Applied Clay Science 74 (2013) 81–86

Contents lists available at SciVerse ScienceDirect

Applied Clay Science

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

Chitosan-modified palygorskite: Preparation, characterization and reactive dye removal

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ARTICLE INFO

Article history:
Received 21 January 2012
Received in revised form 6 July 2012
Accepted 8 October 2012
Available online 7 November 2012

Keywords:
Palygorskite
Chitosan
Surface grafting
Adsorption
Reactive dye
Composite

ABSTRACT

Chitosan-modified palygorskite (CTS-modified PA) was prepared by surface grafting of PA with chitosan, and the CTS-modified PA was used as an effective adsorbent for the removal of reactive dye. The effects of various experimental parameters such as initial pH, adsorbent dosage, contact time and initial dye concentration on adsorption were investigated. The adsorption behavior of CTS-modified PA showed that the adsorption kinetics and isotherms were in good agreement with the pseudo-second-order equation and the Langmuir equation, and the maximum adsorption capacity of CTS-modified PA calculated by the Langmuir model was 71.38 mg g^{-1}, which was much higher than that of the unmodified PA (6.3 mg g^{-1}).

1. Introduction

Wastewater discharged from dyeing and finishing in textile industry contains various dyes, some of which are mutagenic and carcinogenic to human beings (Chatterjee et al., 2010). Therefore, the removal of dyes from waste effluents before discharging into natural water bodies becomes environmentally important. In general, dye effluents are treated by adsorption (Rocher et al., 2008), membrane separation (Ciardelli et al., 2001), coagulation–flocculation (Panswad and Wongchaisuwan, 1986), biological degradation (Gopinath et al., 2009) and chemical oxidation (Khadhraoui et al., 2009), etc. Among these, adsorption has been found to be one of the most popular treatment methods for removing dyes from waste effluents (Garg et al., 2003; Monvisade and Siriphannon, 2009).

Palygorskite (PA) is a hydrated magnesium aluminum silicate with fibrous morphology, large specific surface area and moderate cationic exchange capacity (Kong et al., 2009, 2011a,b). Large reserves of PA are known in China, and therefore PA is widely considered in China as an alternative low-cost adsorbent owning to its abundant resource. Also, surface-modified PA is reported to show a higher adsorption capacity than the raw clay (e.g. Lei and Wen, 2008; Liu and Wang, 2007; Zhao et al., 2009).

Chitosan (CTS) is a linear biopolymer of glucosamine, and exhibits high adsorption capacity towards many contaminations since the amino ($-NH_2$) and hydroxyl (–OH) groups on CTS chains can serve as electrostatic interaction and coordination sites, respectively (Crini, 2006). So it is widely used for the removal of heavy metals and dyes.

Clay-based minerals play an increasing active role in catalysis, environment, biology and nanotechnology (Zhou, 2010). In practice, there have been numerous studies on clay-organic complexes (Lagaly, 1984, 1986; Yariv and Cross, 2002; Zhou, 2011), leading to developments with significant industrial importance. Recently, the CTS/clay composites have attracted attention because of their low production cost and outstanding physico-chemical properties. CTS-coated montmorillonite can be an efficient adsorbent for tungsten removal from contaminated sites, reducing the tungsten concentration in product water to below 1 μg/L (Gecol et al., 2005). CTS/zeolite composites have comparable capacity to other anion exchangers with a nitrate ion exchange capacity of 0.74 mmol NO_3^-/g (Meenakshi et al., 2010). CTS/bentonite has been used in removing Pb (II), Cu (II) and Ni (II) from aqueous solution under static conditions, which established inexpensive large-scale barrier filters for the removal of heavy metals contaminations in wastewater (Futalan et al., 2011). However, there are few reports on CTS-modified PA as an adsorbent (Wang et al., 2009). Considering the fact that PA is an abundant resource in China and the price is around one tenth that of CTS, there may be an economic advantage in developing a CTS–PA composite for the removal of heavy metals and dyes, in place of using pure CTS.

The purpose of the present study was to prepare CTS-modified PA as an effective adsorbent for the removal of reactive dye. Surface

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http://dx.doi.org/10.1016/j.clay.2012.10.002

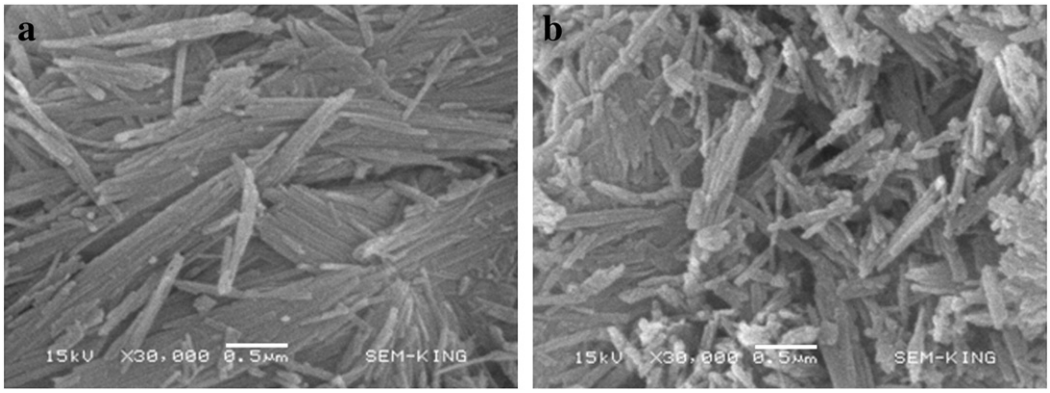

Fig. 1. SEM images of PA (a) and CTS-modified PA (b).

grafting was carried out for the modification of PA by CTS. Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and nitrogen adsorption tests were used to characterize CTS-modified PA. The adsorption behavior for an anionic reactive dye, namely reactive yellow 3RS was studied. The effects of various experimental conditions such as pH, adsorbent dosage, contact time and initial dye concentration on adsorption were investigated.

2. Experimental

2.1. Materials

The acid-activated PA was supplied by Jiangsu Maige Sorbent Co. Ltd. with an average diameter of 200 mesh. 3-Aminopropyl triethoxysilane (KH-550) was provided by Najing Shuguang Chemical Group Co. Ltd. Reactive yellow 3RS was supplied by Zhangjiagang Jinling Textile Co. Ltd. Chitosan (CTS, >90% deacetylation) was purchased from Nantong Xincheng Biology Co. Ltd. Glutaraldehyde, toluene, sodium borohydride, sodium carbonate and acetic acid were purchased from Sinapharm Chemical Reagent Co. Ltd. and were of analytical reagent grade. Distilled water was used in all experiments.

2.2. Preparation of the CTS-modified PA

The coupling reagent KH-550 was firstly used to introduce aminopropyl groups onto the PA surface. The process was as follows: 5.0 g PA (dried at 105 °C) was dispersed in 50 mL toluene, and 10 mL KH-550 was then added and dissolved with the help of stirring for 30 min in a 100 mL flask. The mixture was then refluxed with electromagnetic stirring at 60 °C for 2 h. Finally, the PA was separated by filtration and rinsed, first with toluene and ethanol, and then washed thoroughly with distilled water. The KH-550-modified PA was dried at room temperature in vacuum overnight.

2.5 g of dry KH-550-modified PA was soaked into glutaraldehyde (25 wt.%) for 4 h. 2.0 g of chitosan powder was dissolved in 100 mL acetic acid solution (1 wt.%) using a magnetic stirrer at room temperature. The two materials were mixed with magnetic stirring for 3 h at 30 °C. Then the reacted PA was isolated by centrifugation and added into sodium carbonate solution (1 M) for an hour to solidify and fix the coating. Lastly, the CTS-modified PA was soaked in 100 mL sodium borohydride solution (0.2 M) overnight at room temperature. Finally, the CTS-modified PA was isolated by centrifugation, washed with distilled water, and dried in vacuum.

2.3. Characterization of CTS-modified PA

Scanning electron microscopy (SEM, JSM-6360LA, Japan) was used for characterization of the surface morphology of PA and CTS-modified PA. The FTIR spectra of the samples were recorded on a KBr pellet using a Thermo Corporation Nexus FTIR spectrophotometer (USA). XRD analyses of the powered samples were performed using an X-ray diffractometer with Cu anode (PANalytical Co. X'pert PRO, Netherlands), running at 40 kV and 30 mA with a scan range from 5 to 80° at 3°/min. The specific surface area and pore size of the samples were measured using an Accelerated Surface Area and Porosimetry System (Micromeritics, ASAP 2010) by BET method at 76 K.

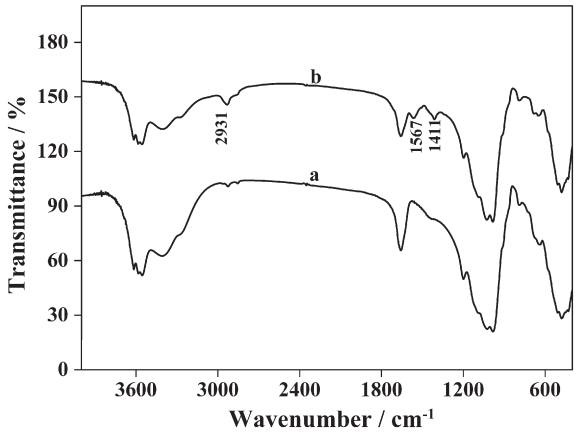

Fig. 2. FTIR spectra of PA (a) and CTS-modified PA (b).

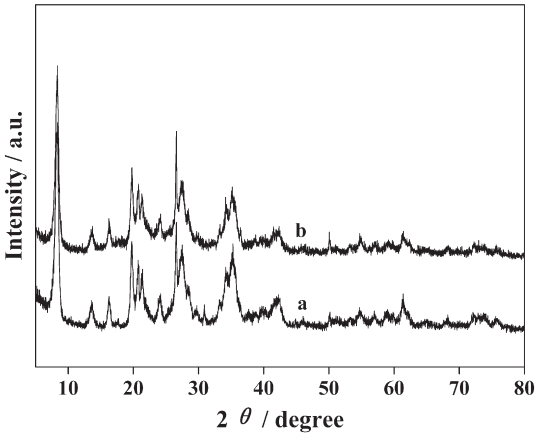

Fig. 3. XRD patterns of PA (a) and CTS-modified PA (b).