

Adsorption of Reactive Black M-2R on Different Deacetylation Degree Chitosan

Fang Li , Chunmei Ding

Anhui University of Polytechnic, Wuhu, Anhui CHINA

Correspondence to:
Chunmei Ding email: zls9390@163.com

ABSTRACT

Different degree of deacetylation (DD) chitosan was prepared and used for the removal of a Reactive black M-2R (RBM) from aqueous solution. The effects of temperature (298 K~323 K), chitosan dosage, degree of deacetylation on RBM removal were investigated. The adsorption equilibrium was reached within one hour. In order to determine the adsorption capacity, the sorption data were analyzed by using linear form of Langmuir, Freundlich and Tempkin isotherm equation. Langmuir equation shows higher conformity than the other two equations. From the kinetic experiment data, it was found that the sorption process follows the pseudo-second-order kinetic model. Activation energy value for sorption process was found to be 58.28 kJ mol⁻¹. Chitosan with 66% deacetylation degree (DD) exhibited good adsorption performance for RBM. In order to determine the interactions between RBM and chitosan, FTIR analysis was also conducted.

Keywords: Chitosan; Reactive Black M-2R; Adsorption; Deacetylation degree

INTRODUCTION

Reactive dyes are widely used for textile dyeing, paper printing, leather dyeing, color photography and as additives in petroleum products. Contamination of water resources with dyes is not desirable since it damages the aesthetic nature of water and reduces the light penetration degree through the water's surface. Furthermore, the colored effluents may contain toxic, carcinogenic, mutagenic or teratogenic chemicals for microbes and fish species. Approximately 10,000 different dyes and pigments are used in industry. Most of them are difficult to biodegrade since they have complex aromatic molecular structures and synthetic origins¹.

The removal of color from dye effluents is a big problem due to the difficulty in treating such waste

waters with conventional treatment methods. The most common used methods of color removal are physical or chemical processes. All these methods have different color removal capabilities, capital costs, and operating rates. The liquid phase adsorption processes have been shown to be highly efficient for the removal of dyes from industrial waste water²⁻⁵. Activated carbon is the most popular adsorbent. It has been used with great success⁶⁻⁷. However, activated carbon is expensive and it is more costly to regenerate and reuse. Sorption process becomes economic, if the adsorbent is inexpensive and does not require any expensive pre-treatment. Thus, there is a continuous search for alternate low cost adsorbent material to replace high cost activated carbon for water and waste water treatment^{8,9}. Many investigators have studied the feasibility of using low cost substances for the removal of various dyes and pollutants from wastewaters¹⁰⁻¹⁴. Chitosan is usually obtained from waste materials from the seafood processing industry, mainly shells of crabs, shrimp, prawns, and krill¹⁵. Shrimp shell waste is a huge waste from China seafood processing industries (more than 1,000,000 tons per year). These wastes are low cost, available in abundance, and suitable for producing chitosan polymer. Chitosan (CS) has linear polymer of acetylamino-D-glucose with a porous structure. Recently, chitosan which is used as an adsorbent has drawn attentions due to its high contents of amino and hydroxyl functional groups showing high potentials of the adsorption of dyes¹⁶⁻²⁰. Deacetylation degree (DD) may have an effect on adsorption capacity of CS, however, there are limited studies about the deacetylation degree effect on adsorption capacity of CS toward dyes.

The aim of the present study was to investigate the effect of temperature (298 K~323 K), chitosan dosage, and deacetylation degree on the adsorption of reactive black M-2R (RBM) (see their molecular

structures in *Figure 1*), and to determine the optimum conditions for the maximum removal of RBM by chitosan from aqueous solution. For this purpose, some known kinetic equations were used to deal with kinetic data. Also, adsorption isotherm equations were used to treat the equilibrium data.

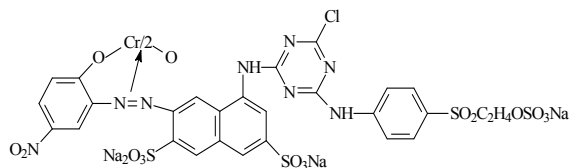


FIGURE 1. The molecular structures of RBM.

MATERIALS AND METHODS

Materials

Chitosan with 92% degree of deacetylation, chitin (Qingdao Jinhua Ocean Biology Co.,Ltd, China), reactive black M-2R, ethanol, acetic acid, and sodium hydroxide used in the experiment were of analytical and purchased from National Medicines Co., Ltd, China.

Preparation Of CS

15 g chitin was treated with 40 mL of 40% sodium hydroxide solution with heating and agitation (60 r/min), The reaction temperature was 110 °C and the reaction time was carried out at 60, 120 and 180 min, in order to obtain 55 ± 5%, 66 ± 3% and 88 ± 3% of deacetylation, respectively.

Batch Kinetic Studies

Experimental kinetic data for RBM adsorption by chitosan were investigated at temperatures of 298 K, 308 K, 318 K and 328 K. All the kinetic experiments were performed at the natural pH of solutions. 0.05 g of CS with 92% DD was contacted with 100 mL RBM solutions in a sealed flask agitated vigorously by a magnetic stirrer using a water bath maintained at a constant temperature. The stirring speed was kept constant at 400 r/min. A volume of 0.5 mL was pipetted and all the samples were centrifuged at 5000 r/min for 5 min and do not settle down easily and the remaining concentration of dye in solution was measured with a visible spectrophotometer model 722-N at a wavelength of 600 nm. After the determination of absorbance, this volume was returned to the flask containing the suspension. In all cases, the working pH (about 6.2-6.6) was that of the solution and was not controlled. The amount of RBM adsorbed on chitosan was calculated by the following equation:

$$q = \frac{(C_o - C_e)V}{m} \quad (1)$$

where q is the amount of RBM adsorbed (mg/g), C_o and C_e the initial and equilibrium concentration of RBM (mg/L), V the volume of the solution (mL) and m the amount of adsorbent (g).

Batch Isotherm Studies

Experimental equilibrium data for RBM adsorption by chitosan were investigated at temperatures of 298 K, 308 K, 318 K and 328 K. 0.05 g of chitosan with 92% DD was mixed separately with 100 mL solutions containing different RBM concentrations (8~18 mg /L). The contact time was determined by kinetic experiments using the same conditions. The suspensions were agitated with a constant speed of 400 r/min for 2 h. Then, the suspensions were decanted and the solutions were analyzed for RBM concentrations using 722-N spectrophotometer. All experiments were conducted in triplicate, and sometimes repeated again and the mean values have been reported.

RESULTS AND DISCUSSION

Adsorption Kinetics

Figure 2 shows the effect of contact time on adsorption at different temperatures. It can be seen from *Figure 2*, equilibrium was almost established within 1 h. To optimize the design of an adsorption system of RBM onto chitosan, it was deemed necessary to establish the most appropriate correlations for the equilibrium data for each system. Therefore, several kinetic models including the pseudo first order equation Eq. (2), pseudo second order equation Eq. (3), and the intraparticle diffusion model Eq. (4) were applied to determine adsorption mechanism.

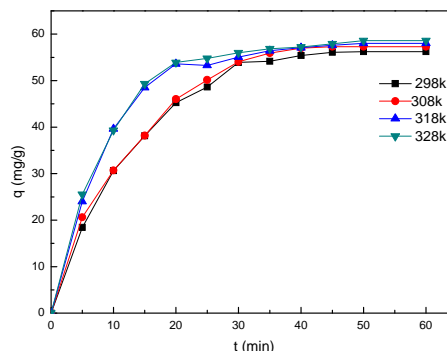


FIGURE 2. Effect of time on the adsorption of RBM on CS at different temperatures.

$$\frac{1}{q_t} = \left(\frac{k_1}{q_1} \right) \left(\frac{1}{t} \right) + \frac{1}{q_1} \quad (2)$$

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

$$q = k_p t^{0.5} + C \quad (4)$$

Where q_t is the amount of RBM adsorbed (mg/g) on chitosan at various time t (min), q_1 the maximum capacity (mg/g) for the pseudo first order adsorption, k_1 the pseudo-first-order rate constant for the adsorption process (min^{-1}), q_2 the maximum adsorption capacity (mg/g) for the pseudo-second-order adsorption, k_2 the rate constant of pseudo-second-order for the adsorption ($\text{g mg}^{-1} \text{min}^{-1}$), k_p the intraparticle diffusion rate constant ($\text{mg g}^{-1} \text{min}^{-0.5}$), C the intercept for the intraparticle diffusion model (mg/g). The results were given in *Table I*.

The Adsorption Isotherms

An adsorption isotherm shows how the adsorbate molecules partition between the liquid and solid phases when the adsorption process reaches equilibrium conditions. Dye concentration plays an important role in affecting the adsorption capacity of CS.

TABLE I. Adsorption kinetic parameters.

	298K	308K	318K	328K
The pseudo-first-order				
q_1	77.76	76.92	74.24	73.15
k_1	15.84	13.69	9.799	9.684
R^2	0.9647	0.9733	0.9813	0.9715
The pseudo-second-order				
q_2	65.18	66.18	62.98	63.29
k_2	0.00187	0.001906	0.003538	0.00369
R^2	0.9978	0.9878	0.9926	0.9936
Intraparticle diffusion				
k_p	7.930	7.919	7.3994	7.3831
C	5.017	5.426	11.158	11.655
R^2	0.9297	0.9331	0.8509	0.8485

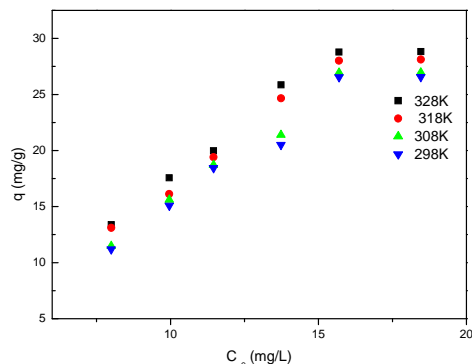


FIGURE 3. Adsorption isotherms of RBM on chitosan at different temperatures.

Figure 3 shows the effect of initial dye concentration on adsorption capacity of RBM for CS. Clearly, adsorption capacity of CS increased sharply with increasing the initial concentration of dye.

Three different adsorption isotherms were used in order to correlate the equilibrium adsorption data. The adsorption isotherms used here were the Langmuir Eq. (5), Freundlich Eq. (6) and the Tempkin isotherm Eq. (7) in liberalized form separately.

$$\frac{C_e}{q_e} = \frac{1}{q_m L} + \frac{C_e}{q_m} \quad (5)$$

$$\ln q_e = \ln K_f + n \ln C_e \quad (6)$$

$$q_e = \frac{RT}{b_T} (\ln A) + \frac{RT}{b_T} (\ln C_e) \quad (7)$$

Where q_m is the maximum adsorption capacity of the adsorbent (mg/g), q_e (mg/g) and C_e (mg/L) are the equilibrium dyestuff concentrations in the solid and liquid phases, respectively, L is Langmuir constant regarding the adsorption energy. K_f is relative adsorption capacity (mg/g), n is heterogeneity factor (adsorption intensity). A (l/g) and b_T (J/mol) are the Tempkin constants. Linear regression was frequently used to determine the most fitted isotherm. The constants together with the R^2 values are shown in *Table II*.

TABLE II. Adsorption Isotherm constants for RBM onto chitosan at different temperatures.

	298K	308K	318K	328K
Langmuir constant				
q_m	31.11	23.26	10.87	8.25
L	0.03946	0.03572	0.08842	0.04128
R^2	0.9889	0.9924	0.9872	0.9898
R_L	0.57-0.762	0.59-0.77	0.37-0.58	0.56-0.75
Freundlich constant				
n	0.5812	0.9802	0.9862	0.9984
R^2	0.9927	0.96	0.96181	0.9599
K_f	2.370	1.670	1.346	1.269
Tempkin constant				
b_t	4111.90	3291.6	1644.7	1272.1
A	0.6456	0.8100	0.3312	0.6874
R^2	0.9800	0.9954	0.8986	0.9531

As it is seen from *Table II*, the correlation factors (R^2) indicates that better applicability was obtained using linearized Langmuir than Freundlich isotherms and Tempkin isotherms. The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant, separation factor or equilibrium parameter, R_L , which is calculated using the following equation Eq. (8):

$$R_L = \frac{1}{1 + LC_0} \quad (8)$$

The range of R_L value is significant in defining the nature of adsorption *Table II*. R_L values lie between 0 and 1, indicating that on-going adsorption process is favorable for the dye using chitosan as adsorbent. The Freundlich parameters K_f values are reduced by increasing temperature. This result shows that adsorption capacities of chitosan increase when temperatures decrease. The values of n are smaller than 1, which also reflecting a favorable adsorption.

Effect Of The Deacetylation Degree On The Adsorption of RBM

Figure 4 shows the effect of amine groups in the chitosan polymer on RBM adsorption for four different deacetylation degrees (55%, 66%, 88%, 92%), in the following conditions: equilibrium pH of 6.6, temperature of 298 K and 0.025 g of chitosan, the best adsorption capacity was observed for a deacetylation degree of 66%. When the deacetylation degree was kept low (55%), it was observed a reduction in the binding capacity of CS. In this case, a smaller number of amine groups in polymer are generated, resulting in less adsorption. A high deacetylation degree does not lead to an improvement of RB binding. Long deacetylation reaction time induces high deacetylation degree. However, it also induces polymer degradation, resulting in chains with low average molecular weight. The polymer chains with either low molecular weight and/or its fragments are released from the coiled structure of CS to the surrounding liquid, affecting the adsorption capacity of CS.

Effect of CS Dosage On Adsorption

The dependence of the dosage of adsorbent used on the adsorption of dye was studied in the condition of a deacetylation degree of 66%, $V=100$ mL, $C_0=19$ mg/L and temperature of 298 K and the results are shown in *Figure 5*. The amount of adsorbents used was varied from 0.01 g to 0.10 g while the other parameters were kept constant. Based on *Figure 5*, when the dosage of chitosan was below 0.01 g, it is found that an increase in the adsorbent dosage can increase the percentage of dye removal from the solution. This is expected because by increasing the adsorbent dosage, the number of adsorption sites available for adsorbent -adsorbate interaction is increased as well. There will be a decrease in the adsorption capacity when the dosage of chitosan was above 0.015 g. The first reason is that an increase in the adsorbent dosage at constant dye concentration and volume, will lead to unsaturation of the adsorption sites, The second is due to the particulate interaction such as aggregation resulting from high adsorbent dosage contributes to this observation. The best adsorption capacity of 146mg/g was observed for a dosage chitosan of 0.01 g.

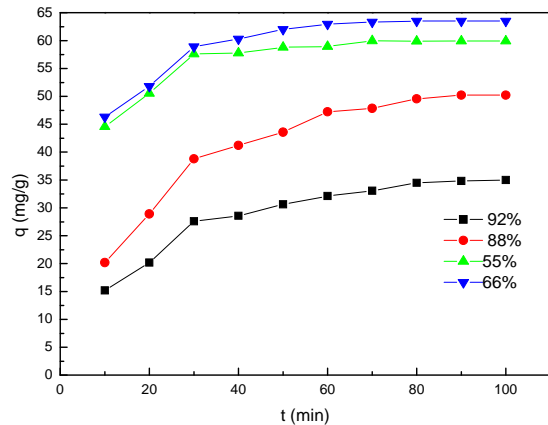


FIGURE 4. Effect of CS deacetylation degree on adsorption of RBM.

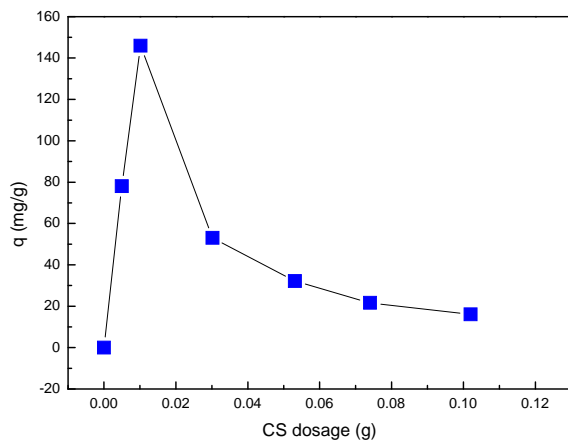


FIGURE 5. Effect of CS dosage on adsorption of RBM.

FTIR Analysis

The FTIR spectra of chitosan before (2) and after adsorption (1) were shown in Figure 6. The wide band at 3430 cm^{-1} shown in the spectrum of chitosan is attributed to stretching vibration of hydroxyl group of chitosan. This band was shifted to 3424 cm^{-1} when RBM was adsorbed. It may indicate a hydrogen bond between RBM and OH groups of chitosan. The band at 2876 cm^{-1} shown in CS is assigned to the C-H stretching vibration of polymer backbone. There was significant decrease for that band in the spectrum of RBM. This band was shifted from 2876 to 2856 cm^{-1} . This can be considered as an evident for the interaction between chitosan and RBM cation¹¹. The band at 1417 cm^{-1} in the spectrum of chitosan is due to C-H bending, which was appeared as a duplicate at 1419 cm^{-1} in

the spectrum of chitosan after adsorption. The bands observed at 1652 and 1596 cm^{-1} correspond to N-H bending vibrations. These bands were shifted from to 1643 and 1560 cm^{-1} when the adsorption of RBM occurs. These changes may be owing to weak interactions between RBM and chitosan.

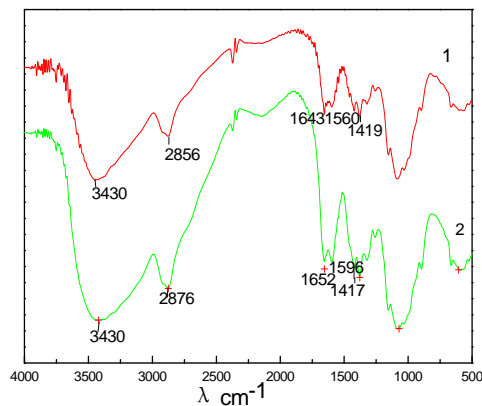


FIGURE 6. FTIR spectra of chitosan (1) before and (2) after adsorption of RBM.

SEM Analysis

The surface morphology Figure 7 of chitosan before and after adsorption was examined by means of scanning electron microscopy (SEM, S4800) at an accelerating voltage of 5 kV. As it is known, SEM is one of the most widely used surface characterization method. Chitosan has heterogeneous surface and micro-pores smaller than $5\text{ }\mu\text{m}$ as seen from its SEM micrographs. These pores are very suitable places for the sorption of RBM. In addition to this, there are some RBM micro-particles observed as shown from Figure 7(b), which may verify adsorption phenomenon between the RBM and chitosan.

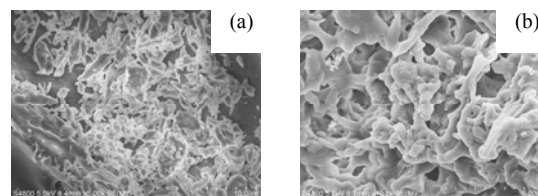


FIGURE 7. SEM spectra of chitosan before (a) and after adsorption (b) of RBM.

CONCLUSIONS

The results in this study show that highly abundance and low cost biopolymer chitosan can be utilized as an adsorbent for the removal of RBM from aqueous solution. The sorption data indicate that Langmuir

equation provides a better fit than Freundlich equation and Tempkin isotherms. Thus, it suggests the monolayer sorption of RBM onto chitosan. The kinetic experiments imply that sorption process obeys the pseudo-second-order kinetic model. The temperature strongly influenced the adsorption process. It is clear that the q_2 (maximum adsorption capacity for the pseudo second-order adsorption) values are decreased by increasing the temperature. From the kinetic study, it was found that activation energy value for RBM sorption onto chitosan was greater than $58.28 \text{ kJ mol}^{-1}$ and CS with 66% deacetylation degree exhibited a good binding for RBM. The best adsorption capacities were found to be 146 mg/g when the conditions for this study were a deacetylation degree of 66%, 0.01 g adsorbent dosage, 298 K and 19 mg/L initial concentration respectively.

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AUTHORS' ADDRESSES

Chunmei Ding

Fang Li

Anhui University of Polytechnic

Beijing Middle Road

Wuhu, Anhui 241000

CHINA