



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

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### ABSTRACT

The adsorption of azobenzene FD&C Red No. 40 (C.I. 16035) from aqueous solutions by chitosan was studied through adsorption isotherms. The effects of pH (5.7, 6.6 and 7.5), particle size ranges ( $0.10 \pm 0.02$ ,  $0.18 \pm 0.02$  and  $0.26 \pm 0.02$  mm), deacetylation degree ( $42 \pm 5\%$ ,  $64 \pm 3\%$  and  $84 \pm 3\%$ ) and temperature (25, 35 and 45 °C) were investigated. Langmuir, Freundlich and Redlich–Peterson (R–P) adsorption models were applied in order to describe the experimental isotherms and isotherm constants. Coefficients of determination ( $R^2 > 0.95$ ) and mean relative error (MRE  $< 0.10$ ) values showed that Langmuir and R–P models presented better fit with the experimental data. The maximum monolayer adsorption value has been found to be  $529 \text{ mg g}^{-1}$ , at pH 6.6, temperature 35 °C, particle size range  $0.10 \pm 0.02$  mm, and deacetylation degree  $84 \pm 3\%$ .

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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 that can be reduced to aromatic amines by the intestinal microflora, have 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, 1982). The azobenzene FD&C Red No. 40 (C.I. 16035) is an azobenzene artificial dye ( $\text{C}_{18}\text{H}_{14}\text{N}_2\text{O}_8\text{S}_2\text{Na}_2$ , molecular weight of  $496.4 \text{ g mol}^{-1}$ ); it is widely used for dyeing sweets, chewing gums, jellies, puddings, juices, jams, mustard, sodas, drugs and cosmetics.

The environmental disposal of untreated effluents to its surroundings often leads to the following consequences: coloration of water bodies with the creation of an aesthetic problem, limitation of reoxygenation capacity of the receiving water, decrease in sunlight penetration which in turn disturbs photosynthetic activities in the aquatic system, and chronic and acute toxicities (Arami et al., 2006; Kadirvelu et al., 2005). 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 adsorption process provides an attractive alternative treatment, especially if the adsorbent is inexpensive and readily available. Activated carbon is the most widely used adsorbent for this purpose because of its high capacity for adsorption, but its use is limited due to its high initial and regeneration

cost (Mane et al., 2007). Consequently, many investigators have studied the feasibility of using low-cost substances for the removal of various dyes, such as sawdust (Garg et al., 2003), rice husk and ash (Mane et al., 2007), hen feathers (Mittal et al., 2007), bentonite (Turabik, 2008) and peat (Sun and Yang, 2003).

Chitin,  $\beta$ -(1 $\rightarrow$ 4)*N*-acetyl-D-glucosamine, is a linear polysaccharide which is found naturally in the exoskeletons of insects, shells of crustaceans, and fungal cell walls (Ravi Kumar, 2000). Chitin can be converted into chitosan by enzymatic means or by alkali deacetylation, with the latter being the most utilized method (Weska et al., 2007). Shrimp shell waste is a plentiful waste from Brazil seafood processing industries. Therefore, these wastes are of low cost and suitable for producing chitosan polymer. During the course of chitin deacetylation, part of the polymer *N*-acetyl links are broken, with the formation of D-glucosamine units, which contain a free amine group. The amino and hydroxyl functional groups present high potentials for the adsorption of dyes (Annadurai et al., 2007; Sakkayawong et al., 2007; Uzun and Güzel, 2005; Wong et al., 2004), metal ions (Franco et al., 2004; Gamage and Shahidi, 2007; Ngah et al., 2006) and proteins (Casal et al., 2006; Xu et al., 2001; Wibowo 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 (Annadurai et al., 2007; Mane et al., 2007; Turabik, 2008; Wong et al., 2004).

The aim of the present work is to explore the possibility of utilizing partially deacetylated chitin and chitosan for the adsorptive removal of FD&C Red No. 40 from aqueous solutions through an

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### Nomenclature

$a_R$	Redlich–Peterson constant in Eq. (4), $((\text{g mg}^{-1})(\text{L mg}^{-1})^{1/\beta})$	$q_e$	adsorption capacity $(\text{mg g}^{-1})$
$C_e$	equilibrium dye concentration in solution, $(\text{mg L}^{-1})$	$q_m$	maximum adsorption capacity in the monolayer $(\text{mg g}^{-1})$
$C_i$	initial dye concentration in solution, $(\text{mg L}^{-1})$	$R_L$	separation factor or equilibrium factor defined in Eq. (5)
$K_F$	Freundlich constant defined in Eq. (3), $((\text{mg g}^{-1})(\text{L mg}^{-1})^n)$	$V$	volume of solution (L)
$K_R$	Redlich–Peterson constant defined in Eq. (4), $(\text{L mg}^{-1})$	<i>Greek symbol</i>	
$K_L$	Langmuir constant defined in Eq. (2), $(\text{L mg}^{-1})$	$\beta$	exponent in Eq. (4) which lies between 1 and 0
$m$	mass of the dry chitosan, (g)		
$n$	sorption intensity defined in Eq. (3)		

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  $25 \text{ mL L}^{-1}$  (2.5 L of acid solution for each kilogram of material mass), for 2 h; deproteinization step, through treatment with sodium hydroxide solution  $50 \text{ g L}^{-1}$  (3.0 L of hydroxide solution for each kilogram of material mass), for 2 h; and deodorization step, through treatment with sodium hypochlorite solution  $3.6 \text{ mL L}^{-1}$  (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 ( $0.425 \text{ kg L}^{-1}$ ) was added to 30 g of chitin. The reaction temperature was  $130^\circ\text{C}$  and the deacetylation was carried out at 5, 25 and 100 min, in order to obtain  $42 \pm 5\%$ ,  $64 \pm 3\%$  and  $84 \pm 3\%$  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  $0.10 \pm 0.02$ ,  $0.18 \pm 0.02$  and  $0.26 \pm 0.02 \text{ mm}$ .

### 2.3. Equilibrium adsorption methodology

The equilibrium adsorption isotherms were determined using batch studies at different temperature conditions (15, 25 and  $35^\circ\text{C}$ ). Adsorbent material chitosan ( $0.05 \text{ g}$ ) 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  $2 \text{ g L}^{-1}$  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)

$$q_e = \frac{C_i - C_e}{m} V \quad (1)$$

### 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).

$$R_L = \frac{1}{1 + K_L C_e} \quad (5)$$

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; Namasivayam 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 1**  
Different isotherm models used to describe adsorption data.

Isotherm	Equation
Langmuir	$q_e = \frac{K_L q_m C_e}{1 + K_L C_e}$ (2)
Freundlich	$q_e = K_F C_e^{1/n}$ (3)
Redlich–Peterson	$q_e = \frac{K_R C_e}{1 + a_R C_e^\beta}$ (4)

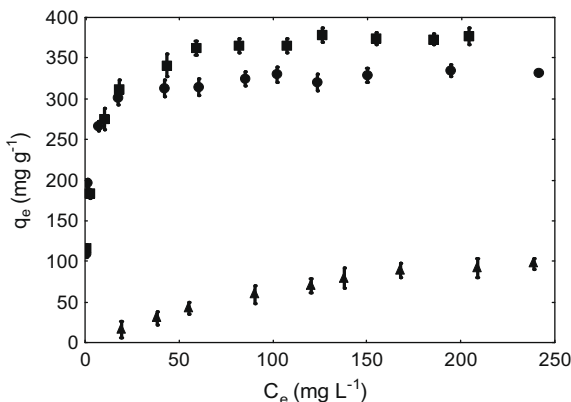
(MRE) and in order to analyze the fit for each model the coefficient of determination ( $R^2$ ) was considered. The software Statistic 6.0 (Statsoft, USA) was used to adjust the models (Eqs. (2)–(4)) to the experimental data

### 3. Results and discussion

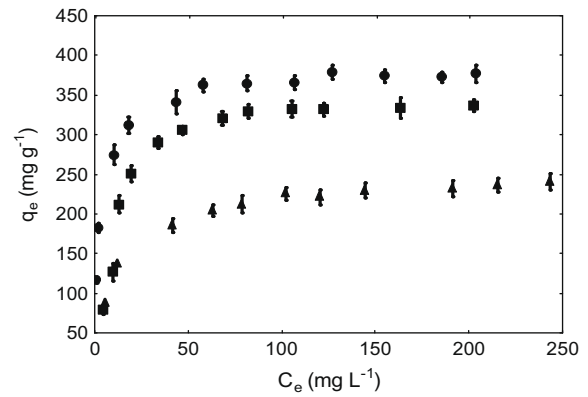
The adsorption capacity ( $q_e$ ) values (Eq. (1)) versus concentration equilibrium ( $C_e$ ) values are presented in Figs. 1–4.

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  $0.10 \pm 0.02$  mm and deacetylation degree of  $84 \pm 3\%$ .

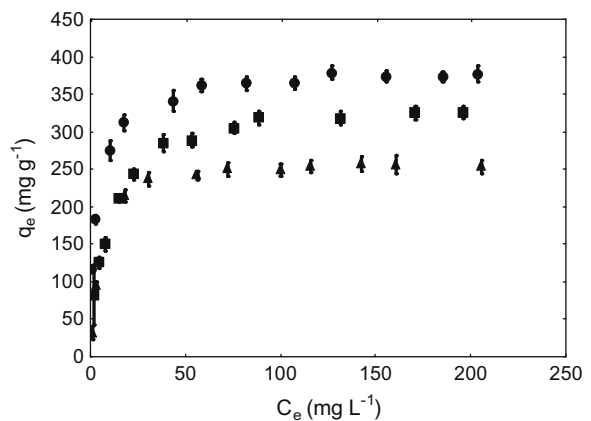
The initial system pH is changed to equilibrium pH during the adsorption process because under acidic conditions hydrogen atoms ( $H^+$ ) in the solution may protonate the amine groups ( $-NH_2$ ) of chitosan (Sakkayawong et al., 2005). Fig. 1 shows that the adsorption capacity increases significantly 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.,



**Fig. 1.** Adsorption isotherm at different equilibrium pHs: ● pH 5.7, ■ pH 6.6 and ▲ pH 7.4.



**Fig. 2.** Adsorption isotherm at different particle size ranges: ●  $d = 0.10 \pm 0.02$  mm, ■  $d = 0.18 \pm 0.02$  mm and ▲  $d = 0.26 \pm 0.02$  mm.



**Fig. 3.** Adsorption isotherms at different deacetylation degrees: ● DD =  $84 \pm 3\%$ , ■ DD =  $64 \pm 3\%$  and ▲ DD =  $42 \pm 5\%$ .

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  $84 \pm 3\%$ .

It can be observed in Fig. 2 that the adsorption capacity increases considerably when decreasing the particle size. Reduction 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 lineal 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 Chiou and Li (2002) for the adsorption of the red color I reactivate No. 189 for quitosana with crossed connection.

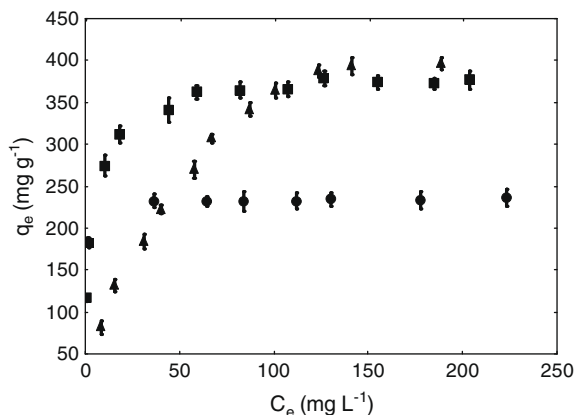


Fig. 4. Adsorption isotherms at different temperature conditions: ●  $T = 15\text{ }^{\circ}\text{C}$ , ■  $T = 25\text{ }^{\circ}\text{C}$  and ▲  $T = 35\text{ }^{\circ}\text{C}$ .

Fig. 3 shows the effect of amine groups in the chitosan polymer on FD&C Red No. 40 adsorption for three different deacetylation degrees ( $42 \pm 5\%$ ,  $64 \pm 3\%$  and  $84 \pm 3\%$ ), in the following conditions: equilibrium pH of 6.6, temperature of  $25\text{ }^{\circ}\text{C}$  and particle size range of  $0.10 \pm 0.02\text{ mm}$ .

Adsorption capacity value increased significantly with the increase 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  $35\text{ }^{\circ}\text{C}$ ) in the following conditions: equilibrium pH of 6.6, particle size range of  $0.10 \pm 0.02\text{ mm}$  and deacetylation degree of  $84 \pm 3\%$ .

Rectangle shapes of the isotherms at 15 and  $25\text{ }^{\circ}\text{C}$ , and logarithm shape of the isotherm at  $35\text{ }^{\circ}\text{C}$  are observed in Fig. 4. With increase in temperature from 15 to  $35\text{ }^{\circ}\text{C}$ , 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 fa-

vored 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 isotherms 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 Red No. 40 by chitosan, due to the fact that the Redlich–Peterson isotherms 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  $529.0\text{ mg g}^{-1}$ , which is observed in the following conditions: equilibrium pH of 6.6, particle size range of  $0.10 \pm 0.02\text{ mm}$ , deacetylation degree of  $84 \pm 3\%$  and temperature of  $35\text{ }^{\circ}\text{C}$ .

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  $494\text{ mg g}^{-1}$ , 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,  $728.2\text{ mg g}^{-1}$ , 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

Table 2

Langmuir, Freundlich and Redlich–Peterson isotherms constants in adsorption of FD&C Red No. 40 by chitosan at different pHs, particle size ranges, deacetylation degrees and temperatures.

Effect	Langmuir					Freundlich				Redlich–Peterson				
	$K_L\text{ (mg L}^{-1}\text{)}$	$q_m\text{ (mg g}^{-1}\text{)}$	$R_L$	$R^2$	MRE (%)	$K_F\text{ (mg L}^{-1}\text{)}$	$n$	$R^2$	MRE (%)	$K_R\text{ (L g}^{-1}\text{)}$	$a_R$	$\beta$	$R^2$	MRE (%)
<i>pH (DD = 84 ± 3%; Temp = 25°C; d = 0.10 ± 0.02 mm)</i>														
5.7	0.829	326.3	0.01	0.97	4.2	185.1	8.32	0.86	9.4	356.6	1.306	0.961	0.98	2.5
6.6	0.395	372.9	0.01	0.97	5.0	175.5	6.38	0.90	9.2	254.1	0.943	0.931	0.98	2.8
7.5	0.006	168.2	0.41	0.98	5.4	3.7	1.64	0.97	10.1	1.0	0.010	0.908	0.98	5.4
<i>Particle range (mm) (DD = 84 ± 3%; Temp = 25°C; pH 6.6)</i>														
0.10 ± 0.02	0.395	372.9	0.01	0.95	5.0	175.5	6.38	0.93	3.0	254.1	0.943	0.931	0.98	4.0
0.18 ± 0.02	0.083	371.0	0.06	0.96	9.0	106.3	4.17	0.80	19.2	20.6	0.052	1.000	0.92	8.1
0.26 ± 0.02	0.090	246.0	0.04	0.98	2.2	92.4	5.59	0.89	5.4	25.4	0.126	0.962	0.99	1.5
<i>Deacetylation degree, DD (%) (Temp = 25°C; d = 0.10 ± 0.02 mm; pH 6.6)</i>														
42 ± 5	0.186	266.4	0.02	0.99	4.7	97.5	4.91	0.82	26.1	47.5	0.178	1.000	0.992	4.3
64 ± 3	0.124	338.0	0.04	0.99	5.3	99.8	4.10	0.91	15.5	42.2	0.138	0.979	0.98	5.1
84 ± 3	0.395	372.9	0.01	0.95	5.0	175.5	6.38	0.93	3.0	254.1	0.943	0.931	0.99	4.0
<i>Temperature (°C) (DD = 84 ± 3%; d = 0.10 ± 0.02 mm; pH 6.6)</i>														
15	2.982	234.1	<0.01	0.97	0.9	187.5	21.5	0.88	2.0	931.8	4.249	0.986	0.97	0.8
25	0.395	372.9	0.01	0.95	5.0	175.5	6.38	0.93	3.0	254.1	0.943	0.931	0.99	4.0
35	0.020	529.0	0.21	0.99	4.7	44.3	2.27	0.95	9.3	11.5	0.023	1.000	0.98	4.3

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 (Namasivayam 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<sup>-1</sup>, respectively. This reports that different adsorbents 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  $K_L$  parameter of the Langmuir model, which corresponds to the inverse of the liquid phase concentration at which adsorption capacity is 0.5  $q_m$ , in relation to increase in pH, particle size and temperature and the decrease in deacetylation degree, suggests that monolayer saturation ( $q_m$ ) values were reached with higher equilibrium concentrations ( $C_e$ ), which results in the presence of larger amount of dye in the final solution.

Values of separation coefficients ( $R_L$ ), adsorption intensity ( $n$ ) and exponent  $\beta$  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<sup>-1</sup>, and the opposite occurred for higher concentrations. Correlation coefficient values ( $R^2 > 0.95$ ) and mean relative error values (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<sup>-1</sup>, 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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