

## Comparison of chitosan with different physical forms to remove Reactive Black 5 from aqueous solutions



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### ABSTRACT

Studies have demonstrated that the chitosan powder (CP) and chitosan films (CF) are attractive alternatives to remove dyes from aqueous solutions, but powder and films were evaluated separately. In this work, CP and CF are compared as adsorbents to remove Reactive Black 5 (RB5), which is a hazardous dye of textile effluents. Chitosan samples were produced with different deacetylation degrees (from 65% to 95%). Adsorption isotherms and kinetics were studied at various values of pH, temperature, stirring rate and deacetylation degree. Adsorption–desorption cycles were performed. CP and CF with deacetylation degree of 95% were the best adsorbents, removing more than 99% of RB5, in pH 4.0 at 298 K. The Langmuir model was the more suitable to fit of the equilibrium data for both adsorbents ( $R^2 \geq 0.9852$  and  $ARE \leq 1.93$ ), and CP showed an adsorption capacity slightly higher. The adsorption kinetics of RB5 onto both adsorbents was better represented by the Elovich model ( $R^2 \geq 0.9990$  and  $ARE \leq 5.21$ ). The interactions analyses indicated that electrostatic interactions occurred between the adsorbents and RB5. CF were easily separated from the liquid phase during the adsorption–desorption cycles and were reused three times, while CP cannot be reused.

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## 1. Introduction

The textile industries generate large amounts of dye containing effluents, once about 40–65 L of effluents are generated per kilogram of cloth produced [1]. The inadequate release of these colored effluents into the water bodies can cause severe damages from the ecological viewpoint [2]. In this way, the treatment of dye containing effluents becomes environmentally and ecologically important. Several biological, physical, chemical and physico-chemical methods have been used to treat these effluents [3]. Among these, adsorption is a good alternative since presents advantages such as, low cost, ease of operation and high efficiency [4]. Activated carbon is the most common used adsorbent, but its use is limited due to the high costs of production and regeneration (generally, the production and regeneration involve high temperatures or many chemicals, leading to the loss of adsorbent and

increasing the costs). The regeneration of saturated carbon is also expensive, not straightforward, and results in loss of the adsorbent. In order to substitute the activated carbon, several alternative adsorbents have been tested to remove dyes from aqueous solutions, such as, citrus waste biomass [5], papaya seeds [6], *Strychnos potatorum* seeds [7], *Aspergillus foetidus* [8], aqai stalks [9], activated carbon from rambutan peels [10], modified tea wastes [11] and low cost activated carbon [12]. In the last years, chitosan has been considered as an alternative and eco-friendly adsorbent, since can be obtained from renewable sources and has high efficiency for dyes removal [13,14].

Regarding to the use of chitosan for dyes removal by adsorption, different physical forms have been employed, such as, powder [15], beads [16], hydrogels [17], flakes [18], hollow fibers [19] and films [20]. Studies demonstrated that chitosan powder and chitosan films are attractive alternatives to remove dyes from aqueous solutions, and both have advantages and drawbacks [20,21]. However, in the mentioned studies, powder and films were used separately, and a direct comparison was not performed. Furthermore, the majority of works about dye removal by chitosan uses commercial chitosan with defined characteristics or chitosan

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derivates to remove textile dyes, however, chitosan with different characteristics and forms is little investigated. Based on the best of our knowledge, a comparative study between chitosan powder and chitosan films with different deacetylation degrees to remove dyes was not presented in the literature.

In this study, the comparison between chitosan powder (CP) and chitosan films (CF) as adsorbents to remove Reactive Black 5 (RB5) from aqueous solutions was performed. At first, chitosan powder was obtained with different deacetylation degrees, and subsequently, the chitosan films were obtained from these samples. Afterwards, the effects of pH and deacetylation degree on the adsorption of RB5 onto CP and CF were evaluated. For both adsorbents, the equilibrium, thermodynamic and kinetic studies were performed under different experimental conditions. Finally, possible interactions CP–RB5/CF–RB5 were elucidated and adsorption–desorption cycles were carried out. We believe that this work can contribute to show the advantages and drawbacks in relation to the use of chitosan based materials as adsorbents.

## 2. Materials and methods

### 2.1. Dye characteristics

The textile dye (purity of 95%), Reactive Black 5 (RB5) (molecular weight  $991.8 \text{ g mol}^{-1}$ ;  $\lambda_{\text{max}} = 596 \text{ nm}$ , Color Index 20505) was supplied by Sigma–Aldrich (Brazil) and used without further purification. This dye was selected due to its presence to be common in textile effluents [22]. Distilled water was used to prepare all solutions. All reagents were of analytical grade. The chemical structure of RB5 is shown in Fig. 1.

### 2.2. Preparation of chitosan powder and chitosan films

Chitosan powder (CP) was obtained from shrimp wastes (*Penaeus brasiliensis*). Firstly, the shrimp wastes were submitted to the demineralization (7 kg of shrimp wastes were mixed with 14 L of HCl solution  $2.5 \text{ g L}^{-1}$  in stirred tank during 2 h at  $25^\circ\text{C}$ ), deproteinization (the demineralized material was mixed with 21 L of NaOH solution  $5.0 \text{ g L}^{-1}$  in stirred tank during 2 h at  $25^\circ\text{C}$ ) and deodorization (the deproteinized material was mixed with 35 L of NaClO solution  $0.4 \text{ g L}^{-1}$  under agitation during 3 h) steps. Then, the deacetylation reaction was carried out according to Moura et al. [23], in order to obtain deacetylation degrees (DD) of 65%, 75%, 85% and 95% (the deacetylation was carried out with 66 g of chitin and

4 L of concentrated sodium hydroxide solution ( $421 \text{ g L}^{-1}$ ) at  $130^\circ\text{C}$ , under constant agitation of 50 rpm. The different DD's were obtained by varying the reaction time). The samples were purified afterwards they were dried in spouted bed and sieved [24]. The mean diameter of powder grains for the adsorption assays was of  $72 \pm 3 \mu\text{m}$ .

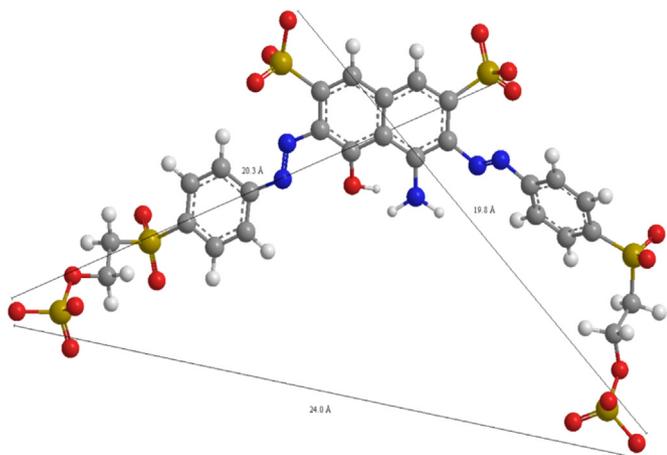
Chitosan films (CF) were obtained using samples with DD from 65% to 95%. Each chitosan powder sample was dissolved in acetic acid solution by moderate stirring (Marte, MAG–01H, Brazil) at room temperature. The solutions were centrifuged (Fanem, 206 BL, Brazil) and poured onto plexiglas plates. Then, CF were obtained by solvent evaporation and conditioned in desiccators prior to the use [21]. For the adsorption assays, samples of CF were divided in size portions of  $1 \text{ cm} \times 1 \text{ cm}$ .

### 2.3. Characterization techniques

Potentiometric titration method was used to determine the deacetylation degrees of the CP samples [25]. The molecular weights were determined by the viscosimetric method [26]. For the CF samples, the tensile strength and elongation were measured by a texture analyzer (Stable Micro Systems, TA–XT–2i, UK) according to the ASTM procedures [27]. The thicknesses were obtained by a digital micrometer (Insize, IP54, Brazil) with  $0.0010 \text{ mm}$  of resolution. Both, CP and CF samples were characterized by scanning electron microscopy (SEM) (Jeol, JSM–6610LV, Japan) [28] and Fourier transform infrared spectroscopy (FT–IR) (Prestige, 21210045, Japan) [29]. SEM and FT–IR were carried out before and after the adsorption process (in the more suitable conditions), in order to elucidate the interactions of CP and CF with the dye.

### 2.4. Adsorption experiments

Batch adsorption assays were carried out in a jar–test (Nova etica, 218 MBD, Brazil). The RB5 stock solutions ( $2.0 \text{ g L}^{-1}$ ) were prepared and its pH values were adjusted (4.0, 6.0 and 8.0) with buffer disodium phosphate/citric acid solution  $0.1 \text{ mol L}^{-1}$  (this buffer was used to keep the pH constant during all the experiment). Preliminary tests showed that there is not significant interaction between buffer and RB5). All tests were performed by diluting these solutions. The assays were carried out in three steps, with adsorbent dosage of  $500 \text{ mg L}^{-1}$ : in the first step, the effects of pH (4.0, 6.0 and 8.0), deacetylation degree (65%, 75%, 85% and 95%) and type of adsorbent (CP or CF) were evaluated with initial dye concentration of  $100 \text{ mg L}^{-1}$ , temperature at 298 K and stirring rate of 100 rpm, being the solutions agitated until the equilibrium; in the second step, equilibrium isotherms were obtained for CP and CF samples under the more suitable conditions of pH and deacetylation degree. The solutions were agitated (100 rpm) until the equilibrium (the equilibrium was considered after three consecutive measurements with the same dye concentration in liquid phase. For both adsorbents the equilibrium was established within 480 min) at 298, 308, 318 and 328 K. The initial RB5 concentration ranged from 50 to  $500 \text{ mg L}^{-1}$ ; in the third step, kinetic curves were obtained for CP and CF samples under the more suitable conditions of pH, deacetylation degree and temperature. The initial RB5 concentration was  $100 \text{ mg L}^{-1}$  and the stirring rate effect was evaluated (50, 100, 200 and 300 rpm). For all the above tests, the RB5 concentration was determined by spectrophotometry (Biospectro, SP–22, Brazil). Blank assays were performed and experiments were carried out in replicate. The amount of RB5 adsorbed per gram of adsorbent at equilibrium ( $q_e$ ,  $\text{mg g}^{-1}$ ) (Eq. (1)), at any time ( $q_t$ ,  $\text{mg g}^{-1}$ ) (Eq. (2)) and the



**Fig. 1.** Chemical structure of Reactive Black 5 (grey = C, white = H, yellow = S, red = O and blue = N). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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