

The removal of the indigo carmine dye from aqueous solutions using cross-linked chitosan—Evaluation of adsorption thermodynamics using a full factorial design

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Abstract

A 2³ factorial design was employed to evaluate the quantitative removal of the indigo carmine (IC) dye from aqueous solutions on glutaraldehyde cross-linked chitosan. The variables were chitosan masses of 100 and 300 mg, IC concentrations of 2.0 and 5.0 × 10⁻⁵ mol L⁻¹ and temperatures of 25 and 35 °C. The quantitative and energetic adsorption parameters were analyzed statistically using modeling with bilinear equations. The results indicated that increasing the chitosan mass from 100 to 300 mg decreases the IC adsorption/mass ratio (mol g⁻¹) whereas a temperature increase of 25–35 °C increases it. The principal effect of the IC concentration did not show statistical significance. The factorial experiments demonstrate the existence of a significant antagonistic interaction effect between the chitosan mass and temperature.

The adsorption thermodynamic parameters, namely $\Delta_{\text{ads}}H$, $\Delta_{\text{ads}}G$, and $\Delta_{\text{ads}}S$, were determined for all the factorial design results. Endothermic values were found in relation to the $\Delta_{\text{ads}}H$. The positive $\Delta_{\text{ads}}S$ values indicate that entropy is a driving force for adsorption. The $\Delta_{\text{ads}}G$ values are also significantly affected by important antagonistic and synergistic effects involving all principal and interactive factors. It is concluded that the thermodynamical spontaneity of the IC adsorption parameters are greatly influenced by the interactive factors and not by the temperature changes alone.

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1. Introduction

Chitin is a biodegradable and non-toxic polysaccharide widely spread among marine and terrestrial invertebrates and fungi [1,2]. It is usually obtained from waste materials of the sea food-processing industry, mainly shells of crab, shrimp, prawn and krill. Native chitin occurs in these natural composite materials usually combined with inorganics, proteins, lipids and pigments. Its isolation calls for chemical treatments to eliminate these contaminants [3,4]. By treating crude chitin with aqueous 40–50% sodium hydroxide in the 110–115 °C range chitosan is obtained [5]. Fig. 1 presents a schematic representation of the structures of the partially deacetylated chitosan structure.

Both biopolymers are chemically similar to cellulose, differing only from the R group attached to carbon 2 of the general carbohydrate structure. Chitin and chitosan are closely related since both are linear polysaccharides containing 2-acetamido-2-deoxy-D-glucopyranose and 2-amino-2-deoxy-D-glucopyranose units joined by $\beta(1 \rightarrow 4)$ glycosidic bonds. Due to the features mentioned, the chemical and physical properties of these polymers are different in nature [6]. The fully deacetylated product is rarely obtained due to the risks of side reactions and chain depolymerization [6].

Applications for chitosan currently are found in industrial wastewater treatment and in recovery of feed grade material from food processing plants [7]. Numerous studies have demonstrated the effectiveness of chitosan and derived products in the uptake of metal cations such as lead, cadmium, copper, and nickel and the uptake of oxyanions as well complexed metal ions. In other areas, chitosan has been employed as an excellent adsorbent for

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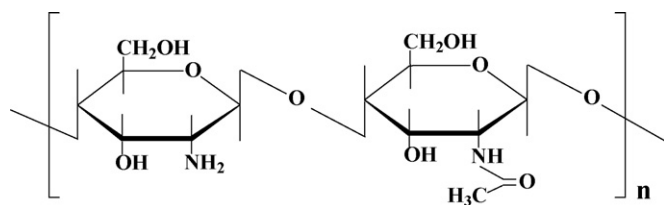


Fig. 1. Structures of partially deacetylated chitosan.

sorption of phenols and polychlorinated biphenyls [8], anionic dyes [9], enzymes [10], and in pollution control, as a chelating polymer for binding harmful metal ions [11].

The extent of metal and/or dye adsorption depends on the source of chitosan, the degree of deacetylation, the nature of the adsorbate molecules, and solution conditions such as the solvent and the adsorption pH value, which makes experimental procedures the only manner to evaluate the interactive chitosan-adsorbate molecule. Since these studies involve a prohibitively large number of experiments, chemometric procedures based on multivariate statistical techniques are employed here. Statistical methods of experimental design and system optimization such as factorial design and response surface analysis have been applied to different adsorption systems because of their capacities to extract relevant information from systems while requiring a minimum number of experiments. Examples of recent applications of the factorial design methodology in adsorption from solution are found, for instance, in the interaction of non-ionic dispersant on lignite particles [12], removal of Ga(III) from aqueous solution using bentonite [13], adsorption of cationic dye on activated carbon beads [14], and optimization of solid-phase extraction and separation of metabolites using HPLC [15]. Since, substantial interactions among the experimental adsorption variables are frequently evidenced, which can predominate over main factor effects, univariate optimization strategies have been shown to be relatively inadequate in these kinds of adsorption studies. Besides economizing experimental effort, multivariate methods are capable of measuring interaction effects on metal adsorption as well as the individual effect of each experimental factor on response properties of interest in the most precise way possible. However, to our knowledge, despite the large number of works concerning adsorption of metals and dyes on chitosan, the role of experimental parameter changes on the thermodynamic of adsorption, such as temperature, amount of chitosan and solute concentration, as well as their interactions, are few and scattered.

In this work, chitosan was cross-linked to improve the chemical and mechanical features of raw chitosan. A 2^3 complete factorial design was used to evaluate the importance of three experimental factors concerning the adsorption quantities and the thermodynamical adsorption of the anionic dye indigo carmine on cross-linked chitosan. The factorial design required the execution of a relatively small number of different experiments. To determine the statistical significance of the effects, duplicate determinations were made for each of these experiments to evaluate experimental error.

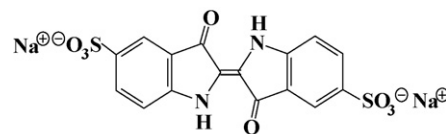


Fig. 2. Chemical structure of indigo carmine dye (IC).

2. Materials and methods

2.1. Materials and preliminary characterization of the raw chitosan sample

Water was used after double-distillation. The indigo carmine dye (disodium salt of 3,3'-dioxo-6,6'-indigo-2,2'-ylidene-5,5'-disulfonate, abbreviated as IC, Merck), whose chemical structure is shown in Fig. 2, was used as-received.

The chitosan powder used was from fresh Norwegian shrimp shells from Primex Ingredients A.S. (Norway/Iceland). The following characterizations were performed (details not shown), in order to check some important aspects, concerning the purity and structural aspects of the chitosan sample. Briefly, the degree of deacetylation was determined by infrared spectroscopy [16]. Solid-state ^{13}C NMR spectroscopy was used to verify the purity of the chitosan sample by the positions and their respective intensities of the ^{13}C absorption peaks, from 20 to 200 ppm [11,16]. The total quantity of nitrogen was determined by the Kjeldhal method.

The raw chitosan powder was cross-linked using a 2% (m/v) glutaraldehyde (VETEC/Brazil) solution as described earlier [1]. Fig. 3 shows a schematic view of the glutaraldehyde-modified chitosan cross-linking reaction. The cross-linked chitosan was sieved and used in the 60–100 mesh range and conditioned in a dark air-free flask, in order to prevent possible interactions between the amine groups and atmospheric CO_2 [17].

The thermogravimetric analyses (TG and DTG) were made using about 10 mg of material, under nitrogen atmosphere from 25 to 600 °C, in a SDT 2960 thermoanalyzer, from TA Instruments. The X-ray analyses were performed with a Rigaku diffractometer, in the 2θ range from 5° to 80° (accumulation rate of 0.02 min $^{-1}$).

2.2. Adsorption experiments

A full 2^3 factorial design was performed to evaluate the importance of the chitosan mass, the IC dye concentration and temperature on the quantity of dye adsorbed. Table 1 summarizes these factors and their respective levels. The adsorptions of

Table 1
Factors and levels used in the 2^3 factorial design study

Factors	Levels	
	(–)	(+)
Quantity of chitosan, Q (mg)	100	300
Concentration of dye, C ($\times 10^{-5}$ mol L $^{-1}$)	2.0	5.0
Temperature, T (°C)	25	35

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