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Adsorption of a model anionic dye on protonated crosslinked chitosan

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ABSTRACT

In the present study, chitosan has been chemically modified by crosslinking and protonation. Protonated crosslinked chitosan (PCC) was employed as an adsorbent to remove amido black 10B from aqueous solution. Adsorption experiments were performed by varying initial dye concentration, pH value of the solution, contact time, and temperature. The adsorption of amido black 10B onto PCC obeyed Langmuir isotherm. The adsorption capacity was 9.43 mg g^{-1} at 293 K. Thermodynamic studies revealed that the nature of amido black 10B adsorption was spontaneous and endothermic. Sorption kinetics was mainly controlled by pseudo-second-order model. About 0.1 M NaOH was identified as the best eluent.

Keywords: Amido black 10B; Adsorption; Isotherm; Protonated Crosslinked Chitosan

1. Introduction

Synthetic dyes are extensively used for textile dyeing, paper printing, color photography, and as additives in petroleum products. During the dyeing process, 10–15% of dye is discharged in the effluent. Approximately, a half of all known dyes are azo dyes. Amido black 10B is a synthetic diazo dye commonly known as naphthol blue black, and is a kind of anionic dye. Symptoms of exposure to amido black 10B may include coughing and shortness of breath. Repeated contact to the dye causes skin and eye irritation and may also develop burns, rashes with redness and pain [1]. Adsorption is the most effective and widely used method because of its ease of operation, low cost, and effectiveness. The efficiency of adsorption technique depends upon the nature of adsorbents used. A large variety of conventional and nonconventional adsorbent materials have been proposed and studied for their ability to remove dyes [2–6]. Chitin is one of the most abundant natural polymers and can be extracted from different sources such as crustaceous shells and fungi. Chitosan is a linear polysaccharide based on a glucosamine unit. Chitosan is considered to be both a versatile and an environmentally friendly raw material as it is nontoxic, biodegradable, and widely distributed. Chitosan exhibits a higher adsorption capacity and faster adsorption rate of anionic dye pollutants than many conventional adsorbents due to the presence of large amounts of amino ($-NH_2$) and hydroxyl (–OH) groups [7,8]. Its higher adsorption capacity was often observed in acidic solution, because the amino groups of chitosan are easily protonated and bounded anionic dye anions under this condition [9]. However,

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chitosan is liable to dissolve in acid, which was not expected during the practical adsorption process.

In this study, in order to effectively utilize the amine groups of chitosan for the removal of anionic dyes, crosslinked chitosan were protonated further. The adsorbent obtained was named as protonated crosslinked chitosan (PCC). The adsorption of amido black 10B onto PCC was investigated in detail.

2. Experimental

2.1. Materials

Chitosan powder (deacetylation degree is 90%) was acquired from Sinopharm Group Chemical Reagent Limited Company (China). Amido black 10B obtained from Guanghua chemical company (Guangdong, China) was used as the adsorbate. Fig. 1 displays the structure of amido black 10B. A stock solution of amido black 10B (1,000 mg/L) was prepared by dissolving appropriate quantity of amido black 10B in 1,000 mL of deionized water. The stock solution was further diluted with deionized water to desired concentrations. The dye concentration was measured at wavelength 618 nm on a UV–vis spectrophotometer. NaOH, HCl, H_2SO_4, glacial acetic acid, glutaraldehyde, and all other chemicals reagents were of analytical grade.

2.2. Preparation of crosslinked chitosan

Chitosan (3.6 g) was dissolved in 2.0 wt% glacial acetic acid solution. The chitosan solution was coated in culture vessels. The dry chitosan membranes were formed after these vessels were placed in an oven. Subsequently, 0.1 M NaOH solution was poured on the surface of dry membranes, and thus these membranes were separated from the culture vessels and washed with distilled water to a neutral pH. After they were dried at 60˚C, these dry membranes were crosslinked with 2.5 wt% glutaraldehyde solution and the ratio of glutaraldehyde to chitosan membranes was approximately 25 mL g^{-1}. Crosslinking reaction was conducted for 23 h at 60˚C and then the crosslinked membranes obtained were washed with distilled water to remove any free glutaraldehyde.

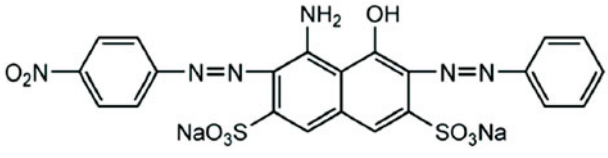


Fig. 1. Structure of amido black 10B.

2.3. Preparation of protonated crosslinked chitosan

PCC was prepared in order to effectively utilize the amino groups of crosslinked chitosan membranes for the adsorption of anion dye. According to the reference [10], the crosslinked chitosan membranes were treated with concentrated HCl for 90 min at 20˚C for the protonation of chitosan. PCC was washed with distilled water to neutral pH, dried at 60˚C, and was ground to obtain particles of 100-mesh size, which would be used for adsorption studies.

2.4. Adsorption studies

Adsorption experiments were carried out by the batch method. Different parameters, including pH (2–9), initial dye concentration (10–100 mg L^{-1}), adsorption temperature (293, 303 and 313 K), and contact time (10–240 min) were assessed. The pH value of the initial amido black 10B solutions was adjusted by adding 0.1 M HCl or 0.1 M NaOH solutions. The adsorbate solutions (50 mL) with initial dye concentration were placed in 250 mL conical flasks. About 0.21 g of PCC was then added to each flask and was equilibrated in a shaker at 200 rpm. The solutions were filtered and then subjected to quantitative analyses. Isotherm experiments were conducted according to the following method. The dye solutions with different dye concentrations in the range 10–100 mg L^{-1} were equilibrated in a shaker at 200 rpm by using 0.21 g PCC at different temperature (293, 303 and 313 K). The adsorption capacity values at equilibrium (q_e) were calculated by using the following equation:

$$q_e = \frac{V \times (C_0 - C_e)}{w} \quad (1)$$

where C_0 is the initial adsorbate concentration (mg L^{-1}), C_e is the adsorbate concentration at equilibrium (mg L^{-1}), V is volume of the solution (L), and w is mass of the adsorbent (g). Kinetic experiments were conducted at 303 K using three different concentrations viz, 20, 30, and 40 mg L^{-1}.

2.5. Desorption study

Desorption was conducted to investigate the regeneration and reuse ability of PCC. Desorption studies were performed in batch with 0.1 M HCl, 0.1 M H_2SO_4, and 0.1 M NaOH. Initially, 0.21 g of

adsorbent was agitated with dye with 20 mg L^{-1} of concentration for 60 min. After the equilibrium time, the saturated dye adsorbent was separated, washed with distilled water to remove the traces of unadsorbed dye, and agitated with 50 mL of eluent for 60 min. The amount of the dye released into the eluent solution was determined by:

$$\text{Desorption } (\%) = \frac{C_e}{C_a} \quad (2)$$

where C_a is the concentration of dye adsorbed on adsorbent, while C_e is the concentration of dye in the eluent solution after its desorption from the adsorbent.

3. Results and discussion

3.1. Adsorption studies

3.1.1. Effect of initial dye concentration

Effect of initial concentration on dye adsorption by PCC was studied by carrying out the experiments at different initial concentrations (10–100 mg L^{-1}), natural pH, adsorbent dosage (0.21 g), stirring speed (200 rpm), and temperature (20˚C) constant. The effect of initial concentration on the removal of anionic dye is shown in Fig. 2. The removal decreased from 90.4 to 37.8% as initial concentration increases from 10 to 100 mg L^{-1}. Similar observation has been reported for amido black 10B removal using lignocellulosic waste biomass activated carbon [6]. At low concentration, the ratio of available surface to the initial dye concentration is large, so the removal may become higher. However, in case of higher concentration, this ratio becomes low, so the removal may become lesser [11].

3.1.2. Effects of adsorption temperature

The temperature dependence on amido black 10B sorption onto PCC was studied with various dye concentration (10–100 mg L^{-1}) at natural pH. Fig. 3 illustrates the effect of temperature on the sorption of amido black 10B by PCC. The removals slightly increase when the temperature of dye solution increases from 293 to 313 K for the same dye concentration. This trend can be explained like this. On one hand, the mobility of the dye molecules increases with an increase in temperature; on the other hand, the rise of temperature resulted in increase the number of active surface sites available for adsorption, increase in the porosity, and in the total pore volume of the adsorbent. Therefore, the removal increased due to the above aspects. Similar results have been reported for the adsorption of acidic dye by the gel anion exchanger [5].

3.1.3. Effects of pH value

The initial pH of the dye solutions affects the chemistries of both the dye molecule and the adsorbent. In this study, the pH-dependence of dye adsorption was investigated by keeping initial dye concentration (20 mg L^{-1}), adsorbent dosage (0.21 g),

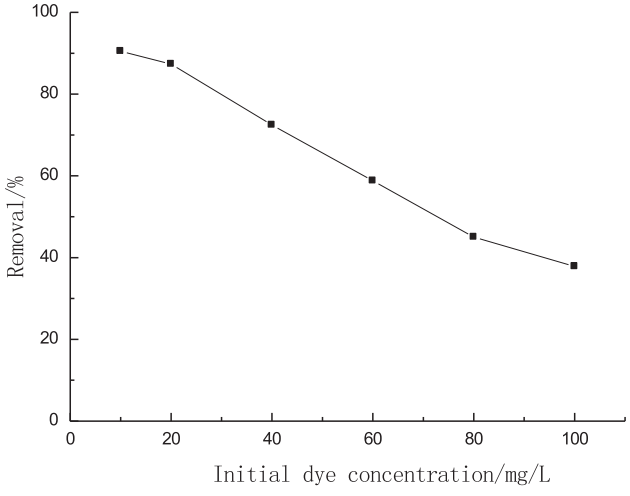


Fig. 2. Effect of initial dye concentration. Adsorbent dosage: 0.21 g; and contact time: 60 min; at 293 K and natural pH.

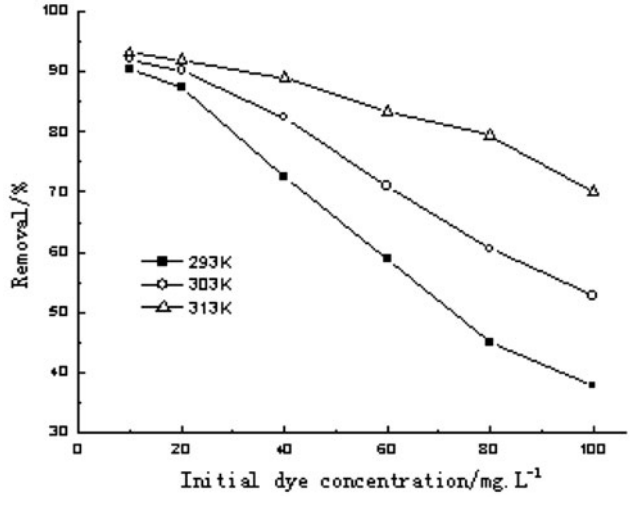


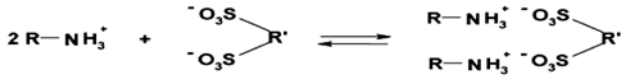
Fig. 3. Effect of adsorption temperature. Initial dye concentration: 20 mg/L; adsorbent dosage: 0.21 g; and contact time: 60 min; at natural pH.

stirring speed (200 rpm), temperature (20 °C), and contact time (60 min) constant and the results were given in Fig. 4. Upon increasing the pH value of solutions from 2 to 11, the removal decreased by 13% or so. A relatively high removal in pH range of 2–7 may be attributed to the protonation of amine groups in chitosan. Adsorption mechanism may be as follows:

First: in aqueous solution, amido black 10B is dissolved and the strongly acidic sulphonate groups of the dye were dissociated and converted to anionic dye ions:

$$R'(SO_3)_2NA_2 \xrightarrow{H_2O} R'(SO_3)_2^{2-} + 2Na^+$$

Second: the adsorption process then proceeded due to the electrostatic attractions between the anionic dye and the functional groups of chitosan.



However, the adsorption weakened with increasing the pH value of dye solution. This decrease can be attributed to the competition of the abundant presence of OH^- ions in basic solution for adsorption sites with anionic dye [12].

3.1.4. Effect of contact time

Adsorption experiments for contact time of sorbent and adsorbate were performed at natural pH by keeping initial dye concentration(20 mg L^{-1}), adsorbent dose (0.21 g), stirring speed (200 rpm), and temperature (30 °C) constant. The results were in Fig. 5. With increasing contact time, the removal increases rather rapidly, but then gradually approaches a more or less constant value. The sorption reaction may be considered to be occurring in two distinct phases. At the start of the adsorption, the removal of dye can be rapid surface adsorption (external surface adsorption). In the following stage, adsorption mainly occurred via transportation of surface-adsorbed dye to the internal adsorption sites of the adsorbent (internal surface adsorption) [13]. After 60 min, the removal was leveled off, denoting attainment of equilibrium and nonavailability of sorption sites.

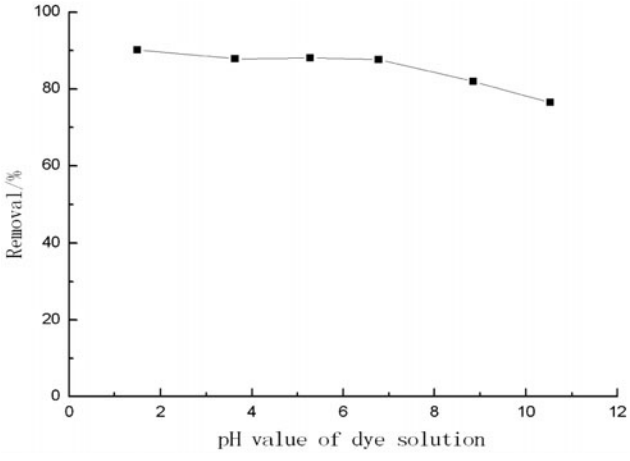


Fig. 4. Effect of pH value of dye solution Initial dye concentration: 20 mg/L; adsorbent dosage: 0.21 g; and contact time: 60 min.

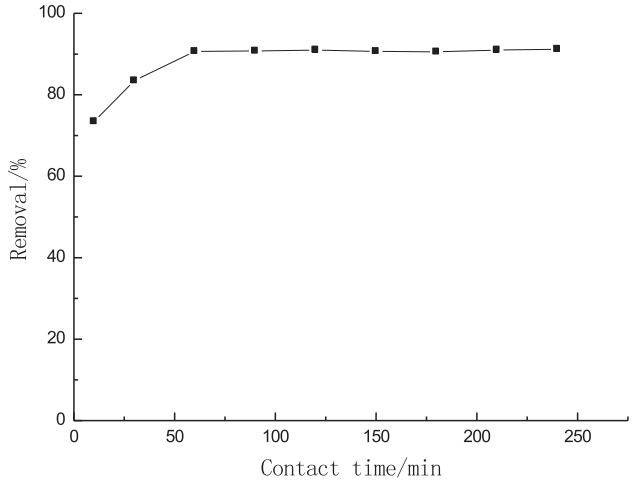


Fig. 5. Effect of contact time Initial dye concentration: 20 mg/L; adsorbent dosage: 0.21 g; at natural pH and 303 K.

3.2. Kinetics of adsorption

To investigate the kinetics behavior of amido black 10B adsorption onto PCC, these experiments were carried out at natural pH and different dye concentrations (20–40 mg L^{-1}) by keeping adsorbent dosage (0.21 g), stirring speed (200 rpm), temperature (30 °C) constant. The fitting of sorption of amido black 10B onto PCC was investigated by two common kinetic models, namely, the pseudo-first-order model and pseudo-second-order model. The pseudo-first-order model was described according to Eq. (3).

$$\lg(q_e - q_t) = \lg q_e - \frac{k_1}{2.303}\, t \tag{3}$$

where q_e and q_t are the amounts of dye adsorbed on adsorbent at equilibrium and at time t, respectively (mg g^{-1}), and k_1 is the rate constant of pseudo-

first-order adsorption (per min). A straight line of $\lg(q_e - q_t)$ vs. t suggests the applicability of this kinetic model to fit the experimental data. Equilibrium adsorption density q_e is required to be known beforehand. However, in many cases q_e remains unknown due to slow adsorption processes. Also, in many cases, the pseudo-first-order equation does not fit well to the whole range of contact time and is generally applicable over the initial stage of the adsorption processes [14].

The pseudo-second-order kinetic model is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

where k_2 (g/mg per min) is the rate constant of pseudo-second-order adsorption. If pseudo-second-order kinetics are applicable, the plot of t/q_t vs. t should show a linear relationship. There is no need to know any parameter beforehand and the equilibrium adsorption density, q_e can be calculated from Eq. (3). Also, it is more likely to predict the behavior over the whole range of adsorption.

The slopes and intercepts of plots of $\lg(q_e - q_t)$ vs. t (Fig. 6) were used to determine the pseudo-first-order rate constant k_1 and equilibrium adsorption density q_e. The slopes and intercepts of plots of t/q_t vs. t (Fig. 7) were used to calculate the pseudo-second-order rate constant k_2 and q_e. Table 1 lists the calculated results and the correlation coefficients (R^2). From Table 1, it is evident that the experimental

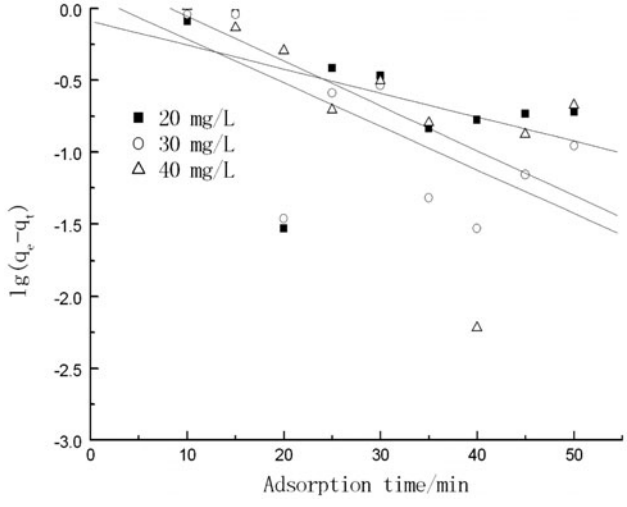


Fig. 6. Plots of pseudo-first-order kinetic model. Initial dye concentration: 20–40 mg/L; adsorbent dosage: 0.21 g; at natural pH and 303 K.

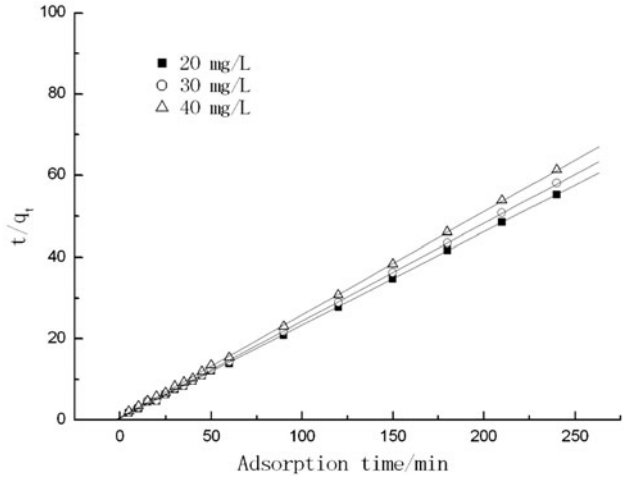


Fig. 7. Plots of pseudo-second-order kinetic model. Initial dye concentration: 20–40 mg/L; adsorbent dosage: 0.21 g; at natural pH and 303 K.

data show a good compliance with the pseudo-second-order model. The values of the correlation coefficients for the pseudo-second-order equations are higher than the pseudo-first-order equations at all of the experimental concentrations, and on the other hand, the calculated q_e values are close to the experimental q_e data for the pseudo-second-order model than the calculated values of the pseudo-first-order model. These observations suggested that the overall rate of amido black 10B adsorption was controlled by pseudo-second-order kinetics. The similar phenomena were also observed in adsorption of reactive red 189 on crosslinked chitosan beads [15].

3.3. Adsorption isotherms

Besides, adsorption data were fitted to the Langmuir and Freundlich isotherms. The Langmuir isotherm is valid for monolayer sorption due to a surface of a finite number of identical sites and expressed in the linear form as follows:

$$\frac{C_e}{q_e} = \frac{b}{Q_0} + \frac{C_e}{Q_0} \quad (5)$$

where C_e is the equilibrium concentration (mg L^{-1}) and q_e is the amount adsorbed at equilibrium (mg g^{-1}). Q_0 (mg g^{-1}) represents the monolayer adsorption capacity and b (L mg^{-1}) is the Langmuir equilibrium constant. The essential feature of the Langmuir adsorption can be expressed by means of R_L, a dimensionless constant is referred to as separation factor or equilibrium parameter for predicting

Table 1
Comparison of the pseudo-first and second-order kinetic models for different dye

Parameters	q_e,exp (mg/g)	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
Dye concentration (mg/L)		k_1 (per min)	q_e,cal (mg/g)	R^2	k_2 (per min)	q_e,cal (mg/g)	R^2
20	4.316	0.0492	1.496	0.9349	0.0966	4.386	0.9999
30	4.149	0.0789	2.023	0.8814	0.1379	4.182	0.9999
40	3.916	0.0510	1.438	0.8934	0.1026	3.963	0.9999

whether an adsorption system is favorable or unfavorable. R_L is calculated using the following equation:

$$R_L = \frac{1}{(1 + bC_0)} \tag{6}$$

where C_0 is the initial dye concentration (mg L^{-1}). If R_L values lie between 0 and 1, the adsorption is favorable.

The Freundlich isotherm describes the heterogeneous surface energies by multilayer adsorption and is expressed in linear form as:

$$\lg q_e = \lg K_f + \frac{1}{n} \lg C_e \tag{7}$$

where K_f indicates adsorption capacity ((mg g^{-1}) (mg $L^{-1})^{1/n}$) and n, an empirical parameter related to the intensity of adsorption, which varies with the heterogeneity of the adsorbent. The greater is the values of n, better is the favorability of the adsorption. Values, n>1 represent favorable adsorption condition.

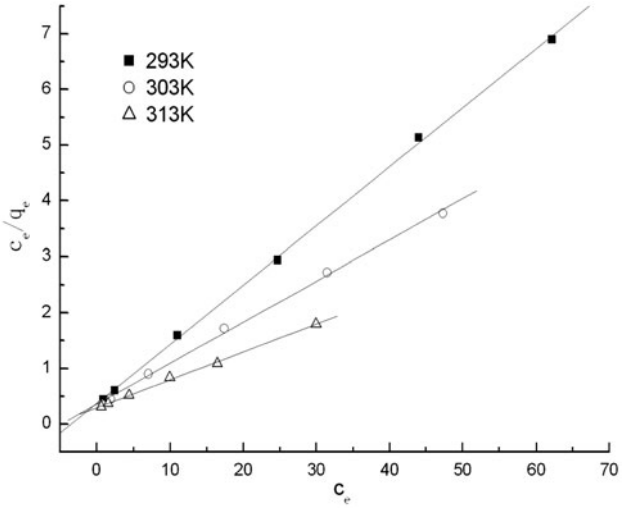


Fig. 8. Langmuir model for dye adsorption. Initial dye concentration: 10–100 mg/L; adsorbent dosage: 0.21 g; contact time: 60 min; at natural pH.

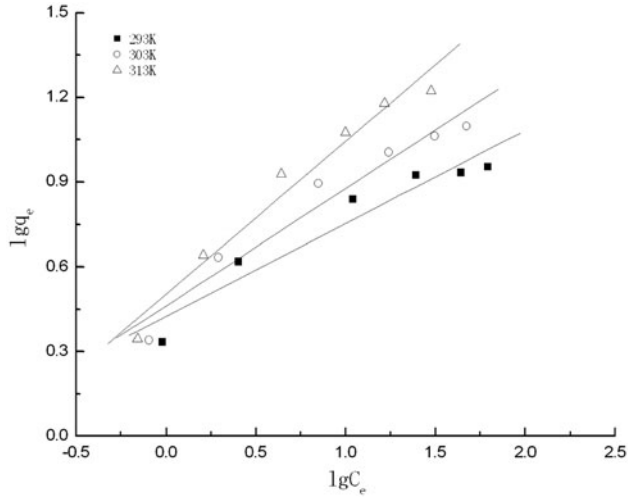


Fig. 9. Freundlich model for dye adsorption. Initial dye concentration: 10–100 mg/L; adsorbent dosage: 0.21 g; contact time: 60 min; at natural pH.

Adsorption data, at different temperature were modeled using both the Langmuir and Freundlich isotherms (Figs. 8 and 9, respectively). Langmuir and Freundlich isotherm constants are presented in Table 2. Apparently, Langmuir adsorption model was better to simulate the adsorption of amido black 10B onto PCC, which indicated that the adsorption of amido black 10B by PCC resulted in a monolayer coverage of PCC by dye molecules. Also, it can be seen that the adsorption of amido black 10B onto PCC was attributed to the favorable adsorption due to R_L values between 0 and 1. The monolayer adsorption capacity, Q_0, slightly increases when the adsorption temperature increased from 293 to 313 K. The fact that the adsorption of amido black 10B was in favor of high temperature was in accordance with the results mentioned in Section 3.1.2. The monolayer adsorption capacity, Q_0, was 9.43 mg g^{-1} at 293 K. Besides, as compared with these adsorbents, viz, the lignocellulosic waste biomass activated carbon (100 lm) [6] and polyaniline/iron oxide composite [13], PCC showed a slightly higher adsorption capacity, indicating that PCC had a potential for the removal of amido black 10B from aqueous solution.

Table 2
Isotherm constants for Langmuir and Freundlich models

T/K	Langmuir				Freundlich		
	Q/mg/g	b/L/g	R^2	R_L	K_f/mg/g	$1/n$	R^2
293	9.427	3.460	0.9997	0.0281–0.0861	2.541	0.3573	0.8618
303	13.59	4.837	0.9990	0.0202–0.1196	2.853	0.4365	0.9123
313	19.94	5.857	0.9990	0.0168–0.1662	3.017	0.5792	0.9494

Table 3
Thermodynamic properties of adsorption

Temperature/K	ΔG^θ (KJ mol^{-1})	ΔH^θ (KJ mol^{-1})	ΔS^θ (KJ mol^{-1} K)
293	−3.02	20.12	0.079
303	−3.97		
313	−4.60		

3.4. Thermodynamic studies

The thermodynamic parameters, standard Gibbs free energy change (ΔG^θ), enthalpy change (ΔH^θ), and entropy change (ΔS^θ) were estimated to evaluate the feasibility of the adsorption process by the following equations:

$$\Delta G^\theta = -RT \ln b \tag{8}$$

$$\ln b = \frac{\Delta S^\theta}{R} - \frac{\Delta H^\theta}{RT} \tag{9}$$

where b is the Langmuir equilibrium constant, R is the universal gas constant (8.314 J mol^{-1} K^{-1}), and T is the absolute temperature (K).

The values of ΔG^θ at a certain temperature were obtained with Eq. (8), while those of ΔH^θ and ΔS^θ were determined by plotting ln b against 1/T based on Eq. (9). The determined values of ΔG^θ, ΔH^θ, and ΔS^θ are given in Table 3. Negative ΔG^θ means spontaneous adsorption of amido black 10B by PCC in the 20–40 ℃ range. Positive ΔH^θ, which is supported by increased adsorption of amido black 10B at high temperatures, suggests that the adsorption of amido black 10B by PCC should be endothermic (Table 3). Considering both positive ΔH^θ and ΔS^θ (Table 3), the driving force for amido black 10B adsorption by PCC may be controlled by an entropy effect rather enthalpy change [16].

3.5. Adsorbent desorption

Desorption studies will help to regenerate this adsorbent so that it can be reused to adsorb dye. All desorption experiments were carried out at room temperature. Desorption efficiency of PCC was checked with acids like HCl and H_2SO_4 and the base, NaOH. Out of the three eluents, 0.1 M NaOH has been identified as the best eluent as it has 90.3% desorption efficiency whereas no desorption was achieved with 0.1 M HCl and 0.1 M H_2SO_4.

4. Conclusions

Protonated crosslinked chitosan (PCC) showed a potential for the removal of the anionic dye(amido black 10B) from aqueous solution. The effect of parameters like pH, contact time, initial dye concentration, and temperature has been investigated and it was found that the adsorption of amido black 10B was dependent on these variables. The adsorption kinetic and isotherm studies showed that the pseudo-second-order model and Langmuir model could well describe the adsorption behavior. Thermodynamic investigation indicated that the amido black 10B adsorption by PCC was a spontaneous and endothermic process.

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