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Kinetics of the adsorption of reactive dyes by chitosan

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Abstract

The effect of initial concentration, temperature, and shaking rate on the adsorption of reactive yellow 2 (RY2) and reactive black 5 (RB5) by chitosan (Sigma C 3646) was investigated. Experimental data obtained at different temperatures for the adsorption of each dyestuff by chitosan were applied to pseudo first-order, pseudo second-order and Weber–Morris equations, and the rate constants of first-order adsorption (k_1), the rate constants of second-order adsorption (k_2) and pore diffusion rate constants (k_p) at these temperatures were calculated, respectively. In addition, the adsorption isotherms of each dyestuff by chitosan were also determind at different temperatures.

Keywords: Adsorption; Chitosan; Reactive dyestuff; Diffusion

1. Introduction

Synthetic dyes are widely used in industries such as textiles, leather, paper, plastics, etc. to colour their final products [1]. Reactive dyes are the most common dyes used due to their advantages, such as bright colours, excellent colourfastness and ease of application [2,3]. They exhibit a wide range of different chemical structures, primarily based on substituted aromatic and heterocyclic groups. A large number of reactive dyes are azo compounds that are linked by an azo bridge [4]. Many reactive dyes are toxic to some organisms and may cause direct destruction of creatures in water [5]. In addition, since reactive dyes are highly soluble in water, their removal from effluent is difficult by conventional physicochemical and biological treatment methods [6,7].

In general, there are five main methods used for the treatment of dye-containing effluent: adsorption, oxidation–ozonation, biological treatment, coagulation–flocculation and membrane processes [8]. The adsorption process is one of the most efficient methods of removing pollutants from wastewater. Also, the adsorption process provides an attractive alternative treatment, especially if the adsorbent is inexpensive and readily available [9]. Many studies have been made on the possibility of adsorbents using activated carbon [2,10,11], peat [12], chitin [13], silica [14], fly ash [15], clay [16] and others [17–21]. However, the adsorption capacity of the adsorbents is not very large, to improve adsorption performance new adsorbents are still under development.

Chitosan is the deacetylated form of chitin, which is a linear polymer of acetylamino-D-glucose (Fig. 1). Recently, chitosan which is used as an adsorbent has drawn attentions due to its high contents of amino and hydroxy functional groups showing high potentials of the adsorption of dyes [22], metal ions [11], and proteins [23]. Other useful features of chitosan include its abundance, hydrophilicity, biocompatibility, biodegradability and antibacterial property [24]. The adsorption of reactive, acidic and direct dyes in neutral solutions using chitosan shows large adsorption capacities [22,25]. The effect of pH is an important factor on the dye-binding capacity of chitosan. Because, the pK_a value

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Nomenclature

C	concentration of adsorbate at time t (ppm)
C_e	equilibrium concentration of adsorbate (ppm)
k_1	the rate constant of first-order adsorption (min^{-1})
k_2	the rate constant of second-order adsorption ($g\,mg^{-1}\,min^{-1}$)
k_p	pore diffusion rate constant ($mg\,g^{-1}\,min^{-1/2}$)
q	amount of adsorbate adsorbed at time t ($mg\,g^{-1}$)
q_e	amount of adsorbate adsorbed at equilibrium ($mg\,g^{-1}$)
S	the BET surface area ($m^2\,g^{-1}$)
t	time (min)

of the amino group ($R{-}NH_2$) in the structure of chitosan is 6.3, and the amino group dissociates partly into $R{-}NH_3^+$ even at pH = 6.9 [26].

The aim of the present study is to investigate the effect of initial concentration, temperature, and shaking rate on the adsorption of reactive yellow 2 (RY2) and reactive black 5 (RB5) being given their molecular structures in Fig. 2, and to determine the optimum conditions for the maximum removal of these dyestuffs by chitosan from aqueous solution. For this purpose, some known kinetic equations have been used. These substances are toxic. In addition, when in contact with the eyes or skin, they cause irritation.

2. Experimental

2.1. Materials

In this study, chitosan (Sigma C 3646, Germany) as adsorbent, and RY2 (Aldrich, Germany) and RB5 (Aldrich, Germany) as adsorbate were used. Some important properties of chitosan are given in Table 1 [22].

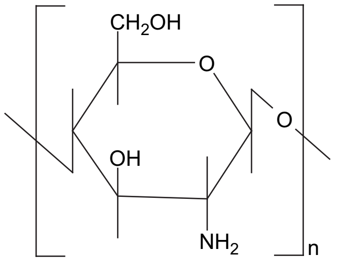
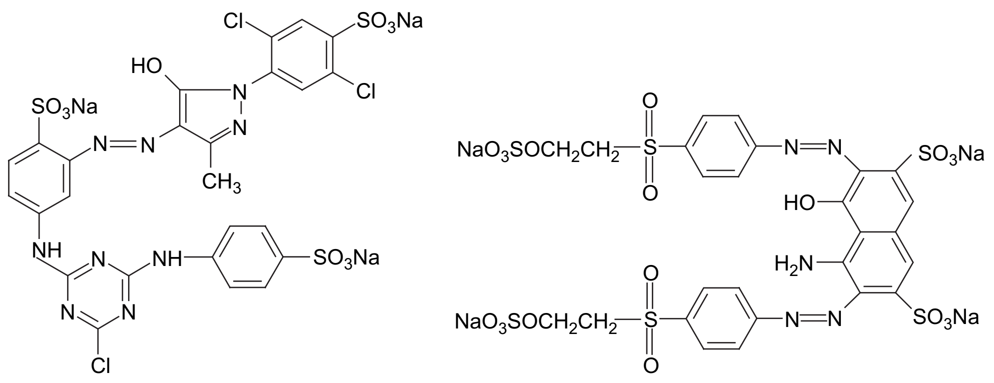


Fig. 1. The molecular structure of chitosan.

2.2. Batch kinetic studies

All the kinetic experiments were performed at the natural pHs of solutions. Acid, base or buffer solution was not added into the solutions of adsorbates. Kinetic study to investigate the effect of initial concentration on the adsorption of RY2 and RB5 by chitosan from aqueous solution was firstly carried out. It was studied at the initial concentrations of 300 ppm (pH = 6.94 for RY2 and pH = 7.12 for RB5) and 600 ppm (pH = 6.98 for RY2 and pH = 7.18 for RB5) of the dyestuffs. Samples of 0.2 g of chitosan with the samples of 50 mL of each dyestuff having a known initial concentration were shaken with a shaker (J.P. SELECTA, s.a., SPAIN). Absorbance values with a SHIMADZU UV-120-02 spectrophotometer after different time intervals were measured at $\lambda_{max} = 404$ nm for RY2 and $\lambda_{max} = 597$ nm for RB5. In addition, the effects of temperature and shaking rate at the initial concentration of 450 ppm (pH = 6.96 for RY2 and pH = 7.15 for RB5) on the adsorption of RY2 and RB5 by chitosan from aqueous solution were similarly investigated. Kinetical data related to the effect of temperature were analyzed using the pseudo first-order [27] (Eq.(1)), the



(a) (b)

Fig. 2. The molecular structures of: (a) RY2 and (b) RB5.

Table 1
Some important properties of chitosan (Sigma C 3646)

Deacetylation degree	Minimum 85%
Formula weight	810,000 g mol^{-1}
BET surface area	0.65 m^2 g^{-1}
Density	0.15–0.30 g mL^{-1}
pK_a	6.3
Colour	Light yellow

pseudo second-order [28] (Eq.(2)) and the intraparticle diffusion [29] (Eq.(3)) equations.

$$\log(q_e - q) = \log q_e - \frac{k_1}{2.303}t \quad (1)$$

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

$$q = k_p t^{1/2} \quad (3)$$

2.3. Batch isotherm studies

Firstly, the samples of 0.2 g of chitosan with the samples of 50 mL of solutions having different initial concentration (C_0) prepared from the stock solutions of each dyestuff were shaken for their equilibrium contact times at 293 K and 150 rpm. After this shaking, the absorbance values of solutions remaining without adsorption were measured. In addition, the adsorption isotherms of each dyestuff were also investigated at 333 K and 150 rpm.

3. Results and discussion

3.1. Effect of initial concentration, temperature and shaking rate

Figs. 3–5 show the effect of initial concentration, temperature, and shaking rate, respectively, on the adsorption of RY2 and RB5 by chitosan from aqueous solution. As can be seen from Figs. 3–5, there are a small effect of initial concentration and shaking rate but a great effect of temperature on the adsorption of RY2 and RB5 by chitosan from aqueous solution. These results are most likely due to the chemical adsorption occurring between these dyestuffs and chitosan. As it is known, chemical adsorption is a type of adsorption occurring with a single layer. These dyestuffs are reactive dyestuffs. There are $-SO_3^-$ groups in their structures. These groups make RY2 and RB5 rather acidic. The amino group in the structure of chitosan is charged positively when chitosan is put into these solutions due to acidity of aqueous solutions of RY2 and RB5, and a chemical affinity forms between this positive charge and negative charges in the structures of RY2 and RB5. As a result of this chemical affinity, the resistance of the boundary layer surrounding the adsorbent weakens. Thus, most probably, the effect of the shaking rate on the adsorption of RY2 and RB5 by chitosan is not too much important.

3.2. Adsorption kinetics

Experimental data related to the adsorption of RY2 and RB5 on chitosan at different temperatures were

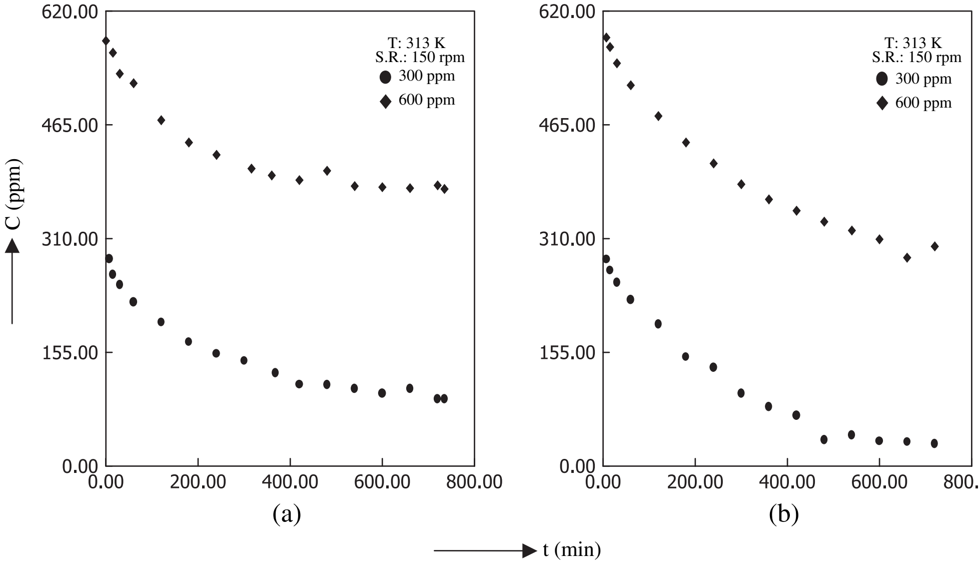


Fig. 3. The effect of initial concentration on the adsorption of two reactive dyestuffs by chitosan from aqueous solution: (a) RY2 and (b) RB5.

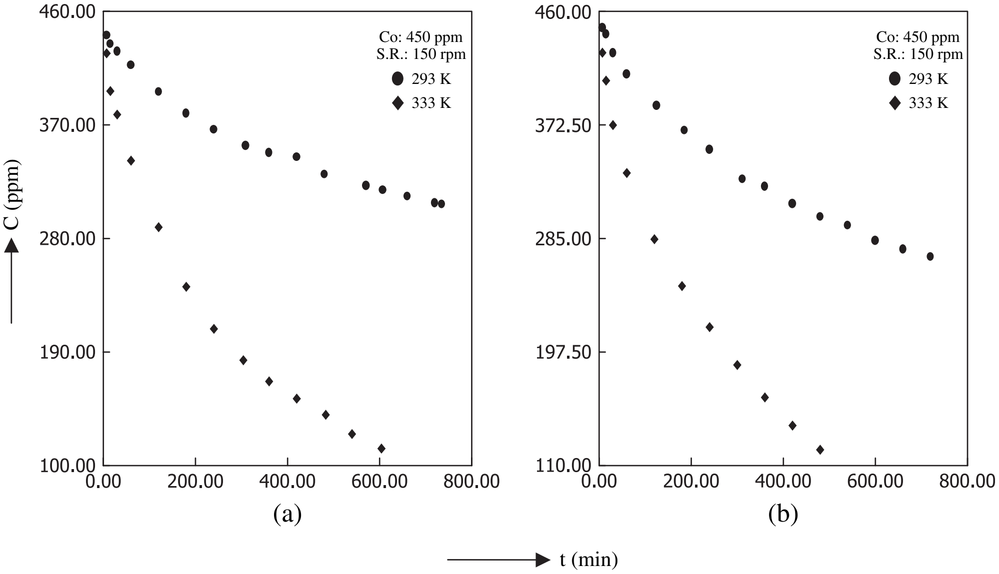


Fig. 4. The effect of temperature on the adsorption of two reactive dyestuffs by chitosan from aqueous solution: (a) RY2 and (b) RB5.

applied to the pseudo first-order equation (Fig. 6), the pseudo second-order equation (Fig. 7) and the intraparticle diffusion equation (Fig. 8), and the rate constants of first-order adsorption (k_1), the rate constants of second-order adsorption (k_2) and pore diffusion rate constants (k_p) in Table 2 were calculated. It was seen that experimental data fitted pseudo first-order equation rather than pseudo second-order equation. As can be seen from k_1 and k_p constants, RY2 and RB5 are adsorbed faster at higher temperature. As for according to k_2 constants, RB5 is adsorbed faster at higher temperature but RY2 is adsorbed faster at lower temperature.

3.3. Intraparticle diffusion

The double nature of intraparticle diffusion plots may be explained as: the initial curved portions are attributed to boundary layer diffusion effects [30], while the final linear portions are due to intraparticle diffusion effects [31]. As it is known, two intraparticle diffusion mechanisms are involved in the adsorption rate: (a) diffusion within the pore volume, known as pore diffusion, and (b) diffusion along the surface of the pores, known as surface diffusion. Pore diffusion and surface diffusion occur in parallel within the adsorbent particle.

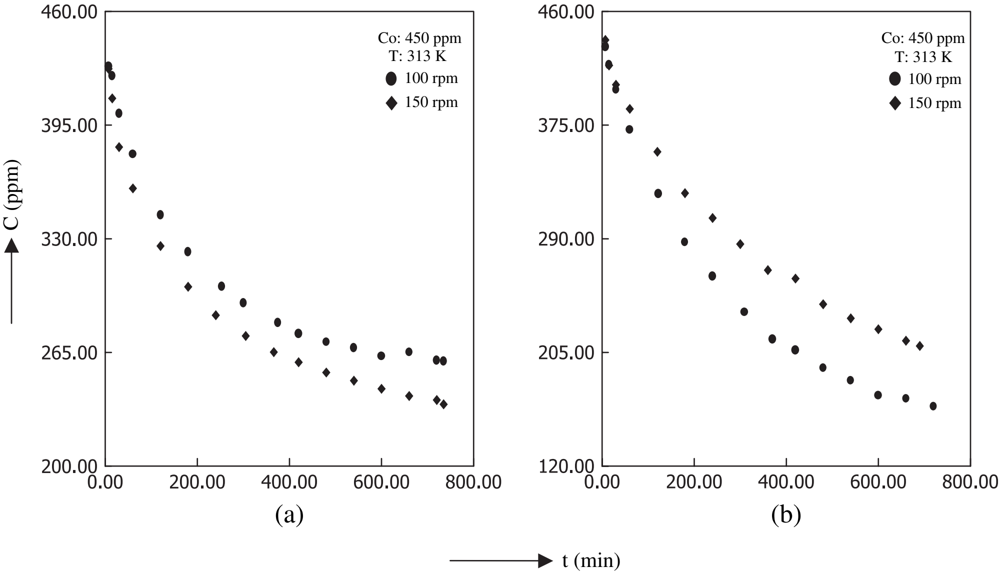
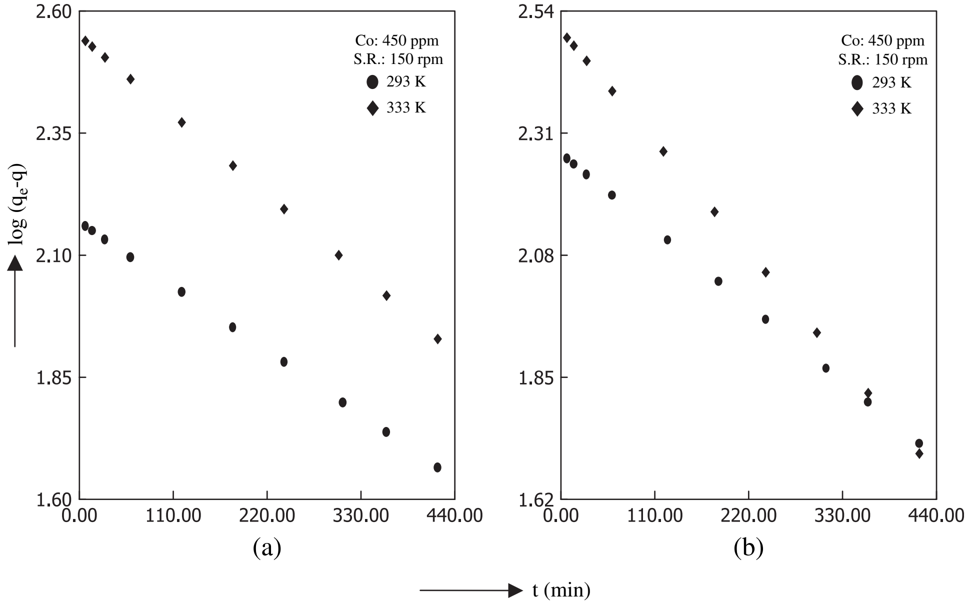


Fig. 5. The effect of shaking rate on the adsorption of two reactive dyestuffs by chitosan from aqueous solution: (a) RY2 and (b) RB5.



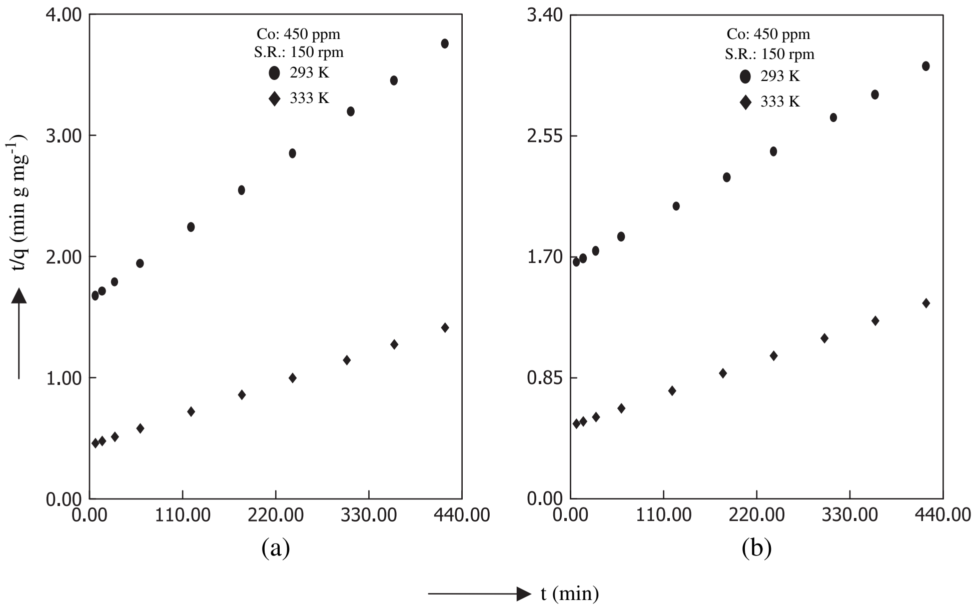
(a) (b)

Fig. 6. Lagergren plots of kinetic curves related to the adsorption of two reactive dyestuffs by chitosan from aqueous solution: (a) RY2 and (b) RB5.

But, because the BET surface area of chitosan used as adsorbent in the present study is very low (0.65 m^2 g^{-1}) [22], adsorption kinetics is controlled by surface diffusion. At particularly lower temperatures, surface diffusion is more dominant.

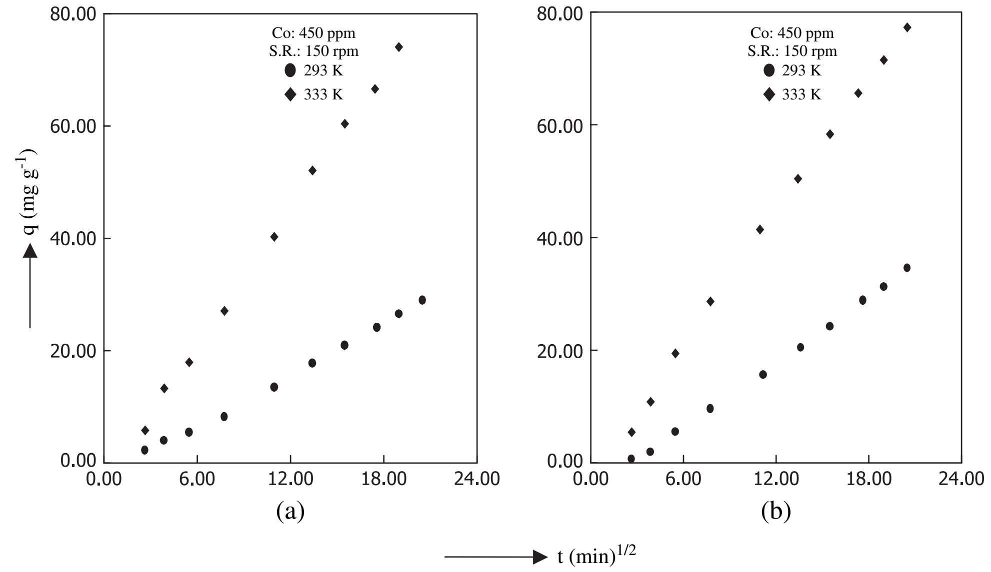
3.4. Adsorption isotherms

Fig. 9 shows the effect of temperature on the adsorption isotherm of RY2 and RB5 by chitosan from aqueous solution. These types of isotherm are known as H-type isotherms (high affinity) according to isotherm classification proposed by Giles et al. The adsorption isotherm of RB5 at 333 K fits subgroup H-4 while its adsorption isotherm at 293 K fits subgroup H-2. In the subgroups H-2 and H-4 we can identify the plateau, which is the end of the turning point, with completion of the first monolayer. The subsequent rise represents the development of a second layer and in subgroup H-4 this is completed [32]. The H-type isotherms are associated



(a) (b)

Fig. 7. Plots of the pseudo second-order model of kinetic curves related to the adsorption of two reactive dyestuffs by chitosan from aqueous solution: (a) RY2 and (b) RB5.



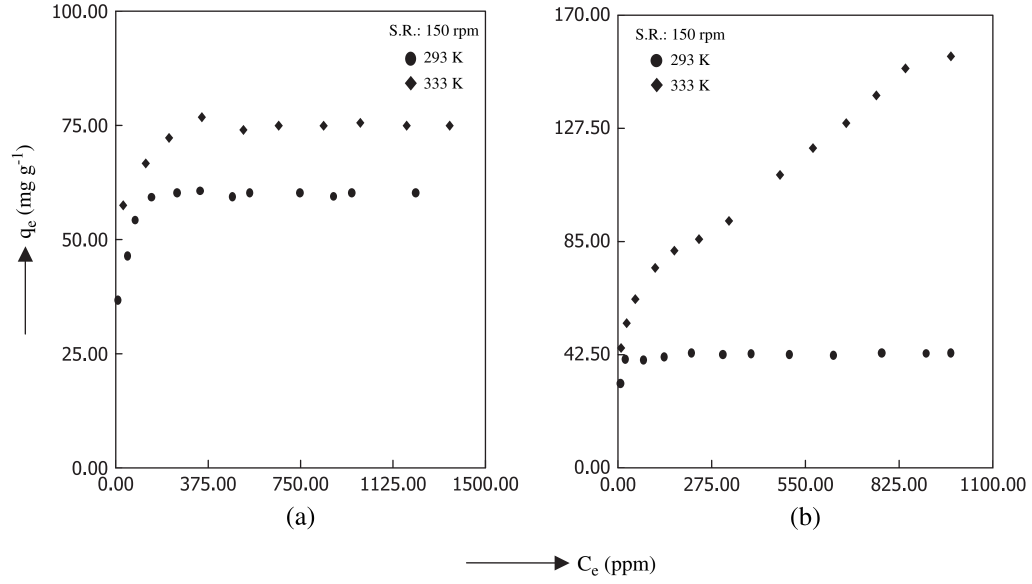
(a)

(b)

Fig. 8. Weber–Morris plots of kinetic curves related to the adsorption of two reactive dyestuffs by chitosan from aqueous solution: (a) RY2 and (b) RB5.

Table 2
The rate constants of first-order adsorption (k_1), the rate constants of second-order adsorption (k_2) and pore diffusion rate constants (k_p) related to the adsorption of RY2 and RB5 by chitosan from aqueous solution

T (K)	RY2			RB5		
	$k_1 \times 10^3$ ($\mathrm{min^{-1}}$)	$k_2 \times 10^5$ ($\mathrm{g\,mg^{-1}\,min^{-1}}$)	k_p ($\mathrm{mg\,g^{-1}\,min^{-1/2}}$)	$k_1 \times 10^3$ ($\mathrm{min^{-1}}$)	$k_2 \times 10^6$ ($\mathrm{g\,mg^{-1}\,min^{-1}}$)	k_p ($\mathrm{mg\,g^{-1}\,min^{-1/2}}$)
293	2.75	1.55	1.58	3.00	6.80	2.03
333	3.40	1.20	4.15	4.37	8.21	3.86



(a)

(b)

Fig. 9. The effect of temperature on the adsorption isotherm of two reactive dyestuffs by chitosan from aqueous solution: (a) RY2 and (b) RB5.

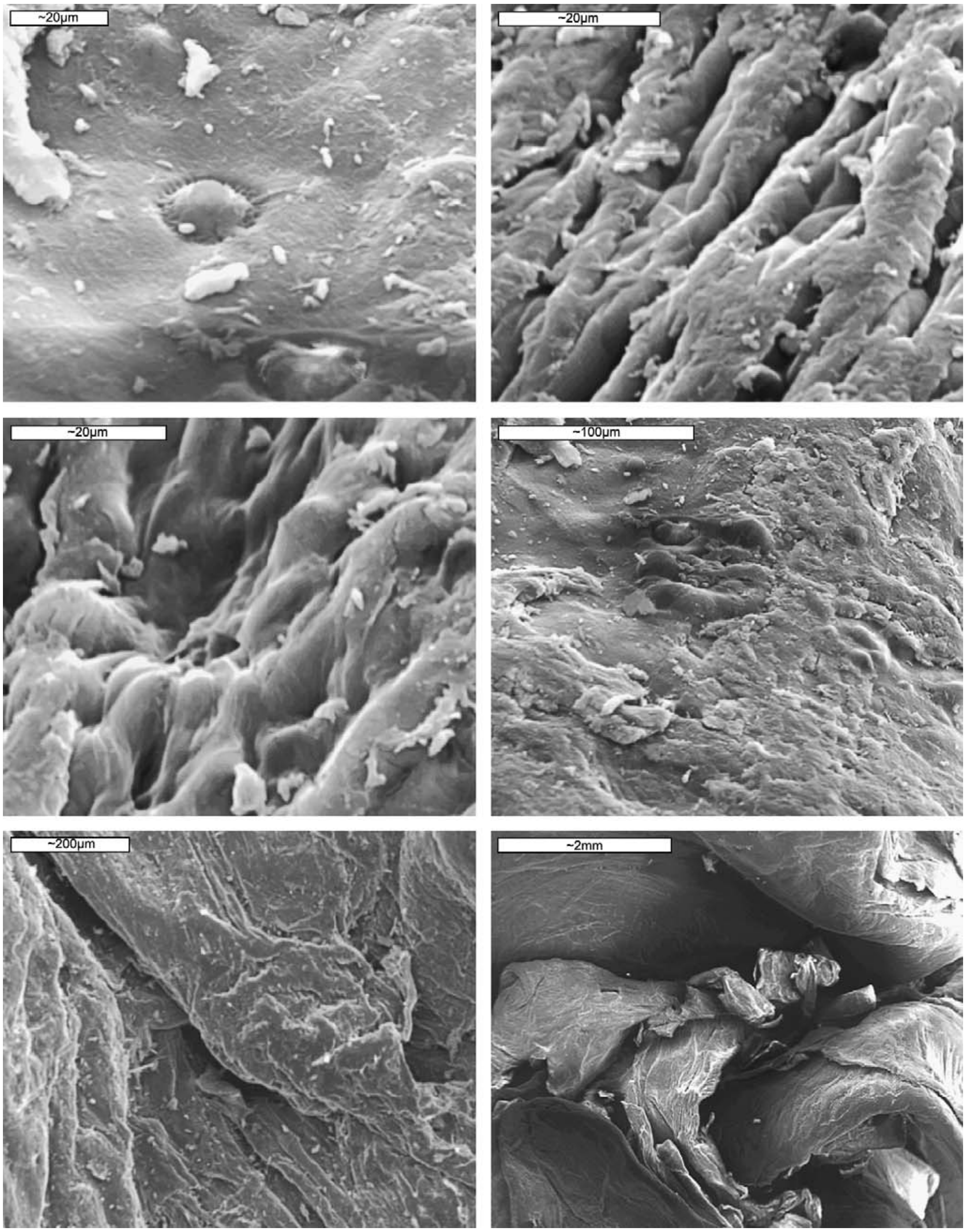


Fig. 10. The SEM micrographs of chitosan (Sigma C 3646).

with chemical bonding rather than physical attractions and are commonly observed in the measurements. Besides, the H-type isotherms have a higher affinity at low concentrations and reach a maximum [33].

Fig. 10 shows the SEM (scanning electron microscopy) micrographs of chitosan. As it is known, SEM is one of the most widely used surface diagnostic tools. Chitosan has heterogeneous surface and macropores as seen from its SEM micrographs. Its BET surface area is confirming that chitosan has macropores. Chitosan is a linear homopolymer of β-(1,4)-2-amino-2-deoxy-D-glucose, and it is similar to cellulose in morphology.

4. Conclusions

For maximum adsorption yield on the basis of experimental results obtained:

1. The adsorption of RY2 and RB5 by chitosan from aqueous solution must be studied at high temperature.
2. It can easily be said that chitosan can be used as adsorbent in the studies of dyestuff adsorption. Because, chitosan is a very better and cheaper adsorbent in comparison with most adsorbents in

the adsorption of particularly heavy metals and acidic dyestuffs from aqueous solution, and it is also found abundantly in nature. In additon, because its BET surface area (S) is very low, the adsorption kinetics in the present study is controlled by surface diffusion.

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