

Adsorption of reactive dye from an aqueous solution by chitosan: isotherm, kinetic and thermodynamic analysis

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Abstract

The adsorption of Remazol black 13 (Reactive) dye onto chitosan in aqueous solutions was investigated. Experiments were carried out as function of contact time, initial dye concentration (100–300 mg/L), particle size (0.177, 0.384, 1.651 mm), pH (6.7–9.0), and temperature (30–60 °C). The equilibrium adsorption data of reactive dye on chitosan were analyzed by Langmuir and Freundlich models. The maximum adsorption capacity (q_m) has been found to be 91.47–130.0 mg/g. The amino group nature of the chitosan provided reasonable dye removal capability. The kinetics of reactive dye adsorption nicely followed the pseudo-first and second-order rate expression which demonstrates that intraparticle diffusion plays a significant role in the adsorption mechanism. Isotherms have also been used to obtain the thermodynamic parameters such as free energy, enthalpy and entropy of adsorption. The positive value of the enthalpy change (0.212 kJ/mol) indicated that the adsorption is endothermic process. The results indicate that chitosan is suitable as adsorbent material for adsorption of reactive dye from aqueous solutions.

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1. Introduction

Various kinds of synthetic dyestuffs found in effluent wastewater from a variety of industries such as for dyestuff, textile, leather and paper production, contain coloring substances which are toxic and need to be removed [1–3]. A wide range of conventional treatment techniques (such as chemical coagulation, activated sludge, trickling filter, carbon adsorption, and photodegradation techniques) for removing dye from aquatic bodies have already been extensively investigated [4–6]. Recently, the possibility of an adsorption process to remove dyestuffs discharged from textile industries has been considered. Dye adsorption is a process of transfer of dye molecule from bulk solution phase to the surface/interface. The adsorption of dyes at the solid–liquid interface plays an important role in much technological and industrial application. The solid–liquid interface is considered to develop a surface charge as a determining ions which give rise to positive, negative and for some system neutral surface sites. This would have the potential advantage of allow-

ing recovery of the dyestuffs in concentrated form [7,8]. The use of adsorption processes for color removal from wastewater has already received considerable attention and several adsorbents have been developed for this purpose [9–10]. Experimental studies have demonstrated the possibility of using activated carbon or chitin in granular form as adsorbents [11–15]. Since the adsorption capacities of the above adsorbents are not very large and the elution of the dye is not easy, the viability of such a process depends on the development of an improved adsorbent. Biosorption—the use of waste biomaterials as sorbents—is a newly developed technique [16–18] for the removal of harmful substances from water bodies, but suffers serious limitations in the case of anionic dyes as most of these biomaterials contain negatively charged cellulosic moieties, which lower adsorption due to coulombic repulsion. Recently, chitosan, a biopolymer of glucosamine, has exhibited a higher capacity for adsorption of colorant than activated carbon. It has been used widely as an adsorbent for transition metal ions and organic species. The amino ($-NH_2$) and hydroxy ($-OH$) groups on chitosan chains can serve as coordination and reaction sites [16–19]. In addition, chitosan is economically attractive, since it can be obtained from the deacetylation of chitin, and chitin is the second most abundant biopolymer in nature, next to cellulose. This present

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investigation reports in detail the adsorption of Remazol black 13 (Reactive dye) onto chitosan. Adsorption of dye is mainly dependent on the dye's properties and structure and to an equal extent on the surface chemistry of the adsorbent. For any batch adsorption process, the main parameters to be considered are the dye concentration, pH, temperature, particle size and time. Hence, it is necessary to investigate extensively the relationship between the adsorption efficiency and the parameters affecting it. The experimental data were correlated by two generalized adsorption isotherm models namely, the Langmuir and Freundlich models. Kinetic experiments were also conducted to determine the rate at which Remazol black 13 (Reactive dye) is adsorbed on chitosan.

2. Materials and methods

2.1. Materials

The chitosan was purchased from Marine Chemicals (Meron India Pvt, Ltd., India). Chitosan is harmless to humans and it has the potential to adsorb dyestuffs. The chitosan was dried at 70 °C in an oven for 8 h and then sieved until the discrete particle size ranged from 0.177, 0.384, 1.651 mm. The fractions were further dried in a vacuum oven for one day, after which it was stored in desiccators. The degree of deacetylation was 85% and the molecular weight was 120,000 g mol⁻¹, pK_a (6.4) and colors (light yellow) were determined. The BET surface area of the chitosan fraction was found by the nitrogen adsorption method to be 0.4976 m²/g, and the average pore diameter was determined to be 67.1023 Å. The pore volume was estimated to be 0.000835 cm³/g. The chemical structure of the Remazol black 13 (Reactive dye) as shown in Fig. 1. The dye used in the tests was the analytical reagent (AR), Remazol black 13 (Reactive dye) with a labeled purity of more than 98%. It was obtained from the Sigma chemical company to be used as the adsorbate. The dye concentration was measured using a UV–vis spectrometer at a wavelength corresponding to the maximum

absorbance for the dye: 597 nm (pH-6.4). The pH was adjusted by adding 0.1 HCl (or) NaOH.

2.2. Equilibrium studies

The equilibrium adsorption isotherm was determined using batch studies. Samples consisting of a portion (1 g) of the adsorbent material chitosan and various initial dye concentrations 20–200 mg/l, were poured into the conical reaction flask. The time required to reach equilibrium as determined in equilibrium studies was 24 h. The effect of the adsorption isotherm was determined by examining the series of isotherms at different temperatures (30, 45 and 60 °C) and for different particle sizes (0.177, 0.384, 1.651 mm) and pH (6.7, 8.5, 9.5), respectively.

2.3. Batch kinetic study

1 g of the adsorbent material chitosan was added to 100 ml of dye solution (100 mg/L). The sample was stirred constantly over a period of time. The different parameters studied included, (i) effect of the dye concentration: (20–200 mg/L) at a constant temperature (30 °C), pH (6.7) and particle size (0.384 mm); (ii) effect of the temperature: (30, 45, 60 °C) at a constant pH (6.7) and particle size (0.384 mm); (iii) effect of the pH: (6.7, 8.5, 9.5) at a constant temperature (30 °C) and particle size (0.384 mm); (iv) effect of the particle size: (1.651 mm, 0.384 mm, 0.177 mm) at a constant temperature (30 °C) and pH (6.7).

2.4. Desorption studies

Samples were prepared by adding 1 g of the chitosan dye adsorbent material (constant particle size 0.384 mm) to 100 ml solution of double distilled water. The solutions were equilibrated for different time periods (min) and stirred constantly. The experimental batches had different pH and temperatures. At preset time intervals, aqueous samples (5 cm³) were taken and the concentration was analyzed. The concentration of the dye was measured with a UV–vis spectrophotometer (Hitachi Model U-2000). Each experiment was duplicated under identical conditions. The amount of adsorption at time *t*, *q_t* (mg/g) was obtained as follows;

$$q_t = \frac{C_0 - C_t}{M} \quad (1)$$

where *C₀* (mg/L) and *C_t* (mg/g) are the liquid-phase concentrations of solutes at the initial and any time *t*, respectively, *M* is the dosage of adsorbent in the solution (g/L).

2.5. SEM studies

SEM images were taken before and after the chitosan was allowed to adsorb the Remazol black 13 (Reactive dye). The analysis of the images showed the height of heterogeneous pores within chitosan particle where adsorption could occur. After adsorption the pores were packed with Remazol black 13 (Reactive dye).

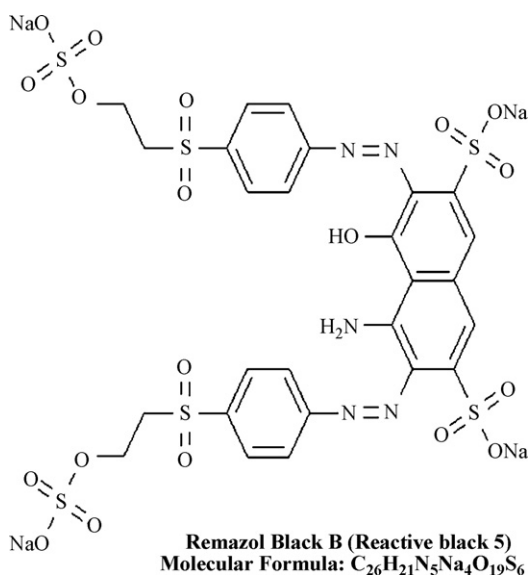


Fig. 1. The chemical structure of the Ramazole Black B (Reactive dye).

3. Results and discussion

The equilibrium adsorption isotherm is of fundamental importance in the design of adsorption systems. The isotherm expresses the relation between the mass of the dye adsorbed at a particular temperature, the pH, particle size and liquid phase of the dye concentration. For any adsorption investigation one of the most important parameters required to understand the behaviour of the adsorption process in the adsorption isotherm. The shape of an isotherm not only provides information about the affinity of the dye molecules for adsorption, but it also reflects the possible mode for adsorbing dye molecules. The most common way of obtaining an adsorption isotherm, is to determine the concentration of the dye solution before and after the adsorption experiments several attempts have been made to find the adsorbed amount.

3.1. Langmuir isotherm

The Langmuir isotherm which has been successfully applied to many other real sorption processes can be used to explain the sorption of dye into chitosan. A basic assumption of the Langmuir theory is that sorption takes place at specific sites within the adsorbent [19–21]. The data obtained from the adsorption experiment conducted during the present investigation was fitted using different particle sizes, pH and temperatures into the isotherm equation. The saturation monolayer can be represented by the expression

$$q_e = \frac{Kq_m C_e}{1 + q_m C_e} \quad (2)$$

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{Kq_m C_e} \quad (3)$$

A plot of $(1/q_e)$ versus $(1/C_e)$ results in a linear graphical relation indicating the applicability of the above model for different particle sizes as shown in (Fig. 2). The values are calculated from the slope and intercept of different straight lines

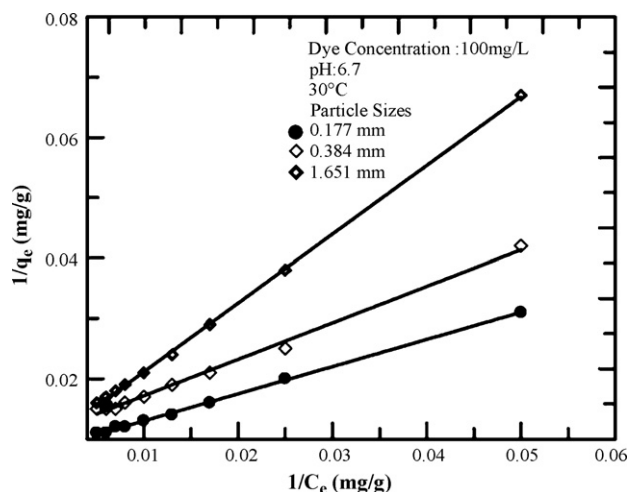


Fig. 2. Langmuir isotherm for the adsorption of reactive dyes using chitosan for different particle sizes.

Table 1

Langmuir isotherm constants at different particle size, pH and temperature

	Langmuir isotherm constants				
	q_m (mg/g)	K (L/g)	R^2	R_L	RMS ^a
Particle size (mm)					
0.177	119.04	0.0186	0.9986	0.7283	5.97×10^{-8}
0.384	91.47	0.0180	0.9964	0.7352	2.83×10^{-7}
1.651	103.1	0.0085	0.9993	0.8532	1.75×10^{-7}
pH					
6.7	91.47	0.0180	0.9964	0.7352	2.83×10^{-7}
8.5	97.08	0.0099	0.9973	0.8347	6.33×10^{-7}
9.5	100.0	0.0076	0.9976	0.8680	8.83×10^{-7}
Temperature (°C)					
30	91.47	0.0180	0.9964	0.7352	2.83×10^{-7}
45	111.11	0.0171	0.9939	0.8834	3.65×10^{-7}
60	130.00	0.0169	0.9930	0.8820	3.21×10^{-7}

^a RMS: residual mean square, sigma-hat-sq'd.

representing the different particle sizes, pH and temperatures (K), energy of adsorption, and (q_m) adsorption capacity. The observed linear relationship is statistically significant (at the 95% confidence level) as evidenced by the R^2 values (which are close to unity). This indicates the applicability of the isotherm (Langmuir isotherm) and the surface. The Langmuir isotherm constants along with correction coefficients are reported in Table 1. It can also be clearly seen from the shape of the adsorption isotherm, that it belongs to the L_2 category of isotherms, which is indicative of the normal (or) Langmuir type of adsorption, [22–25]. Such isotherms are often encountered when the adsorbate has a strong intermolecular attraction to the surface of the adsorbent. The L_2 shaped isotherm observed here clearly implies that the Remazol black 13 (Reactive dye) molecules must be strongly attached to the chitosan. The essential characteristic of the Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter, such as the separation factor (or) equilibrium factor (R_L) used in the following equation

$$R_L = \frac{1}{1 + KC_e} \quad (4)$$

where K is the Langmuir constant introduced in Eq. (2) and C_e is the initial concentration of the adsorbate in solution. This parameter indicates that isotherm will be shaped according to the following adsorption characteristics: $R_L > 1$ unfavourable; $R_L = 1$ corresponds to linear; $0 < R_L < 1$ is favourable and $R_L = 0$ is irreversible as given in Table 1. It can be seen that the adsorption of Remazol black 13 (Reactive dye) onto chitosan will be favorable.

3.2. Freundlich isotherm

The Freundlich isotherm is used for a heterogeneous surface energy system. The sorption isotherm is the most convenient form of representing the experimental data for different particle sizes as shown in (Fig. 3). Fig. 3 show the batch isothermal data fitted to the linear form of the Freundlich isotherm [26–28];

$$q_e = K_F C_e^{1/n} \quad (5)$$

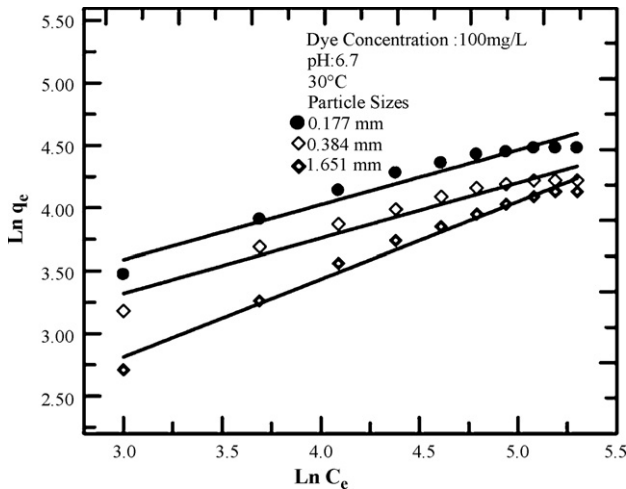


Fig. 3. Freundlich isotherm for the adsorption of reactive dyes using chitosan for different particle sizes.

$$\ln q_e = \frac{\ln K_F}{(1/n) \ln C_e} \quad (6)$$

The various constants associated with the isotherm are the intercept, which is roughly an indicator of sorption capacity (k_f) and the slope ($1/n$) sorption intensity. The values are recorded in Table 2. The Freundlich isotherm has been illustrated to be a special case of heterogeneous surface energies but it can be easily extended to this case. It has been stated by [29,30] that the magnitude of the exponent $1/n$ gives an indication of the favorability and capacity of the adsorbent/adsorbate system. Values where $n > 1$ represent favorable adsorption conditions. In most cases the exponent between $1 < n < 10$ shows beneficial adsorption.

3.3. Adsorption kinetics

The kinetics of adsorption for the treatment of dye-containing industrial effluents has already been studied. Numerous kinetic models elucidating the mechanism by which pollutants are adsorbed have been proposed. The kinetics of adsorption is

Table 2
Freundlich isotherm constants at different particle size, pH and temperature

	Freundlich isotherm constants			
	K_F (mg/g)(L/g) ⁿ	n	R ²	RMS ^a
Particle size (mm)				
0.177	2.27	2.28	0.9451	0.0067
0.384	1.99	2.27	0.9433	0.0071
1.651	0.95	1.62	0.9803	0.0046
pH				
6.7	1.99	2.27	0.9433	0.0071
8.5	1.17	1.73	0.9615	0.0081
9.5	0.77	1.58	0.9712	0.0072
Temperature (°C)				
30	1.99	2.27	0.9433	0.0071
45	2.12	2.20	0.9358	0.0086
60	2.29	2.24	0.9249	0.0097

^a RMS: residual mean square, sigma-hat-sq'd.

important because this is what controls the efficiency of the process. The following dye adsorption kinetic models are utilized to investigate the adsorption mechanism. Various kinetic models have been used and different systems use different models, but the Langergrens rate equations [31] for the sorption of a solute from a liquid solution are commonly used. In order to examine the mechanism controlling the adsorption processes, such as mass transfer and chemical reactions, several kinetic models are used to test experimental data. The large number and array of different chemical groups on chitosan chains (e.g., $-NH_2$, $-OH$) imply that there are many types of chitosan–solute interactions [32–35]. It is probable that any kinetic or mass transfer representation is likely to be global. From a system design viewpoint, a lumped analysis of adsorption rates is thus sufficient for practical operation. A simple kinetic analysis of adsorption gives the pseudo-first-order equation;

$$\frac{dq_t}{dt} = K_1(q_{eq} - q_t) \quad (7)$$

After definite integration by applying the initial conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, equation (7) becomes;

$$\log(q_{eq} - q_t) = \log q_{eq} - \frac{K_1}{2.303} t \quad (8)$$

where q_{eq} and q_t indicate the amount of dye adsorbed at equilibrium and for a specific time, (mg/g) and K_1 (min^{-1}) is the first-order rate constant applied in the present studies of dye adsorption. The values of $\log(q_{eq} - q_t)$ versus t were calculated from the kinetic data at different temperatures (Fig. 4) and plotted against time. The first-order rate constants calculated from the plots are shown in Table 3. The adsorption kinetics of some systems can also be described by a pseudo-second-order reaction [29,30]. The pseudo-second-order equation based on adsorption equilibrium capacity may be expressed in the form;

$$\frac{dq_t}{dt} = K_2(q_{eq} - q_t)^2 \quad (9)$$

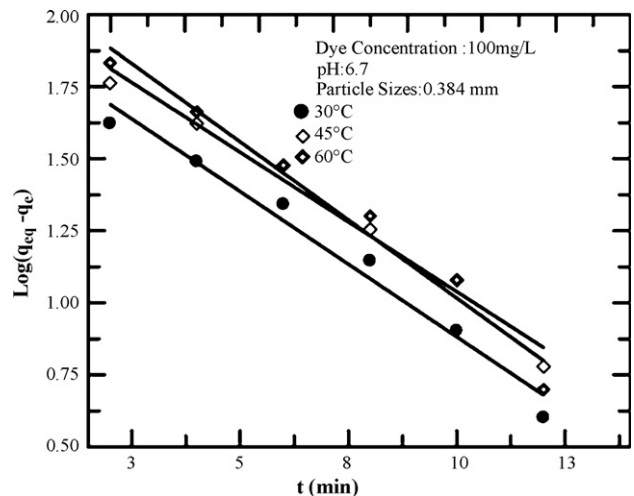


Fig. 4. Pseudo-first-order kinetic for the adsorption of reactive dyes using chitosan at different temperatures.

Table 3

Pseudo-first-order rate constant at different dye concentration, pH, temperature and particle sizes

	Pseudo-first-order rate constant			
	K_1 (min ⁻¹)	q_{eq} (mg/g)	R^2	RMS ^a
Dye concentration (mg/L)				
100	0.232	1.89	0.9753	0.0045
200	0.271	1.98	0.9778	0.0055
300	0.265	2.08	0.9730	0.0064
pH				
6.7	0.232	1.89	0.9753	0.0045
8.5	0.215	1.80	0.9714	0.0044
9.5	0.190	1.65	0.9830	0.0021
Temperature (°C)				
30	0.232	1.89	0.9753	0.0045
45	0.223	2.00	0.9824	0.0029
60	0.249	2.10	0.9741	0.0054
Particle Size (mm)				
0.177	0.234	1.94	0.9571	0.0081
0.384	0.232	1.89	0.9753	0.0045
1.651	0.219	1.83	0.9705	0.0048

^a RMS: residual mean square, sigma-hat-sq'd.

where k_2 is the rate constant of pseudo-second-order adsorption. Integrating equation (9) and applying the initial conditions, we get

$$\frac{1}{q_{eq} - q_t} = \frac{1}{q_{eq}} + K_2 t \quad (10)$$

or equivalently,

$$\frac{t}{q_t} = \frac{1}{K_2 q_{eq}^2} + \frac{1}{q_{eq}} t \quad (11)$$

The equilibrium adsorption capacity (q_{eq}), (mg/g) and the second-order constants k_2 (g/mg min), can be determined experimentally from the slope and the intercept of plot t/q_t versus t . The applicability of the pseudo-second-order models can be examined by the linear plot of t/q_t versus t respectively, as shown in Fig. 5. The correlation coefficient R^2 shows that the pseudo-second-order model is indicative of a chemisorptions mechanism, which fits the experimental data slightly better than the pseudo-first-order model. In other words the adsorption of Remazol black 13 (Reactive dye) can be approximated more favorably by the pseudo-second-order model. This model has been successfully applied to describe the kinetics of many adsorption systems. The calculated correlations are closer to unity for the second-order kinetics model; therefore, the dye adsorption kinetics could well be more favourably when approximated by a second-order kinetic model. The calculated k_2 (g/mg min) and q_{eq} (mg/g) values are listed in Table 4. Kinetic models were tested for chitosan–dye interactions, it was found that the first and second-order kinetic model gave the best fit with the experimental data and therefore, the adsorption followed a mechanism based on order of kinetics. The adsorption coefficients agree well with the conditions supporting favorable adsorption. The temperature were influenced this equilibrium

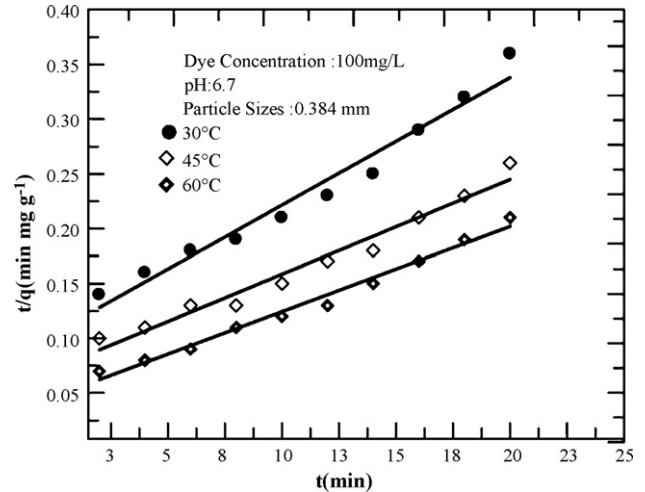


Fig. 5. Pseudo-second-order kinetic for the adsorption of reactive dyes using chitosan at temperatures.

since K is practically decreases in the range of the temperature studied.

3.3.1. Diffusion rate constant study

In the process of the adsorption of dye using chitosan, there is the possibility of intraparticle diffusion;

$$q_t = K_p t^{1/2} + C \quad (12)$$

According to Weber and Morris [25], if the adsorption mechanism follows the intraparticle diffusion processes a plot of q_t versus $t^{1/2}$ should be a straight line with a slope K_p and intercept C . K_p , under different conditions, was calculated from the slope of the linear portions of these respective plots, in units of $(t) \text{ min}^{0.5}$ as shown in Table 5. The double nature of these plots, the initial curved portions and final linear portions, may be explained

Table 4

Pseudo-second-order rate constant at different dye concentration, pH, temperature and particle sizes

	Pseudo-second-order rate constant			
	K_1 (g/mg min)	q_{eq} (mg/g)	R^2	RMS ^a
Dye concentration (mg/L)				
100	0.011	0.010	0.9709	0.00016
200	0.052	0.011	0.9904	4.5×10^{-5}
300	0.040	0.008	0.9894	2.8×10^{-5}
pH				
6.7	0.011	0.010	0.9709	0.00016
8.5	0.028	0.013	0.9685	0.00024
9.5	0.158	0.017	0.9839	0.00020
Temperature (°C)				
30	0.011	0.010	0.9709	0.00016
45	0.072	0.008	0.9686	9.9×10^{-5}
60	0.046	0.007	0.9850	3.7×10^{-5}
Particle Size (mm)				
0.177	0.088	0.010	0.9852	6.7×10^{-5}
0.384	0.011	0.010	0.9709	0.00016
1.651	0.125	0.0126	0.9678	0.00019

^a RMS: residual mean square, sigma-hat-sq'd.

Table 5

Intra-particle diffusion and diffusivity rate constant at different dye concentration, pH, temperature and particle sizes

	Intra-particle diffusion and diffusivity rate constant				
	K_p (mg min ^{0.5} /g)	C	D_p (m ² min ⁻¹)	R^2	RMS ^a
Dye concentration (mg/L)					
100	14.37	1.86	1.04×10^{-13}	0.9345	16.35
200	15.71	10.47	1.24×10^{-13}	0.9019	30.34
300	20.52	14.21	2.11×10^{-13}	0.9004	52.56
pH					
6.7	14.37	1.86	1.04×10^{-13}	0.9345	16.35
8.5	12.48	2.55	7.82×10^{-13}	0.9467	9.89
9.5	9.59	1.28	4.62×10^{-13}	0.9609	4.23
Temperature (°C)					
30	14.37	1.86	1.04×10^{-13}	0.9345	16.35
45	19.60	1.09	1.93×10^{-13}	0.9356	29.89
60	22.18	7.19	2.47×10^{-13}	0.9147	51.82
Particle Size (mm)					
0.177	15.91	0.27	2.79×10^{-16}	0.9385	18.76
0.384	14.37	1.86	1.04×10^{-13}	0.9345	16.35
1.651	12.97	2.63	2.63×10^{-12}	0.9462	10.80

^a RMS: residual mean square, sigma-hat-sq'd.

by the fact that the initial curved portions indicate the boundary layer diffusion effects [23–25,37,38]. The final linear portion is the result of intraparticle diffusion effects. The linear plots are attributed to macropore diffusion the accessible site for adsorption. This can be attributed to the instantaneous utilization of the most readily available adsorbing sites on the adsorbent surface. If the movement of the solute from the bulk film surrounding the adsorbent is ignored, the adsorption process for solids can be separated into three stages: (a) mass transfer (boundary-layer diffusion); (b) sorption of ions onto sites; and (c) intraparticle diffusion. The R^2 values are close to unity, which indicates the appropriateness of the application of this model. The boundary-layer thickness values indicate that, the larger the intercept the greater the boundary layer effect. The divergence in the value of the slope from 0.5 indicates that the contribution of intraparticle diffusion is one of the rate-limiting steps. In addition, there are many other processes controlling the rate of adsorption, all of which are most likely, operating simultaneously. It is possible to determine the intraparticle diffusivity (D_p m² min⁻¹) using the following equations [36];

$$D_p = \frac{k^2 \pi \left(\frac{V}{A}\right)^2}{4} \quad (13)$$

where A/V is the ratio of external area to particle volume and D_p is the intraparticle diffusivity. The intraparticle diffusivity was found under common experimental conditions to be close 10^{-12} – 10^{-16} m² min⁻¹. This low value confirms the idea that intraparticle diffusion is an important kinetic controlling step. The D_p values as shown in Table 5.

3.3.2. Effects of particle-size

The effect of adsorbent particle size on Remazol black 13 (Reactive dye) uptakes for three different particle sizes (1.651, 0.384, 0.177 mm) is shown in Fig. 6. It can be observed that as the

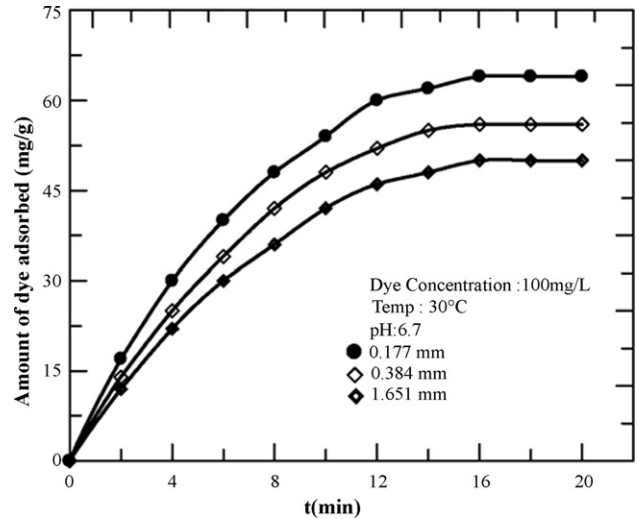


Fig. 6. Effect of specific dye uptake for different particle sizes with time.

particle size decreases, the adsorption of dye increases. It is obvious that for smaller particles, which have a higher solid–liquid interfacial area, the adsorption rates will be higher. A linear relationship exists between the amount of dye adsorbed and the particle size, as evidenced by the R^2 values being close to unity (0.177 mm $R^2=0.9571$; 0.384 mm $R^2=0.9753$ and 1.651 mm $R^2=0.9705$). Such an effect is probably due to the inability of the large dye molecule to penetrate all the internal pore structure of the chitosan. A similar phenomenon in relation to the adsorption of certain dyes on various adsorbents has been reported previously [8–10,13,38,40]. This is due to the larger surface area made available for adsorption.

3.3.3. Effects of pH

The effect of different pH on Remazol black 13 (Reactive dye) uptakes for three different pH values (namely 6.7, 8, 5 and 9.5) is shown in Fig. 7. The glucopyranose unit chitosan contains one amine group, one primary hydroxyl group ($-\text{CH}_2 \text{OH}$) and two secondary hydroxyl group ($-\text{OH}$), the reactive dye tend

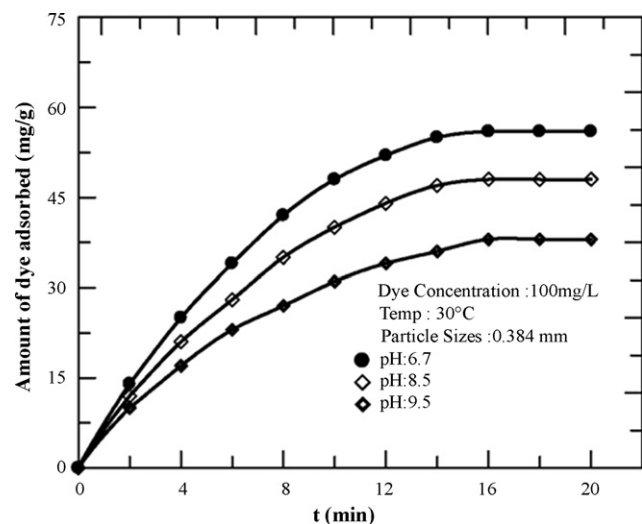


Fig. 7. Effect of specific dye uptake for different pH with time.

to react preferentially with the primary hydroxyl group of the cellulose fiber. However, chemical reactions between the amine groups of chitosan and dye seen highly improbable. The maximum values for the adsorption capacity ratio between acidic and alkaline conditions reach 3.7–6.7 for Remazol black 13 (Reactive dye) on chitosan. According to Yoshida [39–41], at lower pH more protons will be available to protonate amine groups of chitosan molecules to form groups $-\text{NH}_3^+$, thereby increasing electrostatic attractions between negatively charged dye anions and positively charged adsorption sites, and causing an increase in dye adsorption. It can be seen that the pH of aqueous solution plays an important role in the adsorption of Remazol black 13 (Reactive dye) onto chitosan [12]. Similar pH effects have also been observed in the adsorption of reactive dye to cross-linked chitosan fibers [39,40]; for example the adsorption of RR 189 (reactive dye) onto cross-linked chitosan beads [34] and reactive dye (RB2, RB2, RY2, RY86) onto cross-linked chitosan beads [12].

3.3.4. Effects of temperature

Temperature is an important parameter for the adsorption process. A plot of the Remazol black 13 (Reactive dye) uptake as a function of temperature (30, 45 and 60 °C) is shown in Fig. 8. The results reveal that the dye uptake increased with increasing temperature at 30 °C 56.0 mg/g; 45 °C 78.0 mg/g and 60 °C 96.0 mg/g). The adsorption of dye at higher temperatures was found to be greater than that at a lower temperature. The curves indicate the strong tendency for the process for monolayer formation process to occur [9,10,17,33,36–39]. The increase in temperature would increase the mobility of the large dye ions as well as produce a swelling effect with in the internal structure of the chitosan, thus enabling the large dye molecules to penetrate further [39,40]. Therefore, the adsorption capacity should largely depend on the chemical interaction between the functional groups on the adsorbent surface and the adsorbate, and should increase as the temperature rises. This can be explained by an increase in the diffusion rate of the adsorbate into the pores. At higher temperatures the adsorbent might contribute to

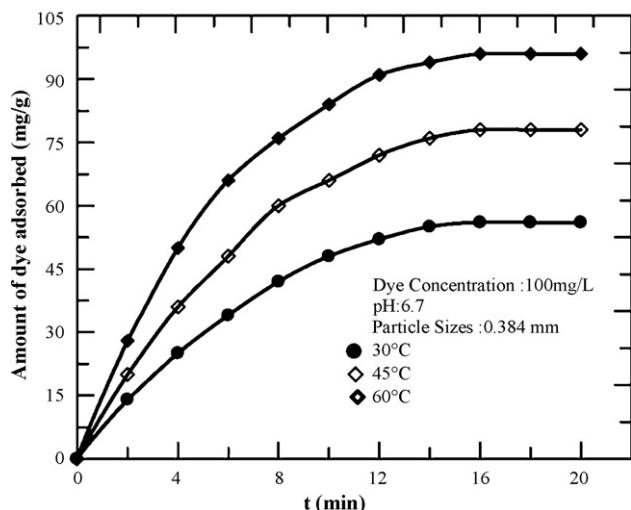


Fig. 8. Effect of specific dye uptake for different temperatures with time.

the adsorption of Remazol black 13 (Reactive dye), as diffusion is an endothermic process.

3.3.5. Effects of temperatures on the adsorption isotherm

The plots of specific adsorption ($1/q_e$) against the equilibrium concentration ($1/C_e$) for dye adsorption onto chitosan at different temperatures were found to be linear over the whole concentration range studied and the linear correlation coefficient (R^2) has a high value (0.9930–0.9964), as shown in Table 1. The correlation coefficient values indicate that the dye and chitosan sorption data satisfactorily follow the Langmuir sorption model. The changes in standard Gibbs free energy (ΔG°), standard enthalpy (ΔH°) and standard entropy (ΔS°) of the adsorption processes were determined from the data obtained at different temperatures using the following equations [41];

$$\Delta G^\circ = -RT \ln K \quad (14)$$

where K is the adsorption equilibrium constant obtained from the Langmuir isotherms, ΔG° is the free energy change, R is the universal gas constant 8.314 J/mol, and T is the absolute temperature. The effect of temperature on the equilibrium constant is determined as follows;

$$\frac{d(\ln K)}{dT} = \frac{\Delta H^\circ}{RT^2} \quad (15)$$

After integration Eq. (14) can be rearranged as;

$$\ln K = \frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (16)$$

ΔH and ΔS were calculated from the slope and intercept of the van't Hoff plots of $\ln K$ versus $1/T$. The equilibrium constants obtained from the best fitting models (Langmuir isotherm K) at 303, 318 and 333 K were used to determine the Gibbs free energy changes. The values of the standard enthalpy and the entropy changes were determined to be 0.212 kJ/mol; -0.0047 kJ/mol K and $R^2 = 0.9997$, respectively. The negative values of ΔG and ΔH (0.212 kJ/mol) indicate that the adsorption of dye onto chitosan is a spontaneous and an endothermic process. These behaviors seem to be explained by the ionic nature of the dye chitosan interaction. The positive value of ΔS suggests that both enthalpy and entropy are responsible for making the ΔG negative, so that the adsorption process is spontaneous, although the enthalpy contribution is much larger than that of the entropy. The negative value of ΔG indicates that the randomness decreases at the solid–solution interface during the adsorption of dye onto the chitosan. Additionally, the monolayer capacity slightly increases from 30 to 60 °C. Adsorption of dye onto chitosan followed an equilibrium, kinetics and the standard enthalpy of sorption was evaluated were 0.212 kJ/mol.

3.3.6. Desorption and regeneration studies

After confirming the fact that, chitosan is capable of adsorbing the dye onto its surface, it becomes necessary and imperative to know the nature, or the process, by which the dye remains adhered to the surface of the material. The nature of the adherence of the dye onto the surface of the material was

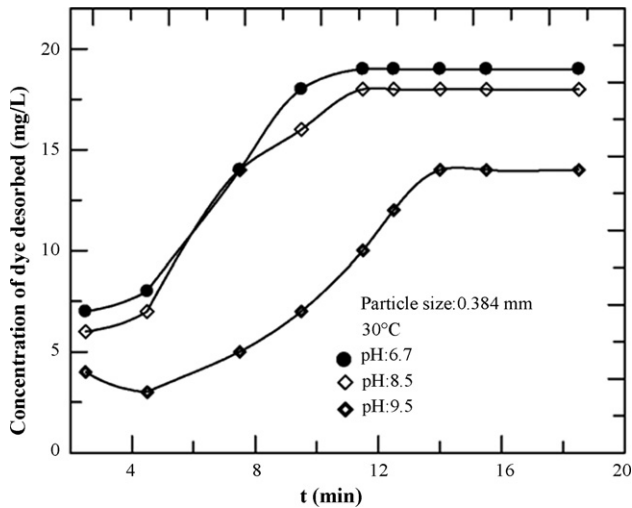


Fig. 9. Effect of pH on dye desorption.

purely chemical, involving chemical binding of the substances. The nature of bonding can be elicited by subjecting the adhered material to desorption and regeneration processes [42]. In the present investigation, experiments were conducted to ascertain the nature of the binding of dye on to the material surface. The desorption of dye at different pH (6.7, 8.5, 9.5) and temperature (30, 45, 60 °C) values is shown in Figs. 9 and 10. The desorbed dye was found to be negligible; one may conclude that the binding of the dye onto the material under study may be purely chemical in nature. Chitosan is a naturally occurring material a chelating polymer. The presence of hydroxyl and amino groups in this polymer make it a potential adsorbent for textile dye effluents. It seems likely that adsorption mechanism may be as follows: first Remazol black 13 (Reactive dye) is dissolved in an aqueous solution after which the sulphonate groups of Remazol black 13 (Reactive dye) (R-SO₃Na) become dissociated and converted to anionic dye ions. The dissociation of the chitosan (R-NH₂)⁺ amino groups into (R-NH₃)⁺ may be formulated as follows;

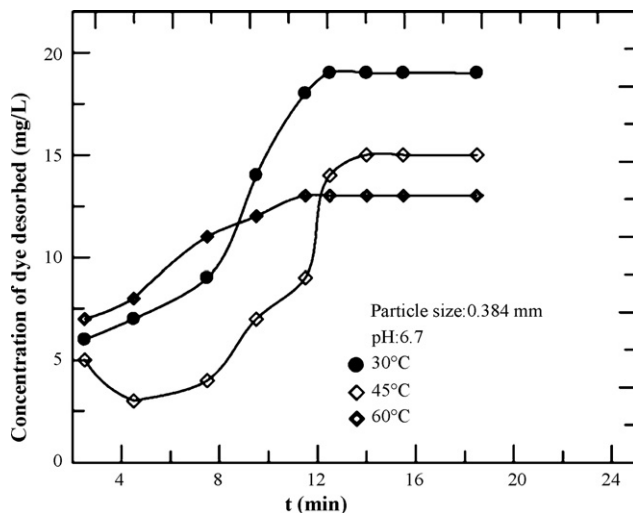
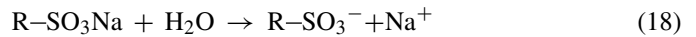


Fig. 10. Effect of temperatures on dye desorption.



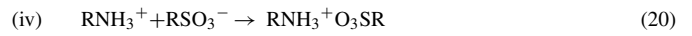
(ii)



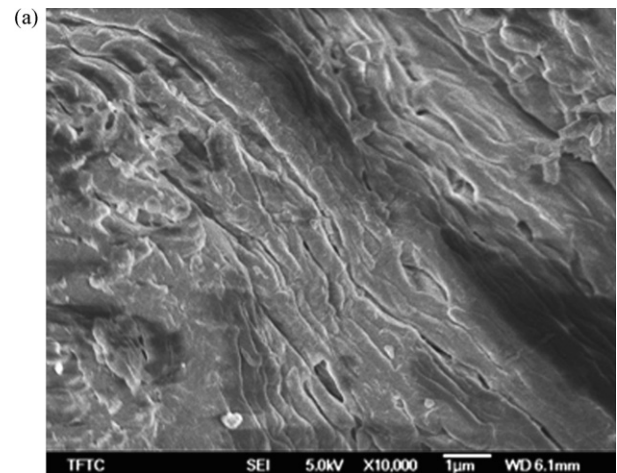
In the presence of H⁺ the chitosan amino groups (R-NH₂) become protonated



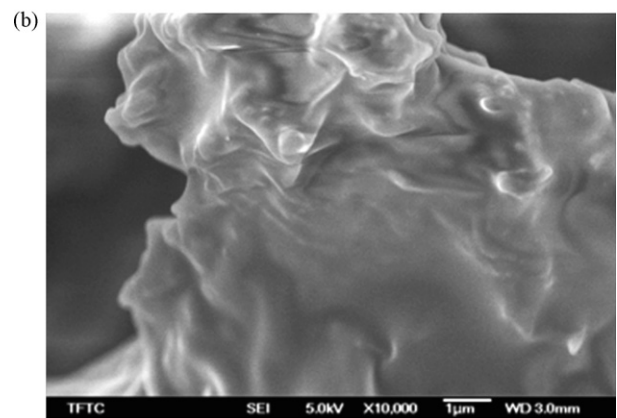
The adsorption process, proceeds due to the electrostatic attraction of these ions



The amino group dissociated into R-NH₃. The anions may be adsorbed by the electrostatic attraction between the Remazol black 13 (Reactive dye) and the R-NH₂ concentration of the amino group. The positive charges may decrease with the increase in the degree of cross-linking. As a consequence, the amount of dye adsorbed may decrease with increasing degree of cross linking [29–31]. Desorption studies help to elucidate the mechanism and recovery of the adsorbate and adsorbent. The Remazole black 13 adsorbed onto sorbents was eluted with different pH and temperature studies. In order to show the reusability of the sorbate the adsorption-desorption cycle



Chitosan



Chitosan adsorbed with Remazol Black B (Reactive dye)

Fig. 11. Scanning electron micrographs for: (a) chitosan (b) chitosan adsorbed with Ramazole Black B (Reactive dye).

of Remazol black was repeated two times using the same experimental studies. These results that recycling of chitosan can be repeated used in dye adsorption studies without detectable losses in their adsorption capacities.

3.3.7. SEM studies

Samples of fresh chitosan were coated under a vacuum with a thin layer of gold and then examined by scanning electron microscopy. SEM is one of the most widely used surface diagnostic tools. The SEM micrograph of the fresh chitosan, Remazol black 13 (Reactive dye) adsorbed chitosan were presented in (Fig. 11) respectively. Its BET surface area is confirming that has macrospores. Chitosan is a linear homopolymer of β -(1,4)-2-amino-2 deoxy-D-glucose and it is similar to cellulose in morphology. The micrograph showed that the dye had densely and homogeneously adhered to the surface of the carrier, as a result of either natural entrapment in to the porous chitosan material, due to physical adsorption by electrostatic forces or to covalent binding between the cellular chitosan and the carrier. The uniform distribution is an important criterion for the proper adsorption Remazol black 13 (Reactive dye) on the whole surface area of the chitosan.

4. Conclusion

The adsorption of dye from an aqueous solution using chitosan has been investigated, under different reaction conditions, in batch and equilibrium modes. The fit of the Langmuir model in the present system shows the formation of a monolayer covering of the adsorbate at the outer space of the adsorbent. The Freundlich model was used to analyze the isotherm. The monolayer adsorption capacity determined was reasonably high at particle size 119.04 (mg/g), temperature (30, 45, 60 °C) 130.0 (mg/g) and pH 100.0 (mg/g) for adsorption of Remazol black 13 (Reactive dye) respectively. The values of dimensionless equilibrium parameters like the separation factor (R_L) (for different particles sizes, pH and temperatures) indicates the favorability of the process described in the present study. The kinetics of Remazol black 13 (Reactive dye) adsorption nicely followed the pseudo-first and second-order rate expression which demonstrates that intraparticle diffusion plays a significant role in the adsorption mechanism. The Langmuir and Freundlich models can be used to describe dye sorption onto chitosan at equilibrium and the kinetic data also give a better fit. Dye sorption at the external surface of the polymer represents a significant part of the sorption process. However, the decrease in sorption capacity observed upon use of large sorbent particles was not proportional to the variation in external surface area. Desorption studies were conducted to elucidate the mechanism and recovery of the adsorbate and adsorbent. As the pH of the system increases, the number of negatively charge sites increased. A negatively charged surface site on the adsorbent favors the adsorption of dye electrostatic repulsion. The data reported here should be useful for the design and fabrication of an economically viable treatment process using batch (or) stirred tank reactors for dye adsorption and for diluting industrial effluents.

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