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CYANOGUANIDINE CROSSLINKED CHITOSAN FOR THE ADSORPTION OF FOOD BLUE 2 IN SIMPLE AND BINARY SYSTEMS

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ABSTRACT: Studies are needed to improve the potential of chitosan as an adsorbent, for example, changes in chemical groups by the insertion of adsorption sites. In this work, chitosan was modified with cyanoguanidine to improve its properties regarding to the adsorption of Food Blue 2 in simple and binary systems. The effects of cross-linking and pH (2-8) on the adsorption of Food Blue 2 in simple and binary (Food Blue 2+Food Yellow 4) systems were investigated. Fourier transform infrared spectroscopy showed that cyanoguanidine was successfully inserted on the chitosan polymeric chains. The crosslinked chitosan presented higher potential that unmodified chitosan for the adsorption Food Blue 2 in simple and binary systems. The adsorption capacities and percentages of removal were higher than 480 mg/g and 94% in simple system and higher than 430 mg/g and 90% in binary system.

KEYWORDS: binary system; chitosan; cyanoguanidine.

1. INTRODUCTION

Many industries employ dyes and pigments to color their products. However, these dyes have been specified to cause hyperactivity in children, and urticaria, asthma, purpura and eczema. Besides these, possess an azo-structure which is carcinogenic. The environmental disposal of untreated colored effluents lead to a coloration of water bodies resulting in an aesthetic problem, limitation of re-oxygenation capacity of the receiving water, decreases in sunlight penetration which in turn disturbs photosynthetic activity (Gupta and Suhas, 2009). For the effluents treatment containing dye , some biological and physicochemical process, such as, electro-coagulation, ozonation, photocatalysis, membrane filtration, activated sludge, adsorption and trickling filters are used (Saratale *et al.*, 2011; Mezohegyi *et al.*, 2012).

Adsorption has been outstanding compared to the conventional methods due to its simplicity and high efficiency, as well as the availability of a wide range of adsorbents (Crini and Badot, 2008). Consequently, many researchers have studied the feasibility of using low-cost substances for the removal of various dyes (Crini and Badot, 2008; Gupta and Suhas, 2009; Srinivasan and Viraraghavan, 2010; Salleh *et al.*, 2011). Among these adsorbents, chitosan is a good alternative (Crini and Badot, 2008; Wan Ngah *et al.*, 2011).

Chitosan is used in order to remove dyes from effluents in adsorption systems, due to its high adsorption capacities and it is obtained from natural resources (Dotto and Pinto, 2011; Dotto *et al.*, 2013) . However, studies are needed to improve the chitosan potential as an adsorbent, for example, changes in chemical groups for the insertion of the adsorption sites. Furthermore, most of the dye adsorption studies using chitosan are focused on the removal of a specific dye. However, from the practical viewpoint, binary mixtures are more realistically to simulate industrial effluents (Gonçalves *et al.*, 2014).

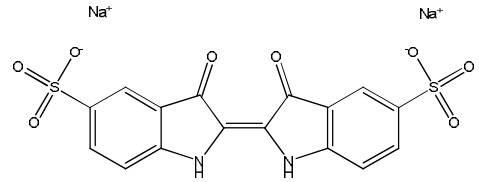
This work aimed to evaluate the applicability of chitosan sample (CS) and chitosan crosslinked with cyanoguanidine (C-CY) for the

adsorption of Food Blue 2 in simple and binary systems.

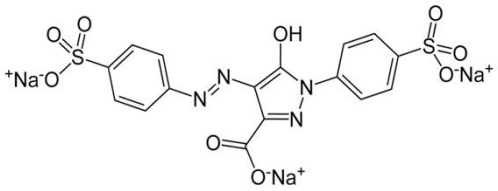
2. MATERIALS AND METHODS

2.1. Adsorbate

Two food dyes were used in this study, Food Blue 2 (indigoid dye, C.I. 73015, molecular weight 466.3 g/mol, λ_{max} 480 nm) and Food Yellow 4 (Azo dye, C.I. 19140, molecular weight 534.4 g/mol, λ_{max} 425 nm). These dyes were supplied by a local manufacturer (Plury Química Ltda.), with purity higher than 85%. The chemical structures of the dyes are shown in Figure 1.



(a)



(b)

Figure 1. Chemical structure of the dyes: (a) Food Blue 2 and (b) Food Yellow 4.

2.2. Preparation of Cyanoguanidine Crosslinked Chitosan

Chitosan samples (CS) in powder (molecular weight of 150±3 kDa, deacetylation degree of 75±1% and particle size of 72±3 µm) was obtained from shrimp wastes (*Penaeus brasiliensis*) according our previous works (Weska *et al.*, 2007; Piccin *et al.*, 2009; Dotto *et al.*, 2011).

Cyanoguanidine crosslinked chitosan (C-CY) was the prepared as follows: 1.00 g of chitosan was dissolved in 100 mL of 1% (v/v) hydrochloric acid solution, and 0.53 g of cyanoguanidine (99.9% sigma-Aldrich) was added under 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. The solution was oven dried at 40 °C, and a powder was obtained (Wang *et al.*, 2013).

To verify the insertion of the cyanoguanidine on the chitosan polymeric chains, Fourier transform infrared spectroscopy (FT-IR) (Prestige, 21210045, Japan) was performed for CS and C-CY.

2.3. Adsorption Experiments

Adsorbent samples (CS or C-CY) (250 mg) were added to 80 mL of water, and it had the pH corrected to 2,3,4,5,6,7 and 8 by 10 mL of buffer solutions (phosphate/citric acid 0.1 mol/L). The buffered dye solutions containing 1 g/L were added to the adsorbent solutions and completed to 200 mL (in order to obtain initial dye concentration of 120 mg/L). The solutions were placed in 500 mL flasks and agitated at 100 rpm using a thermostated type Wagner agitator (Fanem, 315 SE, Brazil) for 24 h at 298 K. The same procedure was used for the binary mixture, but, in this case, the initial dye concentration was 60 mg/L for each dye.

The chitosan and adsorbed dyes were removed from the liquid through filtration with Whatmann filter paper 40, which showed no interaction with the dyes and the dyes concentration was determined by spectrophotometry (Biospectro, SP–22, Brazil). All experiments were carried out in replicate (n = 3 for each experiment) and blanks were performed.

In the simple system, the Food Blue adsorption capacity (q) (mg/g) and the percentage of removal ($\%R$) were calculated by Equations 1 and 2, respectively:

$$q = \frac{C_0 - C_f}{m} V \quad (1)$$

$$\%R = \frac{C_0 - C_f}{C_0} 100 \quad (2)$$

where, C_0 the initial dye concentration (mg/L), C_f the final concentration of Food Blue 2 (mg/L), m is the adsorbent amount (g), and V is the volume of solution (L).

For the binary system, the final concentration (mg/L) of Food Blue 2 (C_f) was calculated by Equation 3 (Mahmoodi *et al.*, 2011):

$$C_f = \frac{k_{B2} d_1 - k_{B1} d_2}{k_{A1} k_{B2} - k_{A2} k_{B1}} \quad (3)$$

where, k_{A1}, k_{B1}, k_{A2} and k_{B2} are the calibration constants for: Food Blue 2, Food Yellow 4, Food Blue 2 at 480 nm and Food Yellow 4 at 425 nm, respectively, d_1 and d_2 are the absorbance values.

3. RESULTS AND DISCUSSION

3.1. FT-IR Analysis

Figure 2 shows the FT-IR spectrums of (a) pure chitosan (CS) and (b) Cyanoguanidine crosslinked chitosan (C-CY).

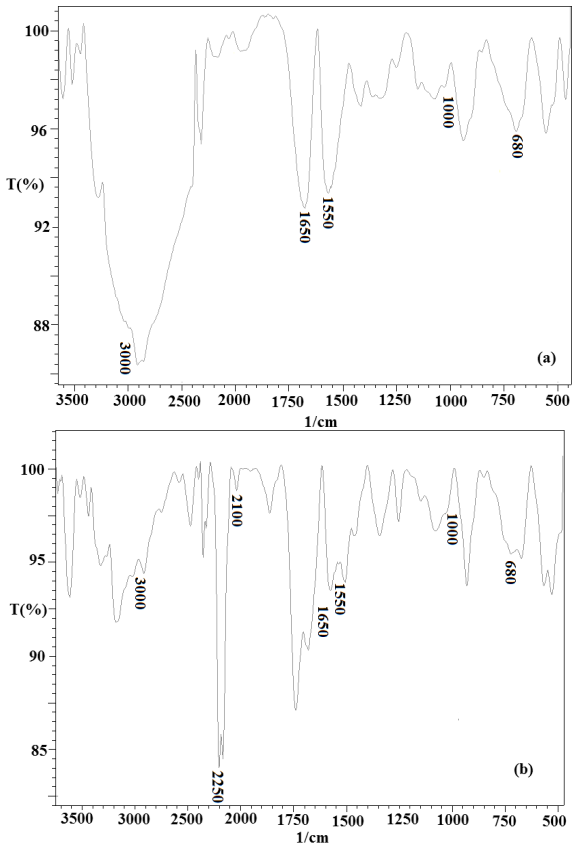


Figure 2. FT-IR spectrums of (a) pure chitosan (CS) and (b) Cyanoguanidine crosslinked chitosan (C-CY).

The characteristic bands of chitosan can be observed in Figure 2 (a). The broad band around 3000 cm^{-1} can be assigned to the typical N–H and O–H stretchings (Dotto *et al.*, 2013). Stretching vibrations of C=O were observed at 1650 cm^{-1}. At 1550 cm^{-1}, the C–N stretching vibration of amide is observed. The band around 1000 cm^{-1} could be assigned to a C–O stretching. It can be seen at 680 cm^{-1}, the angular deformation of H–N–H (Cadaval Jr. et al., 2013). After the modification with cyanoguanidine (Figure 2 (b)), an intense band around 2250 cm^{-1} appeared. This is a bond of doped quaternary ammonium salt formed (Zhao *et al.*, 2012). A little C≡N band of cyanoguanidine appeared at 2100 cm^{-1}. Furthermore, the broad band around 3000 cm^{-1} decreased due to the insertion of cyanoguanidine into the amino group of chitosan. Based on these statements, it can be seen that cyanoguanidine was successfully inserted on the chitosan polymeric chains according to the mechanism proposed by Wang et al. (2013):

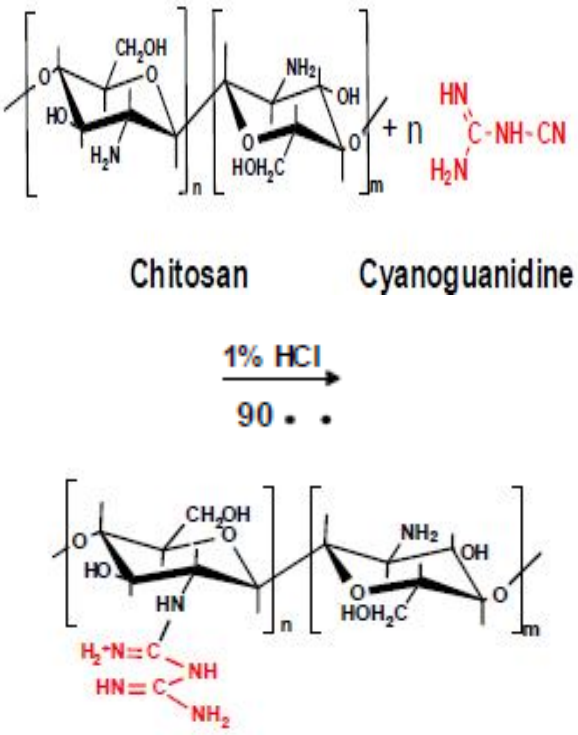


Figure 3. Cross-linking reaction of chitosan/cyanoguanidine proposed by Wang et al. (2013).

From Figure 3, it can be observed that the modification with cyanoguanidine provide more NH and NH_2 groups, which can be available and protonated for interaction with the anionic dye Food Blue 2.

3.2. Effects of pH and Cross-linking

Figure 4 shows the pH effect on the adsorption of Food Blue 2 by pure chitosan (CS) and Cyanoguanidine crosslinked chitosan (C-CY) in simple system.

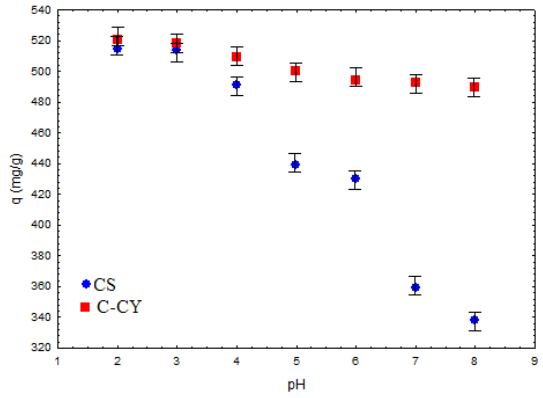


Figure 4. pH effect on the adsorption of Food Blue 2 by CS and C-CY in simple system.

Figure 4 shows clearly that the pH increase caused a strong decrease (from 520 to 340 mg/g) in the adsorption capacity of Food Blue 2 onto CS. This fact is explained because at lower pH values, the CS amino groups are more protonated to interact with the sulfonated groups (Figure 1 (a)) of Food Blue 2 (Crini and Badot, 2008; Dotto and Pinto, 2011). However, for the adsorption onto C-CY, the pH increase from 2 to 8 caused a decrease of only 6.0%. This reflected a decrease in the percentage of removal from 99.9 to 94.1%. This probably occurred because the insertion of more N groups on the chitosan structure due to the cross-ling reaction, which allows the interaction with Food Blue 2, even at highest pH values. These results showed that the modification of chitosan with cyanoguanidine improved its adsorbent characteristics for Food Blue 2 in simple systems, since high values of q and $\%R$ were found in a wide range of pH.

3.3. Adsorption in Binary System

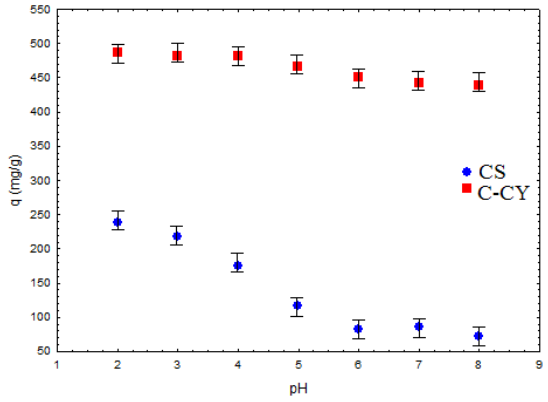


Figure 5. pH effect on the adsorption of Food Blue 2 by CS and C-CY in binary system.

Figure 5 shows the pH effect on the adsorption of Food Blue 2 by pure chitosan (CS) and Cyanoguanidine crosslinked chitosan (C-CY) in binary system (Food Blue 2+Food Yellow 4).

It was found that in the binary system (Figure 5), CS presented maximum adsorption capacity of about 250 mg/g (at pH=2), i.e., a reduction of 52% in relation to the simple system (Figure 4) occurred. This is explained because in the binary system a competition between Food Blue 2 and Food Yellow 4 occurred. So, the adsorption sites were occupied for both dyes. On the other hand, even in a binary system, C-CY maintained its adsorption capacity in the range of 450-500 mg/g and the Food Blue 2 percentage of removal remained from 90 to 99.9%.This is a result of the new adsorption sites on the chitosan structure, which are able to adsorb Food Yellow 4 without harming the adsorption of Food Blue 2.

4. CONCLUSION

In this research, chitosan was modified with cyanoguanidine in order to improve its adsorption characteristics in relation to the Food Blue 2 in simple and binary systems. The results revealed that cyanoguanidine was successfully inserted on the chitosan polymeric chains. The modification of chitosan with cyanoguanidine improved its adsorbent characteristics for Food Blue 2 in simple systems, since high values of q (490-520 mg/g) and $\%R$ (94.1-99.9%) were found in a wide range of pH. Even in a binary system, C-CY maintained its adsorption capacity and the Food Blue 2 percentage of removal remained from 90 to 99.9%.

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