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Adsorptive removal of Congo red from aqueous solutions using crosslinked chitosan and crosslinked chitosan immobilized bentonite

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ABSTRACT

Batch experiments were executed to investigate the removal of Congo red (CR) from aqueous solutions using the crosslinked chitosan (CCS) and crosslinked chitosan immobilized bentonite (CCS/BT composite). The CCS and CCS/BT composite were characterized by X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) techniques. The removal of CR was examined as a function of pH value of CR solution, contact time, and inorganic sodium salt and ionic strength. The equilibrium data of CCS and CCS/BT composite agreed well with the Langmuir model. The adsorption capacities of CCS and CCS/BT composite at 298 K and natural pH value were 405 and 500 mg/g, respectively. The kinetic data correlated well with the pseudo-second-order model. The adsorption of CR onto the CCS was mainly controlled by chemisorption while the adsorption of CR onto the CCS/BT composite was controlled by chemisorption and the electrostatic attraction.

1. Introduction

The treatment and disposal of dye-contaminated wastewater is one of the most serious environmental problems faced by the textile, papermaking, printing, and related industries. Dyes are among the most hazardous materials found in industrial effluents, which needs to be treated, because its presence in water bodies prevents sunlight and oxygen penetration and then has a derogatory effect on photosynthetic activity in aquatic systems [1].

Various treatment processes including biological treatment [2,3], membrane filtration [4], photocatalytic degradation [5] and adsorption [6], have been developed to remove these compounds from colored effluents. Among these methods, adsorption is considered as one of the most competitive methods due to its low-cost, simplicity of operation, as well as the availability of a wide range of adsorbents [7,8]. In recent years, a considerable number of studies have focused on low-cost alternative materials including bentonite [1], agricultural wastes [9,10] and zeolites [11], for the removal of dyes by adsorption method.

Bentonite, which is mainly composed of montmorillonite, is a layered mineral with a crystalline structure and net negative surface charge. bentonite application in wasterwater treatment has received much attention in the past decades. However, bentonite in natural form often shows a low adsorption capacity for anionic dyes due to the net negative surface charge. Modification of bentonite through acid treatment, calcinations, functionalization, compositing with other material and pillaring is employed to enhance its adsorption capacity. Chitosan is a product of the partial *N*-deacetylation of chitin, which has several desirable properties like biodegradability, hydrophilicity, anti-bacterial property, and non-toxicity [12,13]. It contains amino ($-NH_2$) and hydroxyl ($-OH$) groups that can serve as adsorptive sites for heavy metals or dyes. However, chitosan has weak mechanical and chemical properties where it easily dissolves in dilute acids, and agglomerates to form a gel in aqueous solution [14,15]. In order to overcome these limitations, the physical and chemical modification needs to be carried out on chitosan. Chemical cross-linking is an effective method to improve its mechanical strength and its chemical stability in acidic media. However, these improvements were at the cost of the loss of amino ($-NH_2$) or hydroxyl ($-OH$) groups, which often resulted in the decreased adsorption capacity [16]. In this study, bentonite would be composited with cross-linked chitosan. Cross-linked chitosan was intercalated in bentonite, resulting in an increase in the layer spacing of bentonite. This increase would allow an easy access to its binding sites. Therefore, it was expected that the combination of chitosan with bentonite may create a more efficient adsorbent as compared with single crosslinked chtosan and bentonite. Congo red (CR) [-naphthalene sulfonic acid, 3,3′-(4,4′-biphenylenebis(azo))bis(4-amino-) disodium salt] (Fig. 1) was chosen as the model anionic dye in this study. CR is seriously haz-

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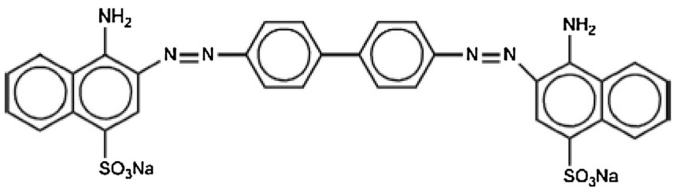

Fig. 1. Molecular structure of Congo red (CR).

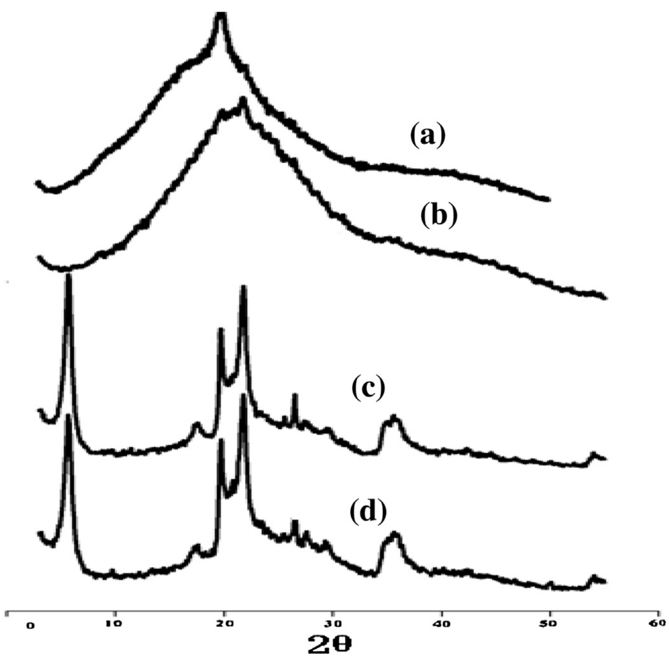

Fig. 2. XRD patterns of (a)CCS, (b) CR loaded CCS, (c) CCS/BT composite and (d) CR loaded CCS/BT composite.

ard to aquatic living organisms and can cause human carcinogen [16]. Removal of CR from aqueous solutions was investigated using crosslinked chitosan (CCS) and crosslinked chitosan immobilized bentonite composite (CCS/BT composite). Effects of pH value of CR solution, the presence of other anions, and contact time on the CR adsorption by CCS and CCS/BT composite were examined. The equilibrium data were analyzed using Langmuir and Freundlich isotherm models. The kinetic data were determined using the pseudo-first order and pseudo second order equations. Surface structural analysis of CCS and CCS/BT composite was done by XRD and FTIR techniques.

2. Materials and methods

2.1. Materials

Chitosan (CTS) was purchased from the Sinopharm Group Chemical Reagent Limited Company (China). Bentonite powder with a particle size of 200-mesh was acquired from the chemical factory of Shentai, Xinyang, Henan, China. Congo red (CR) was supplied by Sigma chemical company, and used as adsorbate in this study. Congo red concentrations were measured at 497 nm using a UV–vis spectrometer (754N) which was provided by Shanghai Precision & Scientific Instrument Co., Ltd. (China). All other reagents were of analytical grade. pH value of CR solutions was adjusted by adding 0.1 M HCl or NaOH solutions.

2.2. Preparation of crosslinked chitosan (CCS)

The crosslinked chitosan particles were prepared by dissolving 2.000 g of chitosan in 100.0 mL of 2% (v/v) acetic acid and were continuously stirred for 30 min. 25 wt% glutaraldehyde (GLA) solution was dropped slowly into the viscous solution of chitosan and the ratio of GLA to chitosan was approximately 5 mL/g of chitosan. Cross-linking reaction occurred for 22 h at 60 °C and then the crosslinked chitosan was washed with distilled water to remove any free GLA and dried in an oven at 60 °C for 24 h. After drying, the dry crosslinked chitosan was ground to obtain 100-mesh size particles, which were used for adsorption studies.

2.3. Preparation of crosslinked chitosan immobilized bentonite composite (CCS/BT composite)

This composite was prepared by adding 2.000 g of chitosan to 5.000 g of bentonite dispersed in 100 mL of 2% (v/v) acetic acid, and the solution was continuously stirred for 2 h. 25 wt% GLA solution was dropped slowly into the viscous chitosan–bentonite solution. The following operations were similar to the preparation of CCS.

2.4. Adsorption studies

For studying the effect of pH value on CR adsorption by CCS and CCS/BT composite, 40 mg of the power samples (CCS and CCS/BT composite) were added in 50 mL 200 mg/L CR solution. The samples were agitated on a thermostated shaker for 100 min at 298 K.

Adsorption kinetics experiments at different concentrations (100, 200, 300 and 500 mg/L) were performed by the batch method, where approximately 40 mg of power samples (CCS and CCS/BT composite) were added in 50 mL CR solution. The samples were agitated for times varying from 5 to 400 min. At the end of the each adsorption period, the samples were collected by filtration, and the concentrations of the residual CR in the filtrates were then determined. The removal toward CR, R, and the adsorption capacity, q_e (mg/g), at equilibrium, were calculated as follows:

$$R = \frac{(C_0 - C_e)}{C_0} \times 100 \tag{1}$$

$$q_e = \frac{(C_0 - C_e) \times V}{M} \tag{2}$$

where C_0 and C_e are the concentrations of CR in the initial solution and at equilibrium, respectively; V is the volume of CR aqueous solution (L) and M is the mass of adsorbent (g).

Adsorption equilibrium isotherm experiments at different temperatures (298, 308, 318 and 328 K) were carried out by varying the concentrations of CR solution from 100 to 800 mg/L. 40 mg of power samples (CCS and CCS/BT composite) was added in 50 mL CR solution. The samples were agitated for 360 min. After equilibrium, the samples were separated by filtration, and the final concentrations of CR in the filtrates were analyzed similarly.

2.5. Characterization of the CCS and CCS/BT composite

The X-ray diffraction (XRD) patterns were obtained using a Shimadzu XD3A diffractometer equipped with a monochromatic Cu Kα source operating at 40 kV and 30 mA. The diffraction patterns were recorded from 5° to 50° with a scan rate of 0.02°/s. The FTIR spectra of samples dispersed in KBr disks were recorded at room temperature using a FTIR spectrometer (Shimadzu 4100) over a range of 4000–400 cm^{-1}. The pH value at zero point charge (pHzpc) of the adsorbent was determined by the solid addition method [17]. Initial pH of 0.1 mol/L NaCl solutions (pH_i) was adjusted from pH 2 to 11 by adding either 0.1 mol/L HCl or 0.1 mol/L NaOH. Adsorbent dose (40 mg) was added to 50 mL of 0.1 mol/L NaCl solution