



Removal of anionic dyes from aqueous solutions by an ion-exchanger based on pullulan microspheres

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ABSTRACT

Pullulan-graft-poly(3-acrylamidopropyl trimethylammonium chloride) (P-g-pAPTAC) microspheres were prepared by suspension cross-linking of the pullulan previously grafted with cationic moieties. Adsorption of Azocarmine B by the P-g-pAPTAC microspheres was used as a model to demonstrate the removal of anionic dyes from aqueous solutions. Batch adsorption studies concerning the effect of the contact time, pH, initial dye concentration, temperature, grafting, and the nature of sulfonated anionic dyes on the adsorption kinetics were investigated. Adsorption was shown to be independent of pH. The experimental data best fitted to the pseudo-second order model which provided values of the rate constant k_2 of $1.4 \times 10^{-4} \text{ g mg}^{-1} \text{ min}^{-1}$ for 100 mg L^{-1} solution and of $3.7 \times 10^{-4} \text{ g mg}^{-1} \text{ min}^{-1}$ for 500 mg L^{-1} solution. From the Langmuir isotherm linear equation, the maximum adsorption capacity determined was 113.63 mg of Azocarmine B per gram of adsorbent; the negative value of the free energy change indicated the spontaneous nature of the adsorption process.

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1. Introduction

Several industries, such as textile, paper, plastics, and dyestuffs, utilize large volume of water and use chemicals and dyes to color their products; as a consequence they generate a considerable amount of polluted wastewater (Crini, 2006; Pokhrel & Viraraghavan, 2004). Dye wastewater discharge into environmental water bodies deteriorates the water quality, and may cause a major impact on human health due to toxic, carcinogenic, mutagenic, and/or teratogenic effects (Otterburn & Aga, 1985). Wastewaters containing dyes are very difficult to treat, since the dyes are recalcitrant molecules, resistant to aerobic digestion, and stable to oxidizing agents.

Reactive dyes contain one or more reactive groups forming covalent links with oxygen, nitrogen and/or sulfur atoms present in cellulose fibers (hydroxyl groups), protein fibers (amino, hydroxyl,

Abbreviations: AO, Acid Orange 7; APTAC, (3-acrylamidopropyl)-trimethylammonium chloride; AzB, Azocarmine B; CAB, cellulose acetate butyrate; CR, Congo Red; ECH, epichlorohydrin; ESEM, environmental scanning electron microscopy; KPS, potassium peroxydisulfate; MO, Methyl Orange; P, pullulan; P6R, Ponceau 6R; P-g-pAPTAC, pullulan-graft-poly(3-acrylamidopropyl trimethylammonium chloride); pAPTAC, poly(3-acrylamidopropyl trimethylammonium chloride).

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and mercaptan groups) and polyamides (amino group) and providing great stability to the fabric color (Trotmann, 1984).

Some biological, physical, and chemical methods have been employed for dye wastewater treatment (Forgacs, Cserhati, & Oros, 2004). In practice, no single process provides adequate treatment and a combination of different processes is often used to achieve the desired water quality in the most economical way (Gupta & Suhas, 2009). Thus, there is a need to develop new decoloration methods that are effective and acceptable in industrial use.

It is now recognized that adsorption processes using low-cost adsorbents are effective and economic methods for water decontamination. A large variety of non-conventional adsorbent materials have been obtained to remove dyes (Crini, 2006). Much attention has recently been focused on biosorbent materials such as fungal or bacterial biomass and biopolymers that can be obtained in large quantities and that are harmless to nature. Special attention has been given to polysaccharides such as chitosan (Chiou, Ho, & Li, 2004; Chiou & Li, 2003; Dotto & Pinto, 2011; Rosa, Mauro, Riela, & Favere, 2008) and starch or starch-based materials (Delval et al., 2002; Klimaviciute, Riauka, & Zemaitaitis, 2007; Xu, Wang, Wu, Wang, & Li, 2006).

Polysaccharides in the form of cross-linked beads have supplementary advantages such as fast adsorption kinetics, easily operated, and appealing diffusion properties (Bailey, Olin, Bricka, & Adrian, 1999). Due to the hydrophilic nature of the polysaccharides repeating units, these materials possess a remarkably high swelling

capacity in water, and consequently their networks are sufficiently expanded to permit a fast diffusion of the pollutants. Even though neutral cross-linked polysaccharides have good adsorption capacity, this can be improved by grafting various functional groups onto the polymer network or the polymer backbone (Arrascue, Garcia, Horna, & Guibal, 2003; Jeon & Höll, 2003). The insertion of new functional groups on the surface of the beads results in an increase of surface polarity and hydrophilicity and this enhances the adsorption of polar adsorbates and improves the adsorption selectivity for the target pollutant. The grafting of carboxyl groups (Chao, Shyu, Lin, & Mi, 2004), amine functions (Jeon & Höll, 2003), and sulfur compounds (Arrascue et al., 2003; Guibal, Von Offenbergsweeney, Vincent, & Tobin, 2002) has been regarded as an interesting method for these purposes. After adsorption, the cross-linked materials can also be easily regenerated by washing it with a solvent or by solvent extraction.

Among polysaccharides, pullulan (P) is a promising material for biotechnological applications because it is a biocompatible and biodegradable polymer (Xi et al., 1996). Neutral and ionic pullulan derivatives have been also extensively developed for several applications including coating and packaging material, sizing agent for paper or starch substitute in low-calorie food formulations, and cosmetic emulsions (Deshpande, Rale, & Lynch, 1992; Kulicke & Heinze, 2006; Oku, Yamada, & Hosoya, 1979).

Until now, as far as we could ascertain, no data are available concerning the removal of water-soluble anionic dyes by pullulan derivatives. Here, the preparation and characterization of grafted cationic crosslinked pullulan microspheres and their adsorption properties of sulfonated anionic dyes are reported.

2. Materials and methods

2.1. Materials

Pullulan (P) ($M_w = 200,000 \text{ g mol}^{-1}$) was purchased from Hayashibara Lab. Ltd. (Okoyama, Japan). (3-Acrylamidopropyl)-trimethylammonium chloride (APTAC) (75%, w/v in water) was obtained from Sigma–Aldrich (St. Louis, MO, USA). Potassium peroxymonosulfate (KPS), and epichlorohydrin (ECH) were purchased from Fluka (Buchs, Switzerland). Cellulose acetate butyrate (CAB) was purchased from Eastman Inc. (Kingsport, TN, USA). 1,2-Dichloroethane was obtained from Fluka and distilled prior the use. The acid dyes Azocarmine B (AzB), Acid Orange 7 (AO), Methyl Orange (MO), Ponceau 6R (P6R) and Congo Red (CR) were purchased from Sigma–Aldrich. These chemicals are anionic sulfonated dyes with mono azo and multiple azo bonds, and with various degrees and positions of sulfonation (Table 1). All the other reagents were from Fluka. All chemicals were of analytical grade. Unless stated, all chemicals were used without further purification.

2.2. Instrumental analysis

The copolymer composition was determined by nitrogen elemental analysis and ^1H NMR spectroscopy. ^1H NMR spectra were recorded on a Bruker Avance DRX 400 NMR (Rheinstetten, Germany), using deuterated water as the solvent. The morphology of adsorbent microspheres was examined by using an environmental scanning electron microscope (ESEM) type Quanta 200 (Netherlands), operating with secondary electrons in low vacuum.

The absorption spectra of dye solutions before and after dye adsorption were recorded by using UV-VIS Specord 200 spectrophotometer (Analytic Jena, Jena, Germany) between 350 and 700 nm. The concentration of dye solutions was determined at the wavelength corresponding to the maximum of absorbance (λ_{max}) (see Table 1).

2.3. Preparation of pullulan-graft-poly(3-acrylamidopropyl trimethylammonium chloride) microspheres

Two copolymers with different contents of cationic groups (14% and 22%) (i.e., pullulan-graft-poly(3-acrylamidopropyl trimethylammonium chloride); P-g-pAPTAC) were synthesized by graft-polymerization of APTAC onto pullulan in aqueous solution, using potassium persulfate as the initiator (Constantin, Fundueanu, Cortesi, Esposito, & Nastruzzi, 2003). The microspheres were prepared in one step by suspension cross-linking of P-g-pAPTAC with ECH as previously reported (Constantin, Mihalcea, Oanea, Harabagiu, & Fundueanu, 2010). Briefly, the cross-linked polysaccharide microspheres were produced using a specially designed reactor fitted with a mechanical stirrer, a condenser, and a thermometer. The dispersion medium was constituted of 50 ml of dichloroethane in which 0.5 g of the dispersion agent CAB was dissolved. A solution containing 2 g of P-g-pAPTAC and 2 g of NaOH in 12 ml of water was heated at 50 °C and dispersed in the organic phase at 450 rpm. The w/o emulsion was stirred for 1 h. After the complete dispersion, 2 ml of ECH were added. Afterwards, the cross-linking reaction was carried out for 20 h at 55 °C. The resulting microspheres were isolated by filtration and rinsed in the reactor successively with dichloroethane, acetone, deionized water, and methanol, and finally dried under vacuum at 60 °C for 24 h.

The reaction parameters and physico-chemical properties of P-g-pAPTAC microspheres obtained in the present study are reported in Table 2.

2.4. Dye adsorption by P-g-pAPTAC microspheres

Adsorption studies were performed at 25 ± 1 °C by the batch technique.

2.4.1. Effect of pH

The effect of pH on the adsorption capacity of P-g-pAPTAC microspheres was investigated as follows. Briefly, 50 mg of P-g-pAPTAC microspheres was added to each dye solution (50 ml; 100 mg L^{-1}) at 25 °C. The pH of the solution (between 3 and 9) was adjusted adding either HCl or NaOH. The dye solutions were collected after 24 h and assayed by UV-Vis spectroscopy.

2.4.2. Effect of initial dye concentration

The effect of the dye concentration on the adsorption capacity of P-g-pAPTAC microspheres was investigated as follows. Briefly, 50 mg of P-g-pAPTAC microspheres was added to each dye solution (50 ml; 100, 300 and 500 mg L^{-1}) at pH 7.0 and 25 °C. Kinetics of dye adsorption onto P-g-pAPTAC microspheres was investigated to determine the time when the adsorption equilibrium was reached and the maximum removal of the dye was obtained.

The amount of dye adsorbed by the microspheres at time t (q_t) was obtained from the difference between the initial concentration of dye and the dye concentration in the supernatant after adsorption; q_t was calculated from the mass balance equation (i.e., Eq. (1)):

$$q_t = \frac{V(C_0 - C_t)}{m} \quad (1)$$

where C_0 and C_t are the initial and final dye concentration (mg L^{-1}), respectively, V is the volume of the dye solution (L), and m is the mass of the adsorbent used (g).

When t corresponds to the equilibrium time (i.e., $C_t = C_e$) $q_t = q_e$, the amount of the adsorbed dye at equilibrium, q_e , was calculated according to Eq. (2):

$$q_e = \frac{V(C_0 - C_e)}{m} \quad (2)$$

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