An Efficient Removal of Dimozol Red from Waste Water by Adsorption onto Chitosan/Marble Powder Composite: A Novel Low Cost Adsorbent

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Abstract In the present study, chitosan (C)/marble powder (M) composites with different weight ratio percentage (C100M0, C70M30, C50M50 and C30M70) were prepared with marble powder and chitosan and characterized by Scanning Electron Microscopy (SEM). The composites were used for the adsorption of Dimozol Red dye from aqueous solutions. The influence of contact time, pH, adsorbent dosage, initial dye concentration and temperature on Dimozol Red adsorption onto the composites was investigated. Equilibrium data were analyzed by model equations such as Langmuir and Freundlich isotherms and were best represented by Freundlich isotherm model. Kinetic adsorption data were analyzed using the pseudo-first-order kinetic model and the pseudo-second-order kinetic model. The adsorption kinetics well fitted with a pseudo-second-order kinetic model. Thermodynamic parameters, $\Delta G°$, $\Delta H°$ and $\Delta S°$, were calculated, indicating that the adsorption of Dimozol Red onto the composites was spontaneous and exothermic in nature.

Keywords: Adsorption, Chitosan, Dimozol Red, Marble powder

1. Introduction

Synthetic dyes are complex aromatic compounds and recognized as serious pollutants in the environment. These compounds are widely used as a coloring agents in several industries like textile, printing, leather, food and cosmetics. Many of these dyes are toxic and some are carcinogenic in nature. Synthetic dye industries grow vigorously day by day and thereby pose threats to human and other living organisms in the environment. Conventional methods such as precipitation, electrochemical treatment, reverse osmosis, ion exchange and adsorption are presently in use for the treatment of industrial effluent. Adsorption has been found to be effective because of the simplicity in its design and operation, ability to adsorb a broad range of pollutants; and fast processing (Vakili *et al*., 2014). Performance of adsorption processes can vary significantly depending on the adsorbent, dye chemical structure and process conditions. Activated carbon is used as an efficient adsorbent for its high surface area and efficiency, but its wide application is limited due to high cost. In recent years, researchers have been developed several new effective and cheaper adsorbents such as iron-containing solid wastes (Iakovleva *et al*., 2016), sludge (Xu *et al*., 2015), carbonate-based magnetic materials (Islam *et al*., 2017), waste textile fiber (Bediako *et al*. 2016) and agricultural wastes (de Luna *et al*., 2017) for adsorption applications.

The objective of this work was to investigate the potential of the chitosan/marble powder composites as a new low cost adsorbent in the removal of dye from waste water. Adsorption performances were investigated by batch experiments, including the influence of contact time, pH, adsorbent dosage, initial dye concentration and temperature. More important, adsorption isotherm and kinetic were also discussed to analyze the interaction between dye molecules and adsorbent.

2. Materials and methods

2.1. Materials

Chitosan (degree of deacetylation 75-85 %) was purchased from Aldrich. Aqueous acetic acid (Merck) solution was used as a solvent for the chitosan. Glutaraldehyde solution (Fluka, 50 %) was used as a crosslinker. The marble powder was collected from the local marble cutting/processing industry in Bilecik, Turkey. The marble powder was dried in an oven at 80°C for 24 h and then passed through sieve to obtain 90 μm before use. Dimozol Red (purity of 99 %) was obtained from a dye factory in Bursa, Turkey. The effect of pH of solution on the adsorption of Dimozol Red dye was studied at different pH ranges of solution by adjusting the natural pH of the dye solution with HCl (0.1 M) or NaOH (0.1 M) solutions. All other chemicals were analytical grade and used without further purification.

2.2. Preparation and characterization of chitosan/marble powder composites

1 g of chitosan was dissolved in 75 mL of 5 % v/v acetic acid with constant stirring in order to get a homogeneous

mixture. Marble powder was added and the mixture was left overnight with continuous stirring on magnetic stirrer resulting in the formation of the dispersion. The dispersion was taken in a syringe and allowed to fall slowly and dropwise into 1 M NaOH solution with gentle stirring, The composites were kept in the same solution overnight with continuous stirring. After the process, the chitosan/marble powder composites were washed many times with distilled water to attain a neutral pH. As a crosslinker, glutaraldehyde was selected and the rinsed chitosan/marble powder was shaken in 2.5 w % glutaraldehyde ethyl alcohol solution. After 15 h crosslinking reaction at 60 °C, the chitosan/marble powder was washed with water again to remove excess glutaraldehyde and then freeze dried for 48 h. Finally, a series of chitosan/marble powder composites with different weight ratio percentage were synthesized, viz., 100:0 wt.% (C100M0), 70:30 wt.% (C70M30), 50:50 wt.% (C50M50), 30:70 wt.% (C30M70). The surface morphology and internal structure of the composites were observed by scanning electron microscope (SEM, Bruker, Germany).

2.3. Adsorption experiments

The concentrations of Dimozol Red in aqueous solution were determined using a UV–vis spectrophotometer (Agilent Cary 60 UV-Vis) at wavelength 540 nm. The adsorption capacities were calculated according to Equation (1):

$$q_e = \frac{(C_0 - C_e)V}{W} \qquad (1)$$

where q_e was the equilibrium adsorption capacity (mg/g), C_0 and C_e were the initial and equilibrium concentrations (mg/L) of the dyes, respectively. V was the volume (L) of the solution and W was the weight (g) of the adsorbent.

3. Results and discussion

3.1. Surface morphology of chitosan/marble powder composites

SEM images of the cross-linked chitosan/marble powder composites envisioned at modifications of 500 x (20 μm) are shown in Figure 1. From SEM micrograph in Figure 1, it is observed that the composites exhibit porous texture.

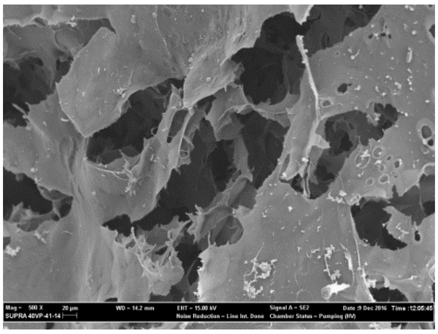

Figure 1. SEM images of chitosan/marble powder composites.

3.2.Effect of contact time and adsorption kinetics

The effect of adsorption time on the adsorption capacity of Dimozol Red dye on the chitosan/marble powder composites was studied, and the results were shown in Figure 2. The rate of adsorption of Dimozol Red was rapid in the beginning, proceeded at a slower rate and finally attained equilibrium at about 72 hours. At equilibrium, the adsorption capacity of Dimozol Red onto C100M0, C70M30 and C50M50 is about 28 mg/g and higher than that onto C30M70. Chitosan/marble powder composite with 50 %: 50 % weight percentage ratio of chitosan and marble powder, C50M50, was more economically than C100M0, C70M30 due to higher marble powder content and hence was selected as an adsorbent for all the other studies.

The controlling mechanism of Dimozol Red dye adsorption on chitosan/marble powder composites was evaluated in terms of adsorption kinetics by measuring adsorption capacity at various time intervals till equilibrium value was reached. For kinetic study, the pseudo-first order model and the pseudo-second order model are used to evaluate the experimental data as the following two equations, respectively (Konicki *et al.*, 2017):

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \qquad (2)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (3)$$

where q_e (mg/g) and q_t (mg/g) are the amount of the dyes adsorbed at equilibrium and at time *t*, respectively. The term k_1 (hour^{-1}) is the rate constant of pseudo-first order kinetic, and the term k_2 (g/(mg·hour)) is the rate constant of pseudo-second order kinetic. The plots of linearized form of the pseudo-first-order and pseudo-second-order equations are shown in Figure 3 (a) and Figure 3 (b), respectively. The characteristics parameters of pseudo-first-order and pseudo-second-order models are given in Table 1. The R^2 values (0.9851–0.9990) for pseudo-second-order kinetic model at all the composites (C100M0, C70M30, C50M50 and C30M70) are higher than those for pseudo-first order model. Also, the theoretical qe,cal values obtained from this model was closer and good agreement with the experimental values (qe,exp). It was suggested that the pseudo-second-order model is more suitable for describing the adsorption of Dimozol Red onto the chitosan/marble powder composites

3.3. Effect of initial solution pH and adsorbent dosage on dye adsorption

The adsorption of Dimozol Red on C50M50 composites was studied in a pH range of 3-11 at 298 K for 72 h. Figure 4 shows the effect of pH on the dye removal efficiency on the C50M50 composites. The highest adsorption capacity of C50M50 composites was achieved at pH 5 and the lowest adsorption capacity at pH 11.

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Table 1. Kinetic parameters for Dimozol Red dye adsorption on different chitosan/marble powder composites.

		Pseudo-first-order			**Pseudo-second-order**		
Adsorbents	**$q_{e,exp}$ (mg/g)**	**$q_{e,cal}$ (mg/g)**	**$k_1(x10^3)$ (hour^{-1})**	**R^2**	**$q_{e,cal}$ (mg/g)**	**$k_2(x10^3)$ (hour^{-1})**	**R^2**
C100M0	27.61	30.65	100.87	0.9309	29.94	4.82	0.9851
C70M30	28.69	16.88	105.94	0.9740	29.59	17.41	0.9990
C50M50	28.00	25.85	79.22	0.9851	29.85	5.81	0.9889
C30M70	20.18	15.69	32.93	0.9718	19.42	9.01	0.9839

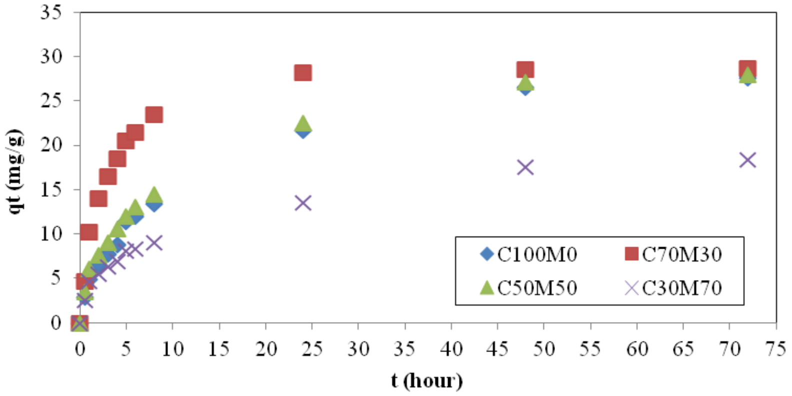
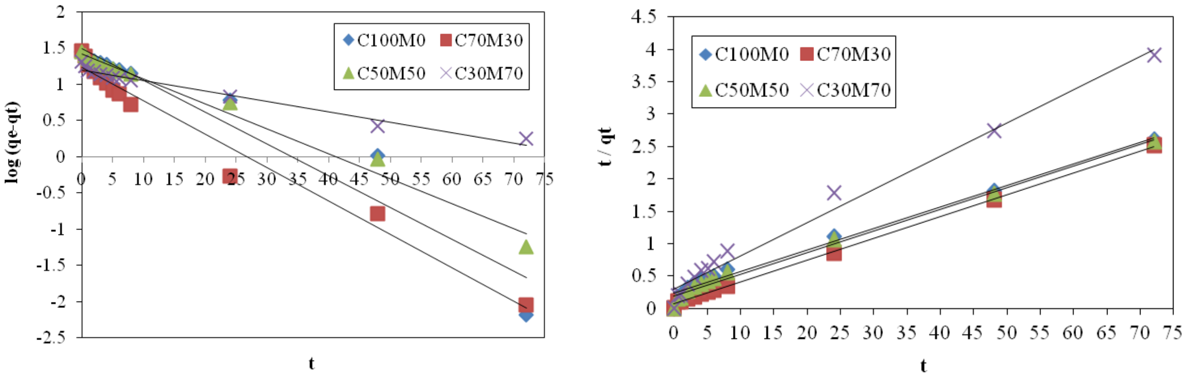


Figure 2. Effect of contact time on the adsorption of Dimozol Red onto different chitosan/marble powder composites (adsorbent: 2 g/L, initial concentration: 60 mg/L, agitation speed: 150 rpm, temperature: 25°C).



(a)

(b)

Figure 3. Kinetic models for the adsorption of Dimozol Red dye onto different chitosan/marble powder composites (a) Pseuso-first order, (b) Pseudo-second-order.

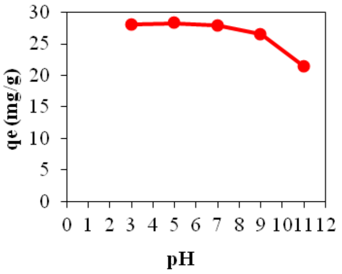


Figure 4. Effect of pH for the removal of Dimozol Red onto C50M50 composites.

The effect of adsorbent dosage on removal of Dimozol Red was conducted in batch experiments by adding various amount of adsorbent in the range of 0.1–0.01 g into the flask containing 50 mL of dye solution. The initial dye concentration and temperature were fixed at 60 mg/L and 25°C, respectively, for all experiments. The results were illustrated in Figure 5. The amount of dye adsorbed onto the C50M50 composites was found to decrease from 199.6 to 28.7 mg/g with increasing adsorbent dose due to the concentration gradient between adsorbent and adsorptive (Zhu *et al*., 2010).

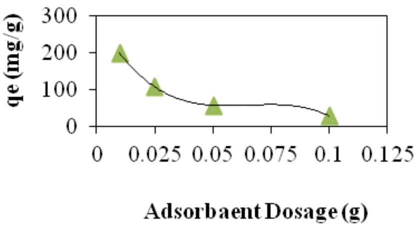


Figure 5. Effect of adsorbent dosage on the adsorption capacity of C50M50 composites.

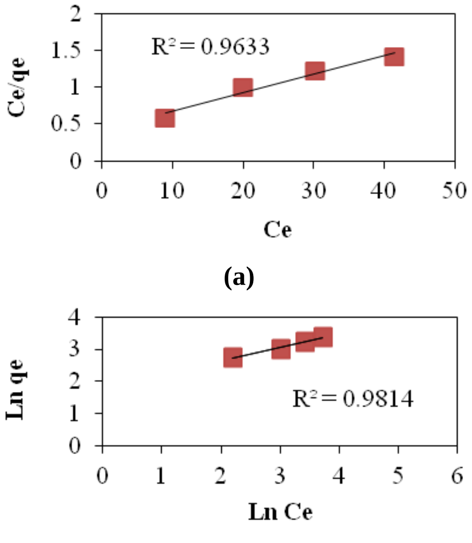
3.4. Equilibrium isotherms

Langmuir and Freundlich adsorption isotherm models were used to design and to understand the mechanism of interaction existing between adsorbate and the adsorbent at equilibrium. The linear forms of the Langmuir and Freundlich isotherms are given by Equation 4 and Equation 5, respectively (Wibowo *et al*. 2017):

$$^{C_e}/_{q_e} = {}^{C_e}/_{q_m} + {}^{1}/_{(q_m.K_L)} \qquad (4)$$

$$\ln q_e = \ln K_F + \left({}^{1}/_{n}\right).(\ln C_e) \qquad (5)$$

Figure 5 shows the plot of ln qe vs. ln Ce for the Freundlich model and the plot of Ce/qe vs. Ce for the Langmuir model. The coefficient of determination R^2 (0.9814) for the Freundlich model is higher than that of the Langmuir model (0.9633). Based on R^2 value, the Freundlich model is more suitable in describing the experimental data for Dimozol Red adsorption onto C50M50 composites. The values of K_f and n calculated from the intercept and slope of the linearized Freundlich model are listed in Table 2. The value of 1/n is lower than 1.0, which indicates the heterogeneity of the adsorption process and also to be favorable.



(a)

(b)

Figure 5. Isotherm models for Dimozol Red dye adsorption by C70M30 composites (a) Langmuir and (b) Freundlich

Table 2. Thermodynamic parameters for the adsorption of Dimozol Red onto C50M50 composites.

Freundlich			***Langmuir***		
K_F	***n***	***R^2***	***q_m***	***K_L***	***R^2***
[mg/g (L/g)$^{1/n}$]			***(mg/g)***	***(L/mg)***	
6.0696	2.4137	0.9814	39.53	0.0604	0.9633

3.5. Effect of temperature and thermodynamic parameters

The effect of temperature on equilibrium adsorption of Dimozol Red onto the C50M50 composites was studied at three temperatures of 25, 45 and 65°C, at 100 mg L^{-1} initial dyes concentration and pH = 5. It was observed that the adsorption equilibrium of Dimozol Red increased with an decrease in temperature, indicating the exothermic nature of the adsorption reaction.

To understand the nature of Dimozol Red adsorption onto the C50M50 composites, thermodynamic parameters, such as free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°) were calculated using the following equations (Konicki *et al*., 2017):

$$\ln K_C = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \qquad (6)$$

$$K_C = \frac{q_e}{C_e} \qquad (7)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \qquad (8)$$

Table 3 presents the thermodynamic parameters of ΔH°, ΔS° and ΔG°. The negative value of ΔH° indicate that adsorption of Dimozol Red onto the C50M50 composites is an exothermic process. The negative ΔS° value suggest the decrease in adsorbate concentration in solid-liquid interface indicating thereby the increase in adsorbate concentration onto the solid phase. It also confirms the decreased randomness at the solid-liquid interface during adsorption of Dimozol Red onto C50M50 composites.

Negative values of ΔGº signify that adsorption of Dimozol Red onto C50M50 composites were spontaneous and thermodynamically favorable processes at all the experimental temperatures. The change in Gibbs free energy for physisorption is between - 20 and 0 kJ mol^{-1}, the physisorption together with chemisorptions is at the range of -20 to -80 kJ mol^{-1} and chemisorption is at the range of -80 to -400 kJ mol^{-1} (Tahir *et al*., 2016). The values of ΔGº for the adsorption of Dimozol Red onto C50M50 composites were in the range of physisorption.

Table 3. Thermodynamic parameters for the adsorption of Dimozol Red onto C50M50 composites.

T (K)	ΔH^o (kJ.mol-1)	ΔS^o ($J.mol^{-1}.K^{-1}$)	ΔG^o ($kJ.mol^{-1}$)
298	- 37.68	- 68.28	- 17.33
318			- 15.97
338			-14.60

4. Conclusions

In the present study, the chitosan/marble powder composites have been synthesized as new adsorbent. The adsorbent was used for removal of Dimozol Red anionic dye from aqueous solution and the influence of several parameters such as contact time, pH, adsorbent dosage, initial dye concentration and temperature was investigated. Under the optimal conditions (pH:5; 298 K; 100 mg/L initial dye concentration, adsorbent dosage:0.01g), the experimental maximum adsorption capacity was achieved as 292.7 mg/g. The results show that chitosan/marble powder composites are an efficient and cost effective adsorbent for removal of Dimozol Red from aqueous solution and is a promising adsorbent for removing dyes from textile and other wastewater.

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