, respectively. The trace amounts of carbon and hydrogen may be from organics, water and carbonates in palygorskite clay. Once the hydrothermal reaction of cellulose occurred (2 h), the pH decreased, the contents of carbon and hydrogen increased and the C/H atomic ratio obviously changed. The pH decreased with reaction time, suggesting that the increased release of organic acid into the liquid phase was produced by cellulose decomposition. As hydrothermal carbonization continued, the carbon content of the solid residue increased from 29.97 wt.% to 32.92 wt.%, and the hydrogen content decreased from 5.44 wt.% to 3.38 wt.%. In addition, an increase in C/H atomic ratio with reaction time suggests an increase in the condensation degree of the hydrochar products (Sevilla and Fuertes, 2010; Wang et al., 2001). Certainly, the weight loss of hygroscopic and zeolitic water may also make some low contribution to the increase of C/H atomic ratio (Liu et al., 2013; Wu et al., 2013). Compared with previously reported hydrothermal carbonization of cellulose, the carbon content was lower in our study because of the presence of palygorskite in the solid residue.

SEM images of the products at different times were shown in Fig. 1. Nearly no carbon particles appeared when the reaction time was less than 8 h. When the reaction time increased (24 h, 48 h), carbon nanoparticles with 10 nm diameter were gradually loaded onto the palygorskite surface. The size of the loaded carbon was significantly smaller than that of the carbon microspheres (diameter: 2 μm to 10 μm) formed from the hydrothermal carbonization of cellulose (Sevilla and Fuertes, 2009a, 2009b). This result implies that palygorskite has an important role as a hard template (Wu et al., 2011). The SEM image of the product after 12 h of hydrothermal carbonization was shown in Fig. 1c. The unclear SEM image for carbonization at 12 h may be attributed to the interference of unstable organics produced during hydrothermal carbonization. Thus, time (12 h) was a critical point during the transformation process. Carbon nanoparticles rather than carbon microspheres were produced after more than 12 h of reaction time, suggesting a remarkable difference between the hydrothermal carbonization of cellulose and glucose. The deposition of nanocarbon from cellulose onto palygorskite will be discussed in detail in the following sections.

Chemical transformation during hydrothermal carbonization was investigated by FTIR, UV, and XPS. Fig. 2 showed the FTIR structures of the products. During reaction time from 2 h to 12 h, the FTIR of the obtained solid residue revealed a collective characteristic of palygorskite (Bradley, 1940; Hisato and Ryohei, 1969) and cellulose. The peaks at 3613, 3550, and 3350 $cm^{-1}$ can be attributed to the −OH stretching vibration, including the Al−Al−OH stretching vibration at 3613 $cm^{-1}$

**Table 1**
pH and elemental changes with reaction time.

| Time (h) | Temperature (°C) | pH | C (wt.%) | H (wt.%) | C/H (at.%) |
|---|---|---|---|---|---|
| 0 | 210 | 5.2 | 1.48 | 2.61 | 0.57 |
| 2 | | 4.0 | 29.97 | 5.44 | 0.46 |
| 4 | | 3.8 | 28.72 | 4.74 | 0.50 |
| 8 | | 2.8 | 28.85 | 4.57 | 0.53 |
| 12 | | 2.9 | 29.81 | 4.41 | 0.56 |
| 24 | | 2.7 | 31.25 | 3.76 | 0.69 |
| 48 | | 2.6 | 32.92 | 3.38 | 0.81 |