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Potential biosorbent based on sugarcane bagasse modified with tetraethylenepentamine for removal of eosin Y

Gang-Biao Jiang[a,*,1], Zuan-Tao Lin[a,1], Xiao-Yi Huang[a], Yu-Qiang Zheng[a], Cui-Cui Ren[a], Chen-Ke Huang[a], Zhi-Jian Huang[b,*]

[a] Department of Pharmaceutical Engineering, College of Natural Resources and Environment, South China Agricultural University, Guangzhou 510642, PR China
[b] School of Marine Sciences, Sun Yat-sen University, Guangzhou 510275, PR China

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ABSTRACT

Tetraethylenepentamine (TEPA) modified sugarcane bagasse (SB), a novel biosorbent (TEPA-MSB), was proved to be an effective adsorbent for anionic dyes due to the introduced functional amino groups. FTIR, TG and DSC analysis were employed to characterize the sorbent. The effects of pH, temperature, contact time and initial concentration of dye on the adsorption of eosin Y were investigated. The experimental data fit very well to the Langmuir model, giving a maximum sorption capacity of 399.04 mg/g at 25 °C. And the kinetic data were well described by the pseudo-second-order kinetic model. pH 6 was the optimal pH for eosin Y adsorption, and the maximum adsorption capacity of TEPA-MSB calculated by Langmuir model was 18 times higher than that of SB.

1. Introduction

Sugarcane bagasse (SB), a kind of abundant agro-industrial residue, is produced from alcohol and sugar industries. It was reported that 1 ton of sugarcane can generate 280 kg of bagasse and the general yield of bagasse is approximately 1×10^7 tons per year [1,2]. Therefore, the salvage of this material is of great importance in alleviating the environmental load and realizing economic benefits as well.

SB contains around 50% cellulose, 27% polyoses and 23% lignin, which have many hydroxyl and/or phenolic functional groups that can be chemically modified to prepare new functional materials easily [3–9]. Lots of literatures reported that SB and its derivatives have substantial adsorption capacity for heavy metals. For instance, Júnior et al. studied the adsorption capacity of modified non-mercerized and mercerized SB for Cu^{2+}, Cd^{2+}, and Pb^{2+} ions, and they found that mercerization resulted in a biosorbent with better properties [10]. Homagai et al. reported that the introduction of xanthate group onto charred SB is essential in enhancing the adsorption capacities of raw SB for cadmium, lead, nickel, zinc and copper from their aqueous solutions [11]. However, research carried out to investigate their removal efficiency of dyes, especially for anionic dye, was not extensive. Recently, Saad et al. used phosphoric acid treated sugarcane bagasse to remove methyl red [12]. More recently, carboxy-methylated sugarcane bagasse chelated Fe^{3+} was employed to adsorb Brilliant Red 2BE by Siva et al. [4]. However, a common disadvantage which both these absorbents share is that the adsorption capacity is limited.

High concentration heavy metal ions and high salinity of tannery wastewater and printing-dyeing wastewater make it very difficult to be treated by conventional treatment. This potent pollutant without complete treatment can cause serious environmental problems due to its high chemical oxygen demand (COD), raised concentration of heavy metals, deep chromaticity and complex ingredient [13]. Since SB and its derivatives have been reported to be considerably effective in the removal of heavy metals [10,11,14,15], it is valuable to develop a new adsorbent based on SB with high dyes adsorption capacity, so as to find out good adsorbent potential for tannery wastewater treatment and printing-dyeing wastewater.

In the light of our early studies, the polyamine derivatives of chitosan modified by ethylenediamine (EDA) or tetraethylenepentamine (TEPA) can improve the adsorption capacity significantly toward anionic dye eosin Y [16,17], in this study, mercerized sugarcane bagasse was modified by TEPA to obtain a biosorbent TEPA-MSB that bears large amounts of amino groups suitable

* Corresponding authors. Tel.: +86 02085280293; fax: +86 02085280292.
E-mail addresses: jgb3h@163.com (G.-B. Jiang), lsshzhj@mail.sysu.edu.cn (Z.-J. Huang).
[1] These authors contributed equally to this work.

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for anionic dye adsorption. The removal efficiency of TEPA-MSB toward anionic dye eosin Y was extensively investigated.

2. Materials and methods

2.1. Materials

Sugarcane bagasse was obtained from a local sugarcane juice workshop. Eosin Y, a model acid dye, was purchased from Hebaochem Co., Ltd. (Shanghai, China). Tetraethylenepentamine (TEPA), epichlorohydrin (ECH) and other reagents used in this experiment were purchased from Damao Chemical Reagent Co., Ltd. (Tianjin, China) and were of analytical grade and used directly.

2.2. Preparation of TEPA modified MSB (TEPA-MSB)

2.2.1. Pretreatment of raw sugarcane bagasse

The raw sugarcane bagasse was dipped in distilled water for 48 h to soak out residual sugars with constant replacement of distilled water. After filtration, they were dried under sunlight and subsequently dried at 105 °C in an oven for 24 h to obtain fragile full dried bits, followed by being milled and sieved size to 60 mesh.

2.2.2. Sugarcane bagasse mercerization

The mercerization process was aimed at enhancing the chemical reactivity of SB. Specifically, 5.0 g of SB was treated with 100 mL of aqueous NaOH solution (10 wt%) at 60 °C for 8 h under constant stirring to obtain mercerized sugarcane bagasse (MSB). Finally, the alkali was removed from bagasse by filtration and washed with distilled water up to pH 7.

2.2.3. Synthesis of TEPA-MSB

The MSB obtained in the above step was reacted with 10 mL of epichlorohydrine (ECH) under ethanol reflux at 45 °C for 24 h. Afterwards, 25 mL of TEPA was added to the system and stirred at room temperature for another 24 h. The product obtained was washed with ethanol up to pH 7 and dried under vacuum (Scheme 1) [8,9].

2.3. Characterization of TEPA-MSB

FT-IR spectra of SB, MSB and TEPA-MSB 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.

Thermal gravimetric analysis (TGA) of SB, MSB and TEPA-MSB were carried out using a TG-209F3 thermogravimetric analyzer (Netzsch Scientific Instruments Co., Germany). Samples were placed in appropriate pans and heated from 40 °C to 900 °C at 20 °C/min under N_2 atmosphere.

Differential scanning calorimetry (DSC) analysis was performed on a 200F3 DSC analyzer (Netzsch Scientific Instruments Co., Germany). Samples were placed in sealed aluminum pans and heated from 20 °C to 210 °C at 10 °C/min under N_2 atmosphere.

2.4. Preparation of eosin Y solution

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).

2.5. Batch adsorption studies

The batch adsorption was carried out on a thermostat shaker at 200 rpm using 50 mL closed plastic bottles resistant to acid and base containing 0.02 g of TEPA-MSB and 20 mL of eosin Y solutions of desired concentration and pH. The effect of pH change on eosin Y removal was carried out by measuring the dye uptake after 6 h immersion at 25 °C. The pH of the dye solution (100 mg/L initial concentration) was adjusted to the range of 5–10, using either hydrochloric acid or sodium hydroxide. The effect of contact time was studied to determine the time taken to reach equilibrium at pH 6 with the initial eosin Y concentration fixed at 100, 200 and 500 mg/L respectively. The eosin Y concentration was measured at different time intervals up to 24 h.

Equilibrium isotherm studies were carried out with different initial concentrations of eosin Y (50–500 mg/L, pH 6) at 25 °C, 35 °C and 45 °C. Langmuir and Freundlich isotherms were used to analyze the equilibrium adsorption data.

Triplicate 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. Concentration of dye in supernatant was analyzed from the linear regression equation of the calibration curve. The amount of eosin Y adsorbed (q, mg/g) were calculated by using the following equation:

$$q_e = \frac{(C_i - C_f) \times V}{1000 \times W} \quad (1)$$

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

3. Results and discussion

3.1. Preparation of TEPA modified MSB (TEPA-MSB)

Before introducing the TEPA to SB, the mercerization process of SB is needed. This is because the order structure, morphology of the fiber of SB, and the conformation of the cellulose chains which shift from cellulose I to cellulose II can be changed by the mercerization process, resulting in the alternations in the strength and adsorption properties of the fiber. During the mercerization process, the SB swells and polysaccharide chains of SB are rearranged, meanwhile, the ordered structure and crystalline part in the fiber is destroyed dramatically. Since mercerization augments the specific surface area of the fiber, the higher adsorption and more facilely accessible the hydroxyl groups of SB can be obtained [18].

3.2. Characterizations of TEPA-MSB

3.2.1. FTIR analysis

The FTIR spectra of SB, MSB and TEPA-MSB are presented in Fig. 1. After the treatment with NaOH, cellulose I was transformed into cellulose II and large amounts of lignin and polyoses were removed together with the hydrolysis of amorphous cellulose fraction. Due to the transformation of cellulose I to cellulose II, typical bands shifted as can be perceived from the Fig. 1a and b. It is worthy of note that the disappearance of bands at 1604 cm^{-1} reveals the removal of lignin and polyoses, as 1604 cm^{-1} is attributed to the aromatic skeletal vibrations. Besides, other characteristic bands of lignin and polyoses at 1735, 1514 and 1325 cm^{-1} are vanished, which could be assigned to that the carbonyl stretching of ketone, skeletal modes and phenolic OH disappear [10,19].

Compared to Fig. 1b, vibration enhancement is observed at 3442 cm^{-1} (O—H and N—H stretch) from the spectrum of TEPA-MSB (Fig. 1c), which indicates that a great deal of amino groups have been introduced into MSB. In addition, Fig. 1c shows an intense peak