Industrial Crops and Products 42 (2013) 153–158

Contents lists available at SciVerse ScienceDirect

Industrial Crops and Products

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

Adsorption of C.I. Reactive Red 228 dye from aqueous solution by modified cellulose from flax shive: Kinetics, equilibrium, and thermodynamics

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ARTICLE INFO

Article history:
Received 21 April 2012
Received in revised form 18 May 2012
Accepted 24 May 2012

Keywords:
Anionic dye
Isotherms
Kinetics
Modified flax shive cellulose
Thermodynamics

ABSTRACT

Cellulose from flax shive was modified with quaternary ammonium groups to facilitate removal of C.I. Reactive Red 228 (RR228) dye from aqueous media. The adsorption of RR228 was investigated at various temperatures, adsorbent doses, initial dye concentrations and pH values. Two kinetic models were used to describe the adsorption process. Two isotherm models were applied to evaluate the adsorption equilibrium, and its thermodynamic parameters were calculated. The maximum capacity of the modified flax shive cellulose for adsorption of RR228 was 190 mg g^{-1} at pH 3 under dose of 0.4 g L^{-1} and initial concentration of 80 mg L^{-1}. The adsorption process and equilibrium of RR228 were well fitted by a pseudo-second-order kinetic model and Langmuir model, respectively. Thermodynamic evaluation indicated that the adsorption is exothermic, spontaneous, and favorable.

1. Introduction

Large quantities of dye waste water are produced by textile dyeing and the dye manufacturing industries. According to incomplete statistics, there are more than 10 000 types of dyes in commercial circulation (Altınışık et al., 2010; Senturk et al., 2010). About 7×10^5 tons of dyes are manufactured worldwide each year, and 10–15% are discharged into water bodies as effluents that seriously pollute the environment and affect aquatic organisms (Thangamani et al., 2011; Moussavi and Khosravi, 2011). Moreover, they may also harm human health because most dyes are toxic (Sun et al., 2007). The conventional treatment methods for dye effluents, such as oxidation (Arslan et al., 2000; Thangamani et al., 2011), coagulation (Panswed and Wongchaisuwan, 1986; Szyguła et al., 2009; Verma et al., 2012), flocculation (Wang et al., 2012), photochemical destruction (Deng et al., 1997), ion exchange, and membrane filtration (Ciardelli et al., 2000), are complicated and costly, in particular as some methods require additional chemicals or produce toxic products. Therefore, these methods are unfit for treating waste water. In fact, the adsorption method is the best alternative and has been widely used for removal of pollutants from effluents. Activated carbon is an effective adsorbent. However, its high cost and difficulty of regeneration restrict its utilization. Recently, many studies have been conducted to investigate the adsorption capabilities of some low-cost bio-adsorbents such as *Loofa egyptiaca* (El Ashtoukhy, 2009), pine needle (Deniz and Karaman, 2011), orange peel (Vieira et al., 2009), sawdust (Hameed and El-Khaiary, 2008), sugarcane bagasse (Orlando et al., 2003), peanut hull (Gong et al., 2005), apple pomace (Robinson et al., 2002), and coconut husk (Manju et al., 1998). These bio-adsorbents were found to have greater affinity for cationic dyes than anionic dyes. Reactive dyes are anionic dyes that can form covalent bonds with fibers and display improved fastness. They are widely applied in dyeing cotton, flax, wool, and silk textiles. During the dyeing process, a small proportion of the reactive dye may be hydrolyzed and lose its binding property and, therefore, flow into waste water.

Flax shive (FS) is the main by-product of fiber separation by retting. FS is a natural material consisting of cellulose and lignin. About 2.5 tons of shives are produced for each ton of fiber separated. In North America, the amount of FS produced annually can be estimated at 2.1 million tons, whereas in China the amount is about 1.0 million tons. FS is usually burned for thermal energy or used as animal bedding or in the manufacture of particle-board. In recent years, it has been used as a culture material for edible mushrooms. Cox et al. (1999, 2000) and El-shafey et al. (2002) studied the carbonaceous material derived from FS treated with sulfuric acid. Feng et al. (2010) separated cellulose from FS and synthesized a super water adsorbent. In our laboratory, the adsorption capacity of two reactive dyes on FS particles was determined to be about 0.5 mg g^{-1}. Chitosan modification improved the adsorption capacity of FS to about 9 mg g^{-1}. In order to make good use of FS as an adsorbent, further chemical conversion is necessary (Feng et al., 2012).

In the present work, we focused our attention on using FS as a starting material for the preparation of cationic cellulose

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http://dx.doi.org/10.1016/j.indcrop.2012.05.031

made by adding quaternary ammonium groups to facilitate the removal of anionic dyes. Specifically, the removal of C.I. Reactive Red 228 (RR228) dye was carried out using this modified cellulose in aqueous solution. X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FT-IR) spectroscopy, and scanning electron microscopy (SEM) were used to characterize the adsorbent before and after adsorption. The equilibrium, kinetic, and thermodynamic data of the adsorption process were analyzed to elucidate the mechanism of adsorption of RR228 molecules onto the modified cellulose.

2. Materials and methods

2.1. Material and chemicals

FS was collected following the process for retting flax stems from the Keshan Flax Fiber Plant, Heilongjiang, China. The FS was washed with tap water four times to remove dust and other impurities and then air-dried. RR228 was kindly offered by Ciba Company. Epichlorohydrin and triethylamine were purchased from Kemiou Chemical Reagent Co. Ltd. (Tianjin, China). All other chemicals and reagents used in this work were of analytical grade.

2.2. Preparation of the dye solution

Reactive red dye (C.I. Reactive Red 228, λ_{max} = 510 nm) was used in this study. An accurately weighed quantity of the dye was dissolved in distilled water to prepare a stock solution (100 mg L^{-1}). Experimental solutions of various concentrations were obtained by further dilution. Standard curves were developed via absorbance measurements of the dye solutions by UV–visible spectrophotometer (TU-1900).

2.3. Preparation of cationic flax shive cellulose (CFSC)

The cellulose was first separated from FS using a cooking method, as described previously (Feng et al., 2010). The cellulose was dried at 102 °C and then milled into particles with a size of 80–120 mesh prior to the synthesis reaction. 10 g of the cellulose particles were treated with 250 mL 20% (w/w) NaOH solution for 2 h at ambient temperature to obtain sodium cellulose. After partially removing the solution, 80 mL of pure epichlorohydrin were added to the system. The mixture was stirred for 6 h at 65 °C to form epoxypropyl-cellulose and then filtered to remove the solution. 110 mL of 34% triethylamine solution was added to the particles and the mixture was stirred for 3 h at 80 °C. The CFSC product was collected and washed with pure ethanol to remove the excess triethylamine, followed by 0.1 mol L^{-1} NaOH solution, 0.1 mol L^{-1} HCl solution, and a large volume of distilled water. The final product was dried at 60 °C.

2.4. CFSC characterization

The nitrogen content (N%) of CFSC was determined using a K-Alpha XPS Analyzer (ThermoFisher Scientific Company). The nitrogen sorption isotherms were measured by the volumetric method on an automatic adsorption instrument (ASAP2020, USA) at liquid nitrogen temperature (77.2 K). The specific surface area was calculated by the Nrumauer–Emmett–Teller (BET) method from the data within a P/P_0 range of 0.06–0.2. The point of zero charge (pH_{PZC}) was determined by the solid addition method (Vieira et al., 2009). To a series of 100-mL conical flasks, 10.0-mL aliquots of NaCl solution were transferred with pH values ranging from 2 to 11. Then, CFSC (0.05 g) was added to each flask, which was securely capped immediately and shaken for 10 h. The differences between the final and initial pH values (ΔpH) were plotted against the initial pH, and the point of intersection on the *X*-axis corresponds to the point of zero charge (pH_{PZC}). The chemical structure of CFSC was characterized by FT-IR using a Nicolet 560 instrument (Nicolet Co., Ltd., USA), after samples were prepared by the KBr tablet method. The surface morphologies of FSC and CFSC were observed using a Quanta 200 SEM. Specimens were observed after spraying with gold.

2.5. Sorption of the dye

Adsorption experiments were conducted in batch mode to evaluate the effects of various parameters, such as initial dye concentration, pH and contact time, on the adsorption of RR228. In each adsorption experiment, 100 mL of dye solution were added to the required amount of adsorbent in a 250-mL conical flask at ambient temperature, and the mixture was shaken at 190 rpm.

The sample was withdrawn from the shaker at the end of the adsorption period, and the adsorbent was separated from the solution by a nylon screen with a pore size of 400 mesh. The absorbance of the residual solution was measured to enable calculation of the dye concentration.

The equilibrium amount of adsorbed dye per unit mass, q_e (mg g^{-1}), and the amount of dye adsorbed on the adsorbent at time t, q_t (mg g^{-1}), were calculated using the following equations:

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

$$q_t = \frac{(C_0 - C_t)V}{W} \quad (2)$$

where C_0 and C_e (mg L^{-1}) are the initial and equilibrium concentrations of the dye solution, respectively. V is the volume of the dye solution (mL) and W is the amount of the adsorbent (g).

To examine the effect of pH on the adsorption of RR228 onto CFSC, the pH was adjusted from 2 to 10 by adding a few drops of NaOH or HCl solution.

2.6. Kinetics and isotherm studies

The kinetics of the adsorption was determined by analyzing the quantity of dye adsorbed from aqueous solution at different time intervals. The initial dye concentration in the test solution and the adsorbent dosage were varied to investigate their effects on the adsorption kinetics. Isotherms of the adsorption at various dosages were analyzed to determine the equilibrium adsorption capacity. Thermodynamic parameters were calculated from the equilibrium adsorption data at different temperatures.

3. Results and discussion

3.1. Characterization of CFSC

3.1.1. FT-IR analysis

The nitrogen content (N%) of CFSC is 1.98%. The FTIR spectra of FSC and CFSC are shown in Fig. 1(A). The FSC spectrum features peaks at around 1060 cm^{-1} and 899 cm^{-1}, which are attributed to a pyranoid ring and a β-D-glucoside bond in the cellulose, respectively. The broad peak at 3382 cm^{-1} is due to the vibration of an —OH group. The band at 1431 cm^{-1} is due to the stretching of C—O in a CH_2—OH group. The peak at 1898 cm^{-1} corresponds to C—H stretching of a —CH_2— group. After modification, the intensity of the peak corresponding to the —OH group decreased and it shifted to 3392 cm^{-1}; however, the intensity of the —CH_2— group increased significantly. Moreover, a new peak at 1457 cm^{-1} is attributed to C—N vibrations of —$N^+(C_2H_5)_3Cl^-$ (Cao et al., 2011). All of those