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Pyridine derivative covalently bonded on chitosan pendant chains for textile dye removal

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ABSTRACT

Chitosan was chemically modified through a sequence of four reactions with immobilized 2-aminomethylpyridine at the final stage, after prior protection of amino group with benzaldehyde. The characterized biopolymers containing free amino and hydroxyl active centers on the biopolymeric structure and pyridinic nitrogen on pendant chains showed combined hydrophobic properties that can potentially favor interactions. Reactive Yellow GR and Blue RN dyes gave the maximum sorption capacities of 2.13 and 1.61 mmol g^{-1}, which were performed as functions of contact time, concentration and dye structure. However, biopolymer/dye interactions are governed by effective hydrogen bond and van der Waals forces for such structural adjustments. The data obtained from the concentration isotherm were applied to non-linear regressions of the Langmuir, the Freundlich and the Sips models, with the best fit to the latter model. The kinetic data was fitted to non-linear regression of pseudo-second-order, indicating that the sorption phenomena are most likely to be controlled by chemisorption process.

1. Introduction

Colored organic effluents originating from the textile, paper, plastic, leather, food, and mineral processing industries constitute undesirable wastewater that aggregate pigments or dyes, which can cause serious water pollution problems (Messina & Schulz, 2006). Small amounts of colored wastes such as dye not only are esthetically displeasing, but also hinder light penetration, to disturb the biological processes in water bodies (Chao et al., 2005; Messina & Schulz, 2006).

Various physical, chemical and biological methods have been extensively explored for dye-containing wastewater management, which include chemical coagulation, flocculation, chemical oxidation, photochemical degradation, membrane filtration, including aerobic and anaerobic biological degradations (Dizge, Aydiner, Demirbas, Kobya, & Kara, 2008; Won et al., 2006). However, dye-contained wastewater is very difficult to amend, since the dyes are recalcitrant organic molecules, resistant to aerobic digestion, stable to light, heat and oxidizing agents and chemical oxidation results in aromatic ring cleavage, generating more toxic chemical sludge or by-products (Won et al., 2006).

Amongst numerous techniques for dye removal, sorption is a choice procedure, which sorbent should have low-cost, be highly efficient, simple, easy to recovery/reuse and be insensitive to toxic substance properties (Alkan, Demirbas, & Dogan, 2007; Wu, 2007). It has also a specific advantage if it removes the dye molecule completely, unlike other techniques applied for this purpose that can destroy only the dye chromophore part, leaving harmful residual moieties in the effluent (Wu, 2007).

Nowadays, attention has been focused on inexpensive and efficient materials, capable of pollutant removal from contaminated aqueous solution to replace the most used activated carbon (Moscofian, Pires, Vieira, & Airoldi, 2012; Tang, Zhang, Guo, & Zhou, 2007). Based on a variety of sorbents, natural polymers such as alginate, pectin, cellulose, chitin and chitosan have attracted attention not only due to their excellent sorption capability, but also some properties associated with environment-friendly behavior such as renewable, biocompatible, biodegradable and nontoxic nature have been considered (Iqbal, Saeed, & Zafar, 2009; Wang & Wang, 2008).

From these biopolymers chitosan, extracted from crustacean shrimp, crab and lobster shells, exoskeleton of insects and the cell walls of some fungi has also been used as sorbent (Juang, Wu, & Tseng, 2002; Lopes, Sousa, & Airoldi, 2009). Chitosan the linear and typically 20% acetylated (1 → 4)-2-amino-2-deoxy-β-D-glucan, is isolated from marine chitin (Muzzarelli, 1977; Muzzarelli et al., 2012). From the structural point of view, chitin and chitosan are very similar, containing reactive hydroxyl and amino groups, being chitosan less crystalline than chitin, which presumably makes it more accessible to reagents, such as aldehydes and ketones in a typical Schiff reaction, in particular, with a series of benzaldehydes (Muzzarellli, 1988; Ravi Kumar, Muzzarelli, Muzzarelli, Sashiwa, & Domb, 2004).

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Chitosan and chemical derivatives have been extensively investigated due to the non-toxicity, hydrophilicity, high biocompatibility and biodegradability properties, in addition to attractive physical and mechanical domains. The low cost and relatively easy preparative methods, these polymers give many academic and also practical uses in medicine, agriculture, food technology and cosmetic applications (Machado, Lopes, Sousa, & Airoldi, 2009), presented also in various forms as powder, paste, film, fiber etc. (Agnihotri, Mallikarjuna, & Aminabhavi, 2004).

The present investigation deals with chemically modified chitosan, using previous protection of the amino group with benzaldehyde. This derivative favors the reaction of the hydroxyl group on carbon 6 with epichlorohydrin molecule, to permit inclusion of the epoxide group, which is easily opened through reagents containing a free electron pair as 2-aminomethylpyridine. After complete reaction, benzaldehyde was eliminated in acidic condition and the available basic active sites have the ability to remove pollutants, as evaluated for Reactive Yellow GR (RY) and Reactive Blue RN (RB) dyes in aqueous solutions.

2. Materials and methods

2.1. Materials

Powered chitosan with 82% degree of deacetylation was obtained by extraction from crab shells and supplied by Primex Ingredients A.S. The reagents benzaldehyde (Aldrich), methyl and ethyl alcohols (Synth), 2-aminomethylpyridine (Aldrich), epichlorohydrin (Synth), hydrochloric acid (Synth), sodium hydroxide (Gold). Reactive Yellow GR and Reactive Blue RN dyes were received as a gift from DyStar Ltda, Suzano, SP, Brazil and were used without prior purification in aqueous solutions.

2.2. Syntheses of chitosan derivatives

2.2.1. Chitosan-benzaldehyde

Chitosan amino groups were initially protected with benzaldehyde to favor the reaction of the more reactive hydroxyl group on carbon 6. For this synthesis 5.0 g of powdered chitosan were suspended in 60.0 cm^3 of methanol, then 20.0 cm^3 of benzaldehyde were slowly added, and the suspension was stirred for 24 h at room temperature (Tang et al., 2007; Yi, Wang, & Ye, 2006). The obtained solid was isolated, washed several times with methanol and dried at 333 K during 8 h, to yield the biomaterial named (1 → 4)-2-amino-2-deoxy-2-N-benzidine-β-D-glucan (BZL).

2.2.2. Chitosan-benzaldehyde with epichlorohydrin

For this synthesis 4.0 g of the preceding biomaterial were suspended in 120.0 cm^3 of a 1.0×10^{-3} mol dm^{-3} sodium hydroxide solution at 323 K, and then 6.0 cm^3 of epichlorohydrin were slowly added. The mixture was stirred for 6 h and the solid obtained was filtered and washed with water and acetone and dried at 333 K during 8 h, to produce the biomaterial (1 → 4)-2-amino-2-deoxy-2-N-benzidine-6-2-(chloromethyl)oxirane-β-D-glucan (EAC).

2.2.3. Chitosan-benzaldehyde with 2-aminomethylpyridine

An amount of 3.0 g of the preceding biomaterial was suspended in 90.0 cm^3 of 1.0×10^{-3} mol dm^{-3} sodium hydroxide at 333 K, and then 3.0 cm^3 of 2-aminomethylpyridine was slowly added. The mixture was stirred, filtered, washed and dried as before, to yield the biopolymer (1 → 4)-2-amino-2-deoxy-2-N-benzidine-6-[O-butyl-4-2aminepyridyl)-β-D-glucan (CTA).

2.2.4. Benzaldehyde removing

This process was performed in acidic medium, using an ethanolic solution containing 0.24 mol dm^{-3} hydrochloric acid. To this solution, 2.0 g of powdered CTA biopolymer was suspended in 60.0 cm^3 of solution and stirred at room temperature for 24 h. The solid obtained (1 → 4)-2-amino-2-deoxy-2-6-[O-butyl-4-2aminepyridyl)-β-D-glucan (CTN), was filtered and washed with water and dried at 333 K for 8 h, as schematically showed in Fig. 1.

2.3. Characterization

Percentages of carbon and nitrogen for chitosan and derivatives were determined through elemental analyses on a Perkin Elmer model PE 2400 elemental analyzer. Infrared spectra of the samples in KBr pellets were obtained by accumulating 32 scans on a Bomem spectrophotometer, MB-series, model B 100, in the 4000–400 cm^{-1} range, with 4 cm^{-1} of resolution. Nuclear magnetic resonance spectra for the carbon nucleus in the solid state were obtained on a Bruker–Avance II^+ 300 spectrometer at room temperature, using the CP-MAS technique, with contact time 4 ms, relaxation time 3 s and frequency of 75.47 MHz. The thermogravimetric curves in an argon atmosphere were obtained on a TA instrument, coupled to a model 2050 thermobalance, using a heating rate of 0.167 K s^{-1}, varying from room temperature to 1073 K. X-ray diffraction patterns were performed on Shimadzu diffractometer, model XRD-7000 (40 kV, 30 mA), in the $2\theta = 2.5–50^\circ$ range using nickel-filtered Cu-Kα radiation, with a wavelength of 0.154 nm. For the determination of zero point charge (pH_{PZC}) for the biopolymers, samples of 15.0 mg were suspended in 15.0 cm^3 of aqueous 0.010 mol dm^{-3} sodium chloride, having pH varying from 3 to 10, adjusted with sodium hydroxide or hydrochloric acid solutions. The suspensions were shaken for 24 h in an orbital bath at 298 ± 1 K. The final pH of the supernatant was then measured using a Metter Toledo pHmeter (Santos, Vilar, & Boaventura, 2008; Vieira et al., 2010; Vieira, Cestari, Carvalho, Oliveira, & Chagas, 2012).

2.4. Sorption experiments

Solutions of RY and RB anionic dyes having concentrations ranging from 1.6×10^{-4} to 3.2×10^{-3} and 1.1×10^{-3} to 3.8×10^{-3} mol dm^{-3}, respectively, were used for all sorption processes. For each experiment, a series of polyethylene flasks, containing about 10 mg of CTN biopolymer was kept in contact with 10.0 cm^3 of dye solutions, using the established concentration ranges. The suspensions were placed in a thermostatic bath at 298 ± 1 K and orbitally stirred for a period of 24 h. Subsequently, in order to determine the concentration of dye in equilibrium, the solid was separated by centrifugation using a Hettich Zentrifugen model Rotina 38 instrument at 4000 rpm for 5 min. The aliquots of supernatant were analyzed by spectrophotometer (UV–vis) at wavelengths of 416 and 592 nm for RY, RB dyes, respectively. The amount of sorbed dye in mmol g^{-1} were calculated by Eq. (1), where N_f is the number of moles of dye sorbed onto the biopolymer, n_i and n_s are the initial number of moles of dye and number of moles in the supernatant at equilibrium number and m is the mass of the sorbent used in each sorption process (Sousa, Silva Filho, & Airoldi, 2009).

$$Nf = \frac{n_i - n_s}{m} \quad (1)$$

2.5. Kinetic studies

The kinetic experiments for RB and RY dyes with CTN were performed with solutions of concentrations of 2.7×10^{-3} and 3.0×10^{-3} mol dm^{-3} at 298 ± 1 K, respectively. In each experiment, about 10 mg of biopolymers were orbitally stirred with 10.0 cm^3 of dye solution. At predetermined times aliquots were taken from the supernatant and analyzed by ultraviolet–visible (UV–vis) absorption spectroscopy. Identically, for all other intermediates BZL, EAC