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Chitosan scaffold as an alternative adsorbent for the removal of hazardous food dyes from aqueous solutions

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ABSTRACT

Hypothesis: The dye adsorption with chitosan is considered an eco-friendly alternative technology in relation to the existing water treatment technologies. However, the application of chitosan for dyes removal is limited, due to its low surface area and porosity. Then we prepared a chitosan scaffold with a megaporous structure as an alternative adsorbent to remove food dyes from solutions.
Experiments: The chitosan scaffold was characterized by infrared spectroscopy, scanning electron microscopy and structural characteristics. The potential of chitosan scaffold to remove five food dyes from solutions was investigated by equilibrium isotherms and thermodynamic study. The scaffold–dyes interactions were elucidated, and desorption studies were carried out.
Findings: The chitosan scaffold presented pore sizes from 50 to 200 μm, porosity of 92.2 ± 1.2% and specific surface area of 1135 ± 2 $m^2 g^{-1}$. The two-step Langmuir model was suitable to represent the equilibrium data. The adsorption was spontaneous, favorable, exothermic and enthalpy-controlled process. Electrostatic interactions occurred between chitosan scaffold and dyes. Desorption was possible with NaOH solution (0.10 mol L^{-1}). The chitosan megaporous scaffold showed good structural characteristics and high adsorption capacities (788–3316 mg g^{-1}).

1. Introduction

Chitosan is a cationic biopolymer obtained from chitin deacetylation, which makes up the exoskeletons of crustaceans, such as, shrimps and crabs [1]. Due to characteristics such as, biocompatibility, hydrophilicity and biodegradability, chitosan is used in a wide range of applications, including dye removal from liquid effluents [2]. In this field, the advantages of chitosan are non-toxicity, cost-effectiveness, high efficiency (because the amino and hydroxyl groups on chitosan chains serve as binding sites) and capacity to development of complex materials [3]. Generally, for dye removal, chitosan is used in powder form [3–5], however, in this form, chitosan has disadvantages, such as, low values of specific surface area and void fraction [6]. These characteristics hinder the diffusion of the dyes within the chitosan structure, limiting the access to the internal adsorption sites [7,8]. These limitations can be overcome by obtaining a chitosan scaffold with high porosity and adsorption capacity.

Dyes are used in the food industries to improve the sensorial, technological and commercial aspects of the products, but, they can cause serious damages to the human health and environment [9,10]. An amount of these dyes is lost during the manufacturing process, resulting in colored effluents, which are characterized by pH values ranging from 5.5 to 8.5 and temperature of approximately 30 °C [2,11]. The inadequate disposal of dye containing effluents into the environment causes limitation in the water reoxygenation ability, reducing the photosynthetic activity of aquatic systems, causing acute and chronic toxicities [2,11,12]. Furthermore, the regulations worldwide regarding the discharge of dye containing effluents are more stringent [11]. In this way, the search for technologies to remove dyes from aqueous solutions has received attention in literature [13].

Several techniques have been used to treat colored effluents, for example oxidation [14], photocatalytic degradation [15], coagulation [16], adsorption [17] and others [2]. Among these, adsorption is a good way to treat colored effluents, because of its advantages compared to the conventional methods, especially from the economical and environmental viewpoints [12,18,19]. In the adsorption field, many adsorbents have been employed to remove dyes from aqueous solutions, including silica microspheres [17], activated carbon [18], agricultural solid wastes [19] and chitosan

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[20]. It is recognized in the literature that the adsorption onto chitosan is an alternative technology to remove dyes from aqueous media [3,4]. The adsorption capacity of chitosan depends on its physical structural parameters, such as, crystallinity, surface area, porosity and particle size [2]. In this way, the development of chitosan scaffold with high values of specific surface area and porosity is an alternative to improve its characteristics as adsorbent.

This study aimed to obtain and characterize a chitosan scaffold in order to apply in the adsorption of hazardous food dyes. The chitosan scaffold was prepared and characterized by Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), and structural characteristics. The potential of chitosan scaffold to remove the hazardous food dyes was investigated by equilibrium isotherms and thermodynamic parameters (ΔG^0, ΔH^0, ΔS^0), at different temperatures (298–328 K). Analyses of Fourier transform infrared spectroscopy, scanning electron microscopy, X-ray mapping and color were performed before and after the adsorption process to elucidate the interactions chitosan scaffold–dyes. Desorption studies were carried out to verify the reuse of the chitosan scaffold.

2. Material and methods

2.1. Preparation and characterization of chitosan scaffold

Chitosan in powder form (molecular weight 150 ± 3 kDa, deacetylation degree of 85 ± 1% and mean diameter of 72 ± 3 μm) was obtained from shrimp (*Penaeus brasiliensis*) wastes, according to the procedures presented in our previous works [21,22]. The chitosan megaporous scaffold was prepared as follows: chitosan sample (2.0 g) was dissolved in 100 mL of 1.0% acetic acid solution under magnetic stirring for 24 h at room temperature. Afterwards, the chitosan solution was homogenized at 10,000 rpm for 5 min (Dremel, 1100-01, Brazil), and it was maintained at 193 K during 48 h in an ultra-freezer (Indrel, IULT 90-D, Brazil). Finally, it was carried out in freeze drying at 219 K for 48 h under vacuum of 44 mmHg (Liobras, L108, Brazil). The sample was conditioned in a desiccator prior to the characterization and use. The mentioned procedures were based in preliminary tests and literature [23,24].

The functional groups on chitosan scaffold were identified by Fourier transform infrared spectroscopy (FT-IR) (Prestige, 21210045, Japan) [25]. Scanning electron microscopy (SEM) (Jeol, JSM-6610LV, Japan) was used to evaluate the textural characteristics [26]. The specific surface area (A_S) was determined by a volumetric adsorption analyzer (Quantachrome Instruments, New Win 2, USA) using the Bennett, Emmet and Teller (BET) method [27]. The solid density (ρ_s) was obtained from the literature [28] and the apparent density (ρ_p) was estimated by mass:volume ratio in an electronic balance (Marte, AY220, Brazil). The porosity (ε_p) and the pore volume (V_p) were calculated by Eqs. (1) and (2), respectively [27]:

$$\varepsilon_p = 1 - \frac{\rho_p}{\rho_s} \quad (1)$$

$$V_p = \frac{1}{\rho_p} - \frac{1}{\rho_s} \quad (2)$$

where ρ_p is apparent density (kg m^{-3}) and ρ_s is solid density (kg m^{-3}).

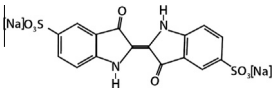
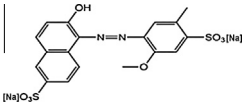
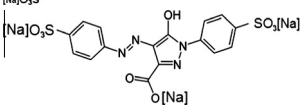
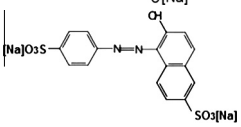
2.2. Food dyes

In this work, five food dyes were used: FD&C blue 2, FD&C red 40, FD&C yellow 5, FD&C yellow 6 and Food red 2. These dyes were supplied by Duas Rodas Ind. (Brazil), with purity higher than 85%, and used without further purification. The characteristics of the food dyes are shown in Table 1. All other reagents were of analytical grade and the experiments were performed with distilled water.

2.3. Equilibrium experiments

The equilibrium isotherms were obtained for the five dyes, at different temperatures (298, 313 and 328 K), and all other experimental conditions were determined by preliminary tests and literature [3,12,29]. Firstly, dye stock solutions (1.0 g L^{-1}) were prepared with distilled water, and the pH was adjusted to 6.0 (this pH is usual for colored effluents [11]) through the buffer disodium phosphate/citric acid solution (0.1 mol L^{-1}), which did not present

Table 1
Characteristics of the food dyes.

Food dye	Color index (C.I.)	Wavelength (λ_{max}) (nm)	Molecular weight (g mol^{-1})	Chemical structure
FD&C blue 2	73,015	610	466.3	
FD&C red 40	16,045	500	496.4	
FD&C yellow 5	19,140	425	534.4	
FD&C yellow 6	15,985	480	452.4	
Food red 2	16,185	521	604.5