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Cross-linked quaternary chitosan as an adsorbent for the removal of the reactive dye from aqueous solutions

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Abstract

Adsorption of reactive orange 16 by quaternary chitosan salt (QCS) was used as a model to demonstrate the removal of reactive dyes from textile effluents. The polymer was characterized by infrared (IR), energy dispersive X-ray spectrometry (EDXS) analyses and amount of quaternary ammonium groups. The adsorption experiments were conducted at different pH values and initial dye concentrations. Adsorption was shown to be independent of solution pH. Three kinetic adsorption models were tested: pseudo-first-order, pseudo-second-order and intraparticle diffusion. The experimental data best fitted the pseudo-second-order model, which provided a constant velocity, k_2, of 9.18×10^{-4} g mg^{-1} min^{-1} for a 500 mg L^{-1} solution and a value of k_2, of 2.70×10^{-5} g mg^{-1} min^{-1} for a 1000 mg L^{-1} solution. The adsorption rate was dependent on dye concentration at the surface of the adsorbent for each time period and on the amount of dye adsorbed. The Langmuir isotherm model provided the best fit to the equilibrium data in the concentration range investigated and from the isotherm linear equation, the maximum adsorption capacity determined was 1060 mg of reactive dye per gram of adsorbent, corresponding to 75% occupation of the adsorption sites. The results obtained demonstrate that the adsorbent material could be utilized to remove dyes from textile effluents independent of the pH of the aqueous medium.

Keywords: Chitosan; Reactive dye; Quaternary chitosan; Adsorption; Cross-linked

1. Introduction

The textile industry consumes a significant volume of water in the process of dyeing fibers and fabrics. This water is highly colored due to the presence of dyes and can affect the photosynthesis process due to the occurrence of reduced water transparency, which makes the penetration of sun rays more difficult [1]. Although many organic molecules are degradable, many others are stable and, due to their complex chemical structures and synthetic organic origin, are not totally degradable [2]. Due to their xenobiotic nature, azo reactive dyes can cause toxicity to aquatic organisms [3].

The classes of dyes mostly used by the textile industry are azo dyes containing reactive groups. Reactive dyes are compounds that contain one or more reactive groups, which form covalent links with oxygen, nitrogen or sulfur atoms from cellulose fibers (hydroxyl group), protein fibers (amino, hydroxyl and mercaptan groups) and polyamides (amino group), providing greater stability to the fabric color [4].

The conventional treatment process of textile effluents involves numerous stages due to the characteristics of the production process. The effluents can exit the processes at high temperature, between 60 and 90 °C, or at ambient temperature. The effluents are collected and receive an injection of carbon dioxide gas to neutralize the pH. In the neutralization tank, new pH measurements are necessary, since the stations are projected to treat effluents with pH varying between 8 and 10 [5].

Conventional treatment involves a process of coagulation/flocculation. This is a versatile process, which can be used alone or combined with biological treatments, as a way of removing suspended solids and organic material, as well as promoting the extensive removal of dyes from textile industry effluents [6,7]. However, this approach presents the disadvantage of generating a large volume of sludge. This sludge is rich in dyes, as well as other substances used in the textile process. This is

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a problem, as the waste must be discarded properly to avoid environmental contamination [5].

Other techniques that have been employed for toxic substance content reduction in industrial wastewater include advanced oxidation; membrane filtration; and reverse osmosis [6–10]. However, these methods are limited due to their high operational costs [2,7].

The adsorption method has been used for dye removal from the aquatic environment [8,11–15]. The major advantage of this technique over others is its low generation of residues and the possibility of adsorbent recycling and reuse [16]. Several literature reports concern the development of more effective, selective and cheaper adsorbent materials [2,8,9,11–13,17,18]. It is important to mention that an increase in adsorption capacity may help compensate for the cost of additional processing.

Biopolymers constitute a promising class of biosorbents used for the removal of pollutant from aquatic environments and among these, chitosan should be highlighted. This polymer is derived from chitin, which is one of the most abundant biopolymer in nature, obtained from crustacean shells of shrimps, crabs and lobsters, which are themselves waste products of the seafood processing industry [19,20].

Chitosan has excellent properties for the adsorption of anionic dyes, principally due to the presence of protonated amino groups ($–NH_3^+$) in the polymer matrix, which interact with dyes in solution by ion exchange, at an appropriate pH [21–23]. The high content of amino groups also facilitates various chemical modifications in the polymer, for the purpose of improving its adsorbent properties and adsorption capacity.

The purpose of this work was to study the kinetics and adsorption equilibrium of reactive dye orange 16, which is used in the dyeing process in the textile industry, in aqueous solution with modified chitosan biopolymer.

2. Experimental

2.1. Materials

Chitosan, used for the preparation of the adsorbent, was obtained from Purifarma (Brazil) and reported to have 90.0% degree of deacetylation, 8.0% water content, 1.0% maximum ash content and pH between 7.0 and 9.0. Glycidyl trimethyl ammonium chloride was purchased from Fluka Biochemica (Switzerland). The dye, reactive orange 16 (RO16, 50%) in sodium form, was acquired from Aldrich (USA). A stock solution of 2000 mg L^{-1} of the reactive dye was prepared by massing an appropriate amount of the dye and diluting to find volume with distilled water. Fig. 1 shows the structure of RO16.

2.2. Instrumentation

Infrared spectra were obtained using a PerkinElmer PC FTIR 16 spectrophotometer. The initial microprobe analysis using energy dispersive X-ray spectrometry (EDXS) of the new adsorbent was realized using Philips equipment, model XL 30, by placing a sample in stabes and covering it in gold. The number of quaternary functional groups was determined by conductometric titration using a Mettler MC 226 conductivimeter from Micronal, model B 330, and a Schott Geräte automatic titrator, model T 80/20. UV–vis absorption measurements using a Micronal B572 spectrophotometer were employed to determine the reactive dye concentration in solution.

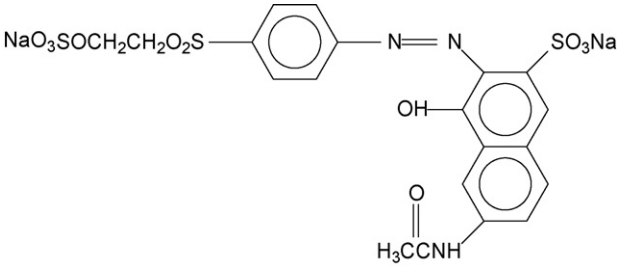

Fig. 1. Structure of RO16.

2.3. Preparation of quaternary chitosan with glycidyl trimethyl ammonium chloride

Quaternary chitosan salt (QCS) was prepared according to the method proposed by Lang et al. [24]. Cross-linking of quaternary chitosan salt was achieved by taking a chitosan suspension in ethanol and adding glutaraldehyde 25% (w/v) to the suspension [25]. The mixture was continuously stirred for 24 h at room temperature. The product was filtered and dried at 50 °C and sieved size using 80–270 mesh. Fig. 2 shows the structure of cross-linked QCS.

2.4. Adsorption experiments

The removal of reactive dyes by the adsorption process in aqueous medium depends on various factors, such as the amount of adsorbent, pH, contact time and temperature. The effect of these parameters with the affinity of the quaternary chitosan to adsorb a model textile azo dye, RO16, from aqueous solution was examined.

A known amount of adsorbent and a measured volume of reactive dye solution were placed in 250 mL closed Erlenmeyer flasks. The system remained under agitation in a thermostatized bath (Shaker Lab-line). The material was separated from the solution by decantation and the non-adsorbed dye concentration was determined by UV–vis spectrophotometry using calibration curve in λ_{max} of 508 nm.

The pH effect on adsorption was conducted using 50 mg of QCS, 50 mL of 170 mg L^{-1} dye solution, shaking rate at 250 rpm and buffered with CH_3COOH/CH_3COONa (pH 3–6); NaH_2PO4/Na_2HPO4; (pH 7 and 8); NH_4OH/NH_4Cl (pH 9 and 10).

The adsorption kinetics were carried out in closed flasks each containing 100 mg of QCS and 100 mL of dye solutions 500 and 1000 mg L^{-1} buffered at pH 4.0. At predetermined times, the shaker was turned-off and immediately thereafter the adsorbent material was decanted for 15 min, and 200 μL aliquots of the 1000 mg L^{-1} solution was removed, diluted with 3 mL of distillated water in a cuvette, and the absorbance was determined. The