Adsorption of FD&C Red No. 40 by chitosan: Isotherms analysis


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1. Introduction

Many industries, especially food and textile industries, often use dyes and pigments to color their products. Although not strongly hazardous, dyes that possess an azo-structure can be reduced to aromatic amines by the intestinal microflora, which has been found to be carcinogenic. Also, these dyes have been reported to cause hyperactivity in children, and urticaria, asthma, purpura and eczema (McCann et al., 2007; Moutinho et al., 2007; MacCara et al., 2007). Biological and physicochemical processes, such as electro-coagulation, ozonation, photocatalysis, membrane filtration, activated sludge and trickling filters have been employed for the treatment of dye-containing wastewater (Mane et al., 2007). The equilibrium adsorption isotherm is of fundamental importance in optimizing the design of an adsorption system for dye adsorption. Moreover, the shape of an isotherm not only provides information on the affinity of the dye molecules for adsorption, but also reflects the possible mechanism for adsorbing dye molecules.
adsorption isotherm technique. The effects of factors such as pH, particle size, deacetylation degree and temperature were investigated. The experimental data were fit by Freundlich, Langmuir and Redlich–Peterson isotherms equations in order to determine the best-fitting isotherm model.

2. Materials and methods

2.1. Materials

The commercial dye (FD&C Red No. 40) was supplied by a local manufacturer, Plury Chemical Ltda., with a labeled purity of more than 85%. All other utilized reagents were of analytical-reagent grade. Distilled water was used to prepare all solutions.

2.2. Chitosan production methodology

The raw material used for chitin production was shrimp waste, which was obtained from fishery local industries. Chitin was obtained by demineralization step, through treatment with hydrochloric acid solution 25 mL L\(^{-1}\) (2.5 L of acid solution for each kilogram of material mass), for 2 h; deproteinization step, through treatment with sodium hydroxide solution 50 g L\(^{-1}\) (5.0 L of hypochlorite solution for each kilogram of material mass), for 3 h, which were carried out in an agitated tank and at room temperature, according to Weska et al. (2007).

Deacetylation was carried out in a reactor, with heating and agitation (50 rpm), where 2 L of sodium hydroxide solution (0.425 kg L\(^{-1}\)) was added to 30 g of chitin. The reaction temperature was 130 °C and the deacetylation was carried out at 5, 25 and 100 min, in order to obtain 42 ± 5%, 64 ± 3% and 84 ± 3% of deacetylation, respectively. Only chitosan samples obtained at 100 min of deacetylation reaction were purified according to the method described by Weska et al. (2007). Deacetylation degree was determined by the potentiometric titration method described by Broussignac, reported by Tolaimatea et al. (2000), and these experiments were carried out in triplicate.

All chitosan samples were dried in a tray dryer till commercial moisture content (7.0–10.0%, wet basis) according to Batista et al. (2007). They were ground by using a mill (Wiley Mill Standard model No. 03, Philadelphia, USA) and were sieved until the discrete particle size ranged 0.10 ± 0.02, 0.18 ± 0.02 and 0.26 ± 0.02 mm.

2.3. Equilibrium adsorption methodology

The equilibrium adsorption isotherms were determined using batch studies at different temperature conditions (15, 25 and 35 °C). Adsorbent material chitosan (0.05 g) was added to 100 mL of water. The pH of chitosan solutions was adjusted to 5.0 at 7.0 by 10 mL of buffer solutions of citric acid/sodium diphosphate (0.1 N each) and equilibrium pH was measured after the adsorption process. Afterwards, different volumes (2–40 mL) of the buffer dye solution containing 2 g L\(^{-1}\) were added to the adsorbent solutions and completed to 200 mL with distilled water. The solutions were placed in 500 mL flasks and agitated at 100 rpm using a thermostated type Wagner agitator (FANEM model 315 SE, São Paulo, Brazil). The experiments were carried out in replicate.

Samples were analyzed every 8 h. The equilibrium was judged to have been attained when the dye concentration in the liquid did not present difference between three consecutive measures. The chitosan and adsorbed dye were removed of liquid through a filtration with Whatmann Filter Paper No. 40, which did not present interaction with the dye, and the dye concentration was determined by spectrophotometer (QUIMIS mod Q108 DRM, São Paulo, Brazil) at 500 nm. The adsorption capacity \(q_e\) was determined according to Eq. (1), where \(q_e\) is dependent of the added mass chitosan \(m\).

\[
q_e = \frac{C_i - C_e}{m} V
\]  

(1)

2.4. Isotherms analyses

Adsorption isotherms are described in many mathematical forms, some of which are based on a simplified physical model of adsorption and desorption, while others are purely empirical and are intended to correlate the experimental data. Various isotherm equations, such as Langmuir (Eq. (2)), Freundlich (Eq. (3)) and Redlich–Peterson (Eq. (4)) models, have been used to describe the equilibrium characteristics of adsorption. These models are shown in Table 1.

A basic assumption of the Langmuir theory is that adsorption takes place at specific homogeneous sites within the adsorbent, and once a dye molecule occupies a site, no further adsorption can take place at that site. Another essential characteristic of the Langmuir isotherm can be expressed by the separation factor or equilibrium factor \(R_L\) according to Eq. (5).

\[
R_L = \frac{1}{1 + K_L C_e}
\]  

(5)

The Freundlich isotherm is used for a heterogeneous surface energy system and for the description of multilayer adsorption with interaction between adsorbed molecules (Annadurai et al., 2007; Mittal et al., 2007; Namasiyam and Kavitha, 2002). The Redlich–Peterson isotherm is used to represent adsorption equilibrium over a wide concentration range, and can be applied either in homogeneous or in heterogeneous systems due to its versatility.

The parameters values of models were calculated by linearization method, and the experimental data were compared with the calculated values by the models from the mean relative error

<table>
<thead>
<tr>
<th>Nomenclature</th>
<th>(q_e)</th>
<th>adsorption capacity (\text{mg g}^{-1})</th>
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<tr>
<td>(q_{\text{m}})</td>
<td>maximum adsorption capacity in the monlayer (\text{mg g}^{-1})</td>
<td></td>
</tr>
<tr>
<td>(R_L)</td>
<td>separation factor or equilibrium factor defined in Eq. (5)</td>
<td></td>
</tr>
<tr>
<td>(V)</td>
<td>volume of solution (\text{L})</td>
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Greek symbol

\(\beta\) exponent in Eq. (4) which lies between 1 and 0
and in order to analyze the fit for each model the coefficient of determination \( R^2 \) was considered. The software Statistic 6.0 (Statsoft, USA) was used to adjust the models (Eqs. (2)–(4)) to the experimental data.

### 3. Results and discussion

The adsorption capacity \( (q_e) \) values (Eq. (1)) versus concentration equilibrium \( (C_e) \) values are presented in Figs. 1–4.

**Fig. 1** shows the equilibrium adsorption data of FD&C Red No. 40 for three different systems' equilibrium pH, at 25°C, particle size in the range of 0.10 ± 0.02 mm and deacetylation degree of 84 ± 3%.

The initial system pH is changed to equilibrium pH during the adsorption process because under acidic conditions hydrogen atoms (H\(^+\)) in the solution may protonate the amine groups (–NH\(_2\)) of chitosan (Sakkayawong et al., 2005). **Fig. 1** shows that the adsorption capacity increases significantly when decreasing the pH value from 7.4 to 6.6 and 5.7. In aqueous solutions, the dye was dissolved and converted to anionic dye ions composed by the sulfonate group (–SO\(_3^-\)). The increase in adsorption capacity under acidic conditions occurs because of protonation of the chitosan’s amino groups and its electrostatic interaction with the dye’s sulfonate groups. Similar pH effects have also been observed in the adsorption of Remazol Black No. 13 (Annadurai et al., 2007), Reactive Red No. 141 (Sakkayawong et al., 2007) by chitosan, Reactive Red No. 189 by cross-linked chitosan beads (Chiou and Li et al., 2003) and Congo Red by chitosan hydrobeads (Chatterjee et al., 2007). Under the acidic conditions the shape of the isotherms appears rectangular because at low equilibrium dye concentrations \( C_e \), the equilibrium adsorption densities \( q_e \) of chitosan are almost similar as those at high \( C_e \), which favors reductions even at low concentrations with high equilibrium adsorption densities \( q_e \). However, this phenomenon does not occur under neutral pH conditions. The rectangular forms of the adsorption isotherms of Reactive Red No. 189 by chitosan in acidic conditions were observed by Chiou and Li (2003).

**Fig. 2** shows the effect of adsorbent particle size on FD&C Red No. 40 for particles in three different size ranges in the following conditions: equilibrium pH of 6.6, temperature of 25°C and deacetylation degree of 84 ± 3%.

The decrease in the particle size causes an increase in the numbers of adsorption sites available on the adsorbent surface, due to its larger superficial area. That does with that more dye is adsorbed in the surface of the adsorbent, increasing the adsorption capacity. According to Annadurai et al. (2007) as there exists a linear relationship between the capacity of adsorption and the superficial area, the dye is not capable of penetrating the interior of the adsorbent. This fact is not observed in this work, demonstrating that the adsorption not only happens on the surface, but also exists inside the adsorbent. Similar results were observed by Guibal et al. (2003) for the adsorption of the color Acid Green No. 25 for quitosana and by Chiu and Li (2002) for the adsorption of the red color I reactivate No. 189 for quitosana with crossed connection.
crease of deacetylation degree (Fig. 3). The increase of deacetylation degree involved an increase in the relative proportion of amine groups, which were able to be protonated, favoring dye adsorption; however, the variation in adsorption properties was not proportional to the deacetylation degree. A similar increase in the adsorption capacity was observed by Sakkayawong et al. (2005).

Fig. 4 shows the effect of temperature on the adsorption of dye FD&C No. 40 by chitosan at three different temperatures (15, 25 and 35 °C) in the following conditions: equilibrium pH of 6.6, particle size range of 0.10 ± 0.02 mm and deacetylation degree of 84 ± 3%.

Rectangle shapes of the isotherms at 15 and 25 °C, and logarithm shape of the isotherm at 35 °C are observed in Fig. 4. With increase in temperature from 15 to 35 °C, the interaction between solvent and solid surface was probably reduced, however a higher number of adsorption sites were exposed. In addition, elevated temperatures caused an increase in free volume, this fact also favored dye adsorption. The temperature increase caused a decrease in the adsorption at low concentrations, therefore the physical interaction between the dye and the chitosan weakened due to decrease in hydrogen bonds and van der Waals interactions. Thus, the temperature increase caused a decrease in the adsorption capacity at low equilibrium concentrations and an increase at high equilibrium concentrations, as observed by Anjos et al. (2002) for the adsorption of Indigo Carmine by chitosan and Chatterjee et al. (2007) for the adsorption of Congo Red by chitosan hydrobeads. All this indicates that the adsorption of FD&C No. 40 by chitosan is controlled by an exothermic process.

3.1. Equilibrium isotherm analysis

The Langmuir, Freundlich and Redlich–Peterson isotherm parameters, their respective coefficients of correlation ($R^2$) and mean relative error values (MRE) are shown in Table 2.

Coefficient of determination ($R^2 > 0.95$) and mean relative error (MRE $< 10\%$) values calculated in Table 2 demonstrate that the Langmuir and Redlich–Peterson models presented good fit with the experimental data. However, it was not verified with the Freundlich model. The Langmuir model can be more useful to describe the adsorption process of FD&C No. 40 by chitosan, due to the fact that the Redlich–Peterson isotherm parameters cannot be determined by linearization because it presented three parameters (Wong et al., 2004).

Table 2 shows that the maximum monolayer adsorption ($q_m$) of FD&C Red No. 40 obtained by chitosan was 529.0 mg g$^{-1}$, which is observed in the following conditions: equilibrium pH of 6.6, particle size range of 0.10 ± 0.02 mm and temperature of 35 °C.

The adsorption capacity is influenced by various factors, such as the chemical structure of the dye and adsorbent, molecule size and origin of adsorbent. Wu et al. (2000) compared the adsorption capacities of dye Reactive Red No. 222 by chitosan produced from crab, lobster and shrimp wastes and the monolayer adsorption capacities were determined to be 293, 398 and 494 mg g$^{-1}$, respectively. Wong et al. (2004) analyzed the adsorption of different dyes, Acid Green No. 25, Acid Orange No. 10, Acid Orange No. 12, Acid Red No. 18, Acid Red No. 73 by chitosan, and monolayer adsorption capacities were determined as 645.1, 922.9, 973.3, 693.2, 728.2 mg g$^{-1}$, respectively. In this study, the adsorption occurs preferentially by ionic interaction in between the sulphonate group of the dye and the amino group of the chitosan, and the
number of sulphonate groups and the molecule size of the dye are among the factors that limit the adsorption capacity.

Adsorption of Congo Red by activated carbon (Namisivayam and Kavitha, 2002), banana peel and orange peel (Annadurai et al., 2002), and chitosan hydrobeads (Chatterjee et al., 2007) was determined to be 5.1, 18.2, 14.0 and 93.7 mg g⁻¹, respectively. This report that different absorbents have different adsorption capacities, and when compared to some data in the literature, the chitosan studied in this work presented good adsorption capacity of FD&C Red No. 40 at acidic pH conditions.

The K₁ parameter of the Langmuir model, which corresponds to the inverse of the liquid phase concentration at which adsorption capacity is 0.5 qₘ, in relation to increase in pH, particle size and temperature and the decrease in deacetylation degree, suggests that monolayer saturation (qₘ) values were reached with higher equilibrium concentrations (Cₑ), which results in the presence of larger amount of dye in the final solution.

Values of separation coefficients (Rₛ), adsorption intensity (n) and exponent 𝜆 of the Langmuir, Freundlich and Redlich–Peterson models, respectively, demonstrate that the reduction in pH, particle size and temperature, and the increase in deacetylation degree, are favorable to the adsorption of dye FD&C Red No. 40 by chitosan.

4. Conclusion

Studies on adsorption isotherms were carried out for the adsorption of FD&C Red No. 40 by chitosan at different pH, temperature, particle size and deacetylation degree conditions. Decrease in pH from 7.5 to 6.6 resulted in an increase in over 80% on the adsorption capacity. Particle size decrease and deacetylation degree increase contributed to the increase in the adsorption capacity. Temperature caused change in the isotherm shape, and low temperatures were better for concentrations lesser than 100 mg L⁻¹, and the opposite occurred for higher concentrations. Correlation coefficient values (R² > 0.95) and mean relative error (MRE < 10%) demonstrated that Langmuir and Redlich and Peterson isotherms showed better fit than the Freundlich equation. Maximum monolayer adsorption value of 529.0 mg g⁻¹, was observed at 35 °C, particle size range of 0.10 ± 0.02 mm, equilibrium pH of 6.6 and deacetylation degree of 84 ± 3%.

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