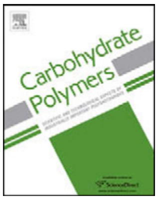
Carbohydrate Polymers 84 (2011) 1350–1356

Contents lists available at ScienceDirect

Carbohydrate Polymers

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



Removal of anionic dye eosin Y from aqueous solution using ethylenediamine modified chitosan

Xiao-Yi Huang[a], Jian-Ping Bin[b], Huai-Tian Bu[c], Gang-Biao Jiang[a,*], Ming-Hua Zeng[d,*]

[a] College of Natural Resources and Environment, South China Agricultural University, Guangzhou 510642, China
[b] Department of Cardiology, Nanfang Hospital, Southern Medical University, Guangzhou 510515, China
[c] SINTEF Materials and Chemistry, P.O. Box 124 Blindern, N-0314 Oslo, Norway
[d] The Key Laboratory for the Chemistry and Molecular Engineering of Medicinal Resources (Ministry of Education), School of Chemistry and Chemical Engineering of Guangxi Normal University, Guilin 541004, China

ARTICLE INFO

Article history:
Received 29 October 2010
Received in revised form 20 January 2011
Accepted 21 January 2011
Available online 28 January 2011

Keywords:
Chitosan
Adsorption
Sorbent
Eosin Y
Chitosan derivative
Effluent treatment

ABSTRACT

In this study, chitosan was cross-linked with ethylenediamine (EDA) to prepare an outstanding sorbent for the removal of anionic dye eosin Y from aqueous solution. FTIR, DTG, XPS and zeta potential analysis were used to characterize the sorbent. The effect of particle size, solution pH, agitation rate, temperature, adsorbent dosage (50–500 mg/L), contact time (10 min–24 h) and initial concentration of dye (50–300 mg/L) on the adsorption process was investigated. Langmuir and Freundlich adsorption models were applied to describe the isotherms and isotherm constants, and the data fitted well with Langmuir model with a maximum adsorption capacity of 294.12 mg/g at 25 °C. Kinetic studies followed the pseudo second-order rate model, which indicated that the chemisorption is the rate-limiting step. Thermodynamic parameters such as enthalpy change ($\Delta H^\circ = -5.004$ kJ/mol), free energy change ($\Delta G^\circ < 0$) and entropy change ($\Delta S^\circ = -11.656$ J/(mol K)) indicate the exothermic and spontaneous nature of adsorption.

1. Introduction

The biopolymer chitin and its derivative chitosan have gained importance in environmental biotechnology due to their very good adsorption capacity towards dyes and metal ions (Crini, 2006; Figueiredoa, Loureirob, & Boaventurab, 2005; Ngah, Ab Ghani, & Kamari, 2005). Chitin is widely found in the exoskeleton of crustaceous, the cuticles of insects and the cell walls of fungi (Crini, 2006). Commercial chitin product is now primarily extracted from the exoskeleton of crustaceans (crab, krill, crayfish), an abundant by-product of food processing (Crini, 2006). Chitosan is a natural cationic polymer obtained by deacetylation of chitin. It is more efficient than chitin in terms of adsorption capacity due to the presence of a large number of free amino ($-NH_2$) groups that can serve as the coordination and reaction sites. However, chitosan is soluble in most dilute acids, limiting its utilization of adsorbent for acidic effluents. Therefore, various physical and chemical modifications have been developed to improve the chemical stability of chitosan in acid media as well as its resistance to biochemical and microbiological degradation (Ngah et al., 2005). Chemically modified sorbent not only posses better adsorption, but also has higher stability in strong acids. Meanwhile, the mechanical strength of chitosan is also improved after modification. Some of the chemical modifications like cross-linking, grafting of a new functional group and acetylation have been applied (Chiou & Li, 2003; Kyzas & Lazaridis, 2009).

The method of amination to prepare adsorbent with high adsorption capacity for anionic dye or reactive dye has been reported using rice hull as the raw material by Ong, Lee, and Zainal (2007). They found that, compared to pure rice hull, the ethylenediamine (EDA) modified rice hull had exceptional higher affinity for reactive dye through electrostatic attraction. In the present study, chemically modified chitosan was prepared by EDA grafting, which was predicted to have higher adsorption capacity towards anionic dyes (acid dyes) by introducing more amino groups. What's more, this product showed satisfactory chemical stability in acid medium, which was confirmed by the fact that it was not dissolved at all in the hydrochloride acid solution with the pH ranging from 2 to 7, while chitosan was completely dissolved in weak acid medium. Eosin Y was chosen as the model anionic dye to evaluate the adsorption capacity of EDA modified chitosan (EDA-CS).

---

* Corresponding author.
E-mail addresses: jgb3h@163.com (G.-B. Jiang), zmh@mailbox.gxnu.edu.cn (M.-H. Zeng).

0144-8617/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2011.01.033

2. Materials and methods

2.1. Materials

Chitosan was obtained from Sanland chemical Co, LTD (Los Angeles CA, USA), the average molecule weight was 45 kDa, and the degree of deacetylation (DD) was above 95%. Eosin Y was an acid dye purchased from Hebaochem Co, LTD (Shanghai, China). Ethylenediamine (EDA), epichlorohydrin (ECH), and other reagents used in this experiment were of analytical grade and used without further treatment.

2.2. Preparation of ethylenediamine modified chitosan (EDA-CS)

The preparation of EDA-CS was carried out with the following steps.

Step 1: preparation of chitosan gel beadsChitosan beads were prepared by dropwise addition of chitosan solution (3%, w/v) in 2% (v/v) acetic acid solution to an alkaline precipitation bath (150 mL of 0.5 mol/L sodium hydroxide aqueous solution) as described by Ngah et al. (2005). The wet chitosan beads were collected and extensively rinsed with distilled water to remove residual NaOH, and stored in distilled water for further use.
Step 2: Reaction with epichlorohydrine (ECH)Chitosan functioned as the nucleophilic reagent to attack ECH, and the amino groups of chitosan was grafted by ECH. Briefly, the chitosan gel beads obtained in the above step was suspended in 300 mL of a mixture of water–ethanol (v/v = 1:1), and then 6 mL ECH was added to the suspension. The mixture was stirred at 60 °C for 16 h and then cooled. The solid product (ECH-CS) was filtered with a filter paper and then washed each three times with ethanol and water to remove the unreacted ECH.
Step 3: Preparation of EDA modified chitosan (EDA-CS)The product got in the preceding step was suspended in 300 mL ethanol/water mixture (1:1, v/v) and then treated with 5 mL EDA. The temperature was set at 60 °C. After stirring for 24 h, the product obtained was washed each three times with water followed by ethanol and air dried. The dry product was ground and sieved size to 100–200 μm, 200–300 μm and 450–900 μm respectively.

2.3. Characterization of EDA-CS

FT-IR spectra of pure chitosan, chitosan gel beads, ECH-CS, EDA-CS and dye loaded EDA-CS were recorded with an FTIR spectrometer (Thermo FTIR-6700, Nicolet Instrument Co., USA) in the range of 4000–400 cm^{-1} using KBr pellets containing the prepared materials.

Differential Thermal Analysis (DTA) and Thermal Gravimetric Analysis (TGA) of chitosan, ECH-CS and EDA-CS were performed with a thermal analyzer (DTG-60, Shimadzu. Japan) at a heating rate of 15 °C/min from 50 °C to 600 °C under a nitrogen flow rate of 20.0 mL/min.

X-ray photoelectron spectroscopy (XPS) was recorded on a Thermo ESCALAB 250 X-ray photoelectron spectroscope using AlKα radiation (1486.6 eV, 15 kV, 150 W). To exclude any effects on the values of binding energies due to charging of the sample during the XPS analysis, all data were corrected by a linear shift such that the peak maximum of the C1s binding energy of adventitious carbon corresponded to 284.8 eV. In order to extract the surface core-level shifts and relative intensities of these components, a curve-fitting procedure was utilized. The fitting of the core-level data was performed using a nonlinear fitting procedure (Software XPSPEAK 41).

To estimate the effect of EDA on the surface charge of chitosan, a certain amount of chitosan and EDA-CS were dispersed in deionized water previously and the zeta potential values of chitosan and EDA modified chitosan were determined using Zetasizer Nano-JS94H (Shanghai Zhongchen Digital Technique Equipment Co, Shanghai, China). Triplicate measurements were carried out and the mean value was presented.

2.4. Adsorption experiments

Stock solution of eosin Y (1 g/L) was prepared in deionized water. The experimental solutions with desired eosin Y concentration were obtained by successive dilution of this stock solution with deionized water. Calibration curve of eosin Y was prepared by measuring absorbance of samples with predetermined concentrations at 516 nm (corresponding to a maximum absorbency of eosin Y) using UV–vis spectrophotometer (UV-2300, Tian Mei CO. LTD. China).

For the adsorption experiment, a known amount of sorbent and a measured volume of eosin Y solution were placed in 50 mL closed plastic bottles resistant to acid or base. The system remained under agitation in a thermostatic bath. Parameters like pH, temperature, agitation rate, adsorbent dosage and particle size, contact time and initial dye concentration were set according to the relevant adsorption studies. Duplicate measurements were carried out for each study, and the mean values are presented, the error obtained was ±2%. The adsorbent was finally separated from the solution by filtration and small amount of dye remaining in the filter is omitted. Concentration of dye in supernatant was analyzed from the linear regression equation of the calibration curve. The removal efficiency (R, %) and the amount of eosin Y adsorbed (q, mg/g) were calculated using the following equations, respectively.

$$R = \frac{100(C_i - C_f)}{C_i} \tag{1}$$

$$q = \frac{(C_i - C_f) \times V}{1000 \times W} \tag{2}$$

where C_i and C_f are the initial and final concentration (mg/L) of dye after adsorption. V is the volume (mL) of experimental solution and W is the weight (g) of the adsorbent.

3. Results and discussion

3.1. Characterizations of EDA-CS

FT-IR spectra of chitosan, chitosan gel beads, ECH-CS, EDA-CS and dye loaded EDA-CS are presented in Fig. 1. Spectrum shows the principal spectral features in chitosan. The broad band at 3380 cm^{-1} could be assigned to the axial stretching vibration of –OH superimposed to the $-\text{NH}_2$ stretching band and inter- and extra-molecular hydrogen bonding of chitosan molecules. The spectrum also exhibits the distinctive absorption bands of chitosan at 2918 cm^{-1} and 2878 cm^{-1} (C–H stretch), 1647 cm^{-1} (amide II band, C=O stretch), 1597 cm^{-1} (NH_2 bending), 1383 cm^{-1} (amide III band, C–N stretch), 1420 cm^{-1} and 1323 cm^{-1} (C–H bending), 1259 cm^{-1} (C–N stretch), 1155 cm^{-1} (bridge C–O–C stretch) and 1082 cm^{-1} (C–O stretch) (Kyzas & Lazaridis, 2009; Ostrowska-Czubenko & Gierszewska-Drużyńska, 2009). Compared to the spectrum of pure chitosan, spectrum of chitosan gel beads presents a much higher peak at 3442 cm^{-1} corresponding to the stretching vibration of O–H overlapped by N–H stretch. Besides, the C–O stretch at 1082 cm^{-1} and NH_2 bending at 1597 cm^{-1} shift to 1068 cm^{-1} and 1603 cm^{-1} respectively, as shown in spectrum b. The reason may lay in that the inter- and extra-molecular hydrogen bonding of chitosan become weaker after dissolution and precipitation process. Spectrum c is corresponding to ECH-CS. It is obvious that a new peak appears at 1458 cm^{-1}, which can be assigned to the deformation of CH_2. The peak at 3370 cm^{-1} is sharper than that