Journal of Molecular Liquids 211 (2015) 425–430

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

# Cyanoguanidine-crosslinked chitosan to adsorption of food dyes in the aqueous binary system

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ARTICLE INFO

*Article history:*
Received 1 June 2015
Received in revised form 17 July 2015
Accepted 25 July 2015
Available online xxxx

*Keywords:*
Binary system
Crosslinked chitosan
Extended Langmuir model

ABSTRACT

The dye adsorption by chitosan is considered an alternative and eco-friendly technology, however, when chitosan structure is chemically modified it can result in a more suitable adsorbent. In this work, cyanoguanidine-crosslinked chitosan (CC-chitosan) was prepared and characterized, and it was applied for the adsorption of Food Blue 2 and Food Yellow 4 in the aqueous binary system. The equilibrium curves showed adequate to fit the extended Langmuir model at different temperatures. The equilibrium results showed that the more suitable conditions for the food dye adsorption in a binary system were at 288 K, and the maximum adsorption capacities were around 595–680 mg $g^{-1}$. Avrami model was the most appropriate to fit the kinetic behavior, and desorption was possible for two cycles. On the basis of FT-IR spectrums, it was shown that cyanoguanidine was successfully inserted on the chitosan polymeric chains. CC-chitosan was an efficient adsorbent in removing dyes from aqueous binary systems.



## 1. Introduction

The food industries consume substantial volume of water, and also they use chemicals and dyes to color its products. Consequently, these industries generate toxic colored effluents, which are the sources of aquatic pollution leading to the limitation of re-oxygenation capacity of the receiving water, decreasing the sunlight penetration, which in turn, disturbs the photosynthetic activity [1,2]. Thus, these effluents should be carefully treated before discharge, and for this purpose, adsorption operation provides significant advantages in relation to the traditional methods, such as, easy operation and application, cost-effectiveness and high efficiency. Generally, the dye adsorption studies are focused on the removal of a specific dye, however, from the practical viewpoint, binary mixtures of dyes in aqueous solutions are more realistic to simulate industrial effluents [3].

In the adsorption field, there is a great availability of adsorbents, becoming the method economically and environmentally feasible, especially when low cost adsorbents are employed [4,5]. Consequently, many researchers have studied the feasibility of using different adsorbents for the removal of various dyes [5–7]. Among these adsorbents, chitin, chitosan or chitosan based materials stand out as good alternatives [5–8].

Chitosan is a polysaccharide composed of glucosamine and N-acetyl glucosamine units, which can be obtained from natural resources, for example, from the deacetylation of crustacean chitin [5,9,10]. Chitosan has some drawbacks, such as, low chemical and mechanical stability, high crystallinity, and low surface area. However, chemically modified chitosan structures can confer different properties and applications for chitosan, resulting in more suitable adsorbents [11]. The crosslinking with cyanoguanidine is a good alternative to improve the chemical stability of chitosan in acid solution, and also increase the adsorption capacity of food dyes [8].

On basis of the literature, there are no studies regarding the adsorption of food dyes using cyanoguanidine-crosslinked chitosan, mainly in binary systems. Then, this work aimed to the application of chitosan crosslinked with cyanoguanidine (CC-chitosan) for the adsorption of food dyes (Food Blue 2 and Food Yellow 4) in the aqueous binary system. Chitosan was obtained from shrimp wastes and was crosslinked with cyanoguanidine. Raw chitosan and CC-chitosan were characterized. The adsorption isotherms were studied at different temperatures by the extended Langmuir model. Pseudo-first order, pseudo-second order and Avrami models were used to investigate the kinetic behavior. In addition, desorption studies were performed.

## 2. Materials and methods

### 2.1. Adsorbate

The commercial food dyes, Food Blue 2 (FB2) (indigoid dye, C.I. 73015, molecular weight 466.3 g $mol^{-1}$, $\lambda_{max}$ 610 nm) and Food Yellow 4 (FY4) (azo dye, C.I. 19140, molecular weight 534.4 g $mol^{-1}$, $\lambda_{max}$ 425 nm) were supplied by a local manufacturer (Plury Chemical Ltda.,

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http://dx.doi.org/10.1016/j.molliq.2015.07.061
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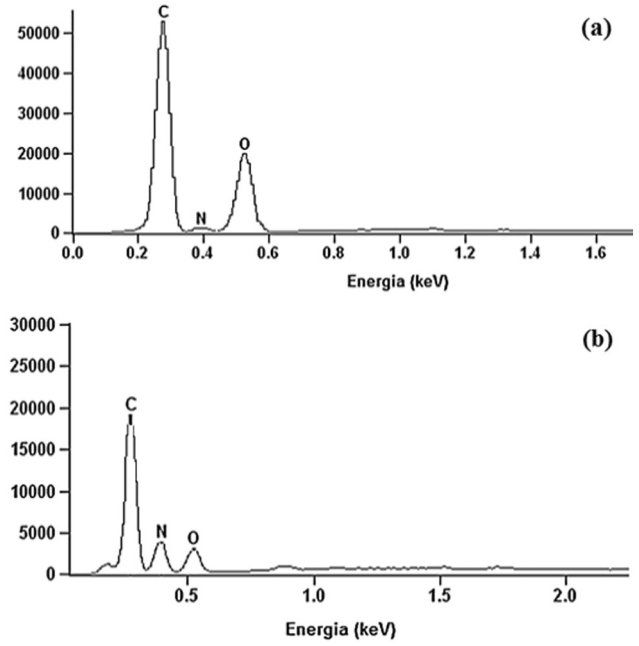


**Fig. 1.** EDS spectrums: (a) raw chitosan and (b) CC-chitosan.

Brazil) with a purity of more than 85%. Distilled water was used to prepare all solutions.

### 2.2. Preparation and characterization of cyanoguanidine-crosslinked chitosan

Chitin was obtained from shrimp wastes (*Penaeus brasiliensis*) by demineralization, deproteinization, deodorization and drying steps [10,12,13]. Chitin was deacetylated to obtain chitosan, which was purified and dried [12,13]. Chitosan samples (deacetylation degree of 85.0 ± 1.5% and viscosity average molecular weight of 150 ± 3 kDa) were sieved, and the particle size of 72 ± 3 μm was used. Detailed procedures can be found in previous works [12–15]. CC-chitosan was prepared as follows: 1.00 g of chitosan was dissolved in 100 mL of hydrochloric acid solution 1% (v/v), and 0.53 g of cyanoguanidine (99.9% Sigma-Aldrich) was added under magnetic agitation. The agitation was carried out for 3 h at 90 °C. Then, the mixture was cooled at room temperature and the cyanoguanidine modified chitosan solution was obtained [16]. The solution was oven dried at 40 °C, and then, CC-chitosan in powder form was obtained.

Raw chitosan and CC-chitosan were characterized according to the elemental composition using the energy dispersive X-ray spectroscopy technique (Jeol, JSM-5800, Japan) [17]. The textural aspects were visualized by scanning electron microscopy (SEM) (Jeol, JSM-6060, Japan) [17]. The possible chemical modifications were assessed by Fourier transform infrared spectroscopy (FT-IR) (Shimadzu, Prestige 21210045, Japan) [18].

### 2.3. Equilibrium experiments

The equilibrium experiments were carried out in a thermostated type Wagner agitator (Fanem, 315 SE, Brazil). CC-chitosan (25 mg, dry basis) was added in flasks with 80 mL of distilled water and the pH was corrected to 3.0 (Marte, MB20, Brazil) through the addition of 10 mL of disodium phosphate/citric acid solution (0.1 mol $L^{-1}$). Thereafter, 10 mL of dye concentrated solutions was added in order to obtain dye solutions' initial concentrations from 50 mg $g^{-1}$ (25 mg $g^{-1}$, for each dye) to 500 mg $g^{-1}$ (250 mg $g^{-1}$, for each dye). The flasks were stirred (100 rpm) at temperatures from 288 to 318 K for 24 h. After the assays, the solutions were filtered (Whatman filter paper) and the remaining dye concentrations were determined by spectrophotometry (Biospectro, SP-22, Brazil). The experimental conditions were determined by preliminary studies. All experiments were carried out in replicate and blanks (dye solutions without adsorbent) were performed. The dye concentrations in the liquid phase (mg $L^{-1}$) for FB2 ($C_A$) and FY4 ($C_B$) in the binary system were determined by Eqs. (1) and (2), respectively [19]:

$$C_A = \frac{(k_{B2}d_1 - k_{B1}d_2)}{(k_{A1}k_{B2} - k_{A2}k_{B1})} \quad (1)$$

$$C_B = \frac{(k_{A1}d_2 - k_{A2}d_1)}{(k_{A1}k_{B2} - k_{A2}k_{B1})} \quad (2)$$

where, $k_{A1}$(0.038), $k_{B1}$ (0.0001), $k_{A2}$ (0.026) and $k_{B2}$ (0.04) are the calibration constants for FB2 and FY4, respectively, and $d_1$ and $d_2$ are the optical densities. The adsorption capacities for Food Blue 2 ($q_{blue}$) and Food Yellow 4 ($q_{yellow}$) (mg $g^{-1}$) were obtained by Eqs. (3) and (4), respectively [20]:

$$q_{blue} = \frac{(C_{A0} - C_A)}{m} V \quad (3)$$

$$q_{yellow} = \frac{(C_{B0} - C_B)}{m} V \quad (4)$$

where $C_{A0}$ and $C_{B0}$ are the initial concentrations of Food Blue 2 and Food Yellow 4 in the liquid phase (mg $L^{-1}$), $V$ is the volume of solution (L) and $m$ is the amount of CC-chitosan (g).

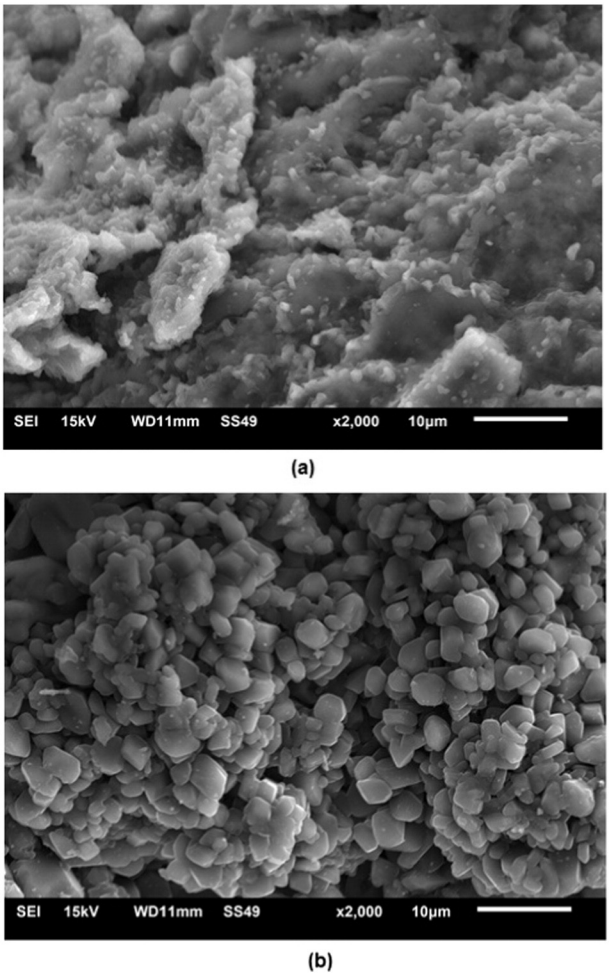


**Fig. 2.** SEM images (×2000): (a) raw chitosan and (b) CC-chitosan.