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Kinetics of the adsorption of reactive dyes by chitin

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Abstract

The effect of initial concentration, temperature, shaking rate and pH on the adsorption of reactive yellow 2 (RY2) and reactive black 5 (RB5) by chitin (Sigma C 9213) was investigated. Experimental data obtained at different temperatures for the adsorption of each dyestuff by chitin 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 chitin were also determined at different temperatures.

Keywords: Adsorption; Chitin; Reactive dyestuff; Diffusion

1. Introduction

Synthetic dyes are extensively used for textile dyeing, paper printing, leather dyeing, colour photography and as additives in petroleum 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 group [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], chitosan [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.

Chitin is a natural polysaccharide found particularly in the shells of crustaceans such as crab and shrimp, the cuticles of insects, and the cell walls of fungi [22]. It is the second most abundant polysaccharide after cellulose. The composition of chitin is similar to cellulose except for the acetylated C-2 hydroxyl groups [23]. Chitin is substantially composed of 2-acetamido-2-deoxy-D-glucopyranose (*N*-acetyl-D-glucosamine, GlcNAc) units linked by β-(1,4-) linkage (Fig. 1) [22]. It has strong inter- and intra-molecular hydrogen bonds between the polymer chains and is water-insoluble due to its rigid crystalline structure [24]. The pK_a of the chitin *N*-acetyl

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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)

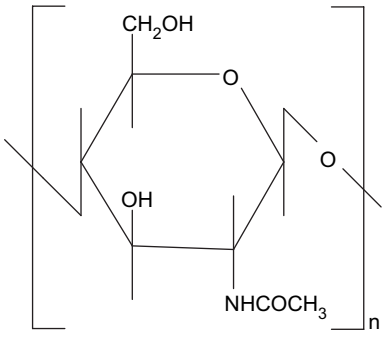
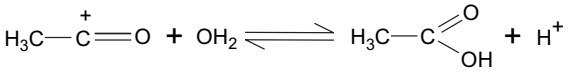


Fig. 1. The molecular structure of chitin.



Scheme 1. The hydrolysis of chitin *N*-acetyl ion.

side chain is 6.1 (Eq. (1)). At pH = 6.1 some 50% of the *N*-acetyl groups are charged.

$$K_a = \frac{[CH_3COOH][H^+]}{[CH_3C^+O]} \text{ and } pK_a = -\log K_a \quad (1)$$

At lower pHs more groups are charged and at higher pHs less of these groups are charged [25] (Scheme 1).

Chitin has been used in agricultural, food, and industrial fields. Recently it has been considered as biomaterial in fields such as biomedicine, pharmacology, and biotechnology due to its biocompatibility, biodegradability, and biological activities [24]. In addition, chitin has been widely used as adsorbent in adsorption studies. But, limited information is available on the adsorption of dyes by chitin.

In previous study [13], the effect of initial concentration, temperature, and shaking rate on the adsorption of reactive yellow 2 (RY2) and reactive black 5 (RB5) (their molecular structures are given in Fig. 2) by chitosan from aqueous solution had been investigated. The aim of the present study is to investigate the effect of above-mentioned factors and pH on the adsorption of these dyestuffs and to determine the optimum conditions for the maximum removal of these dyestuffs by chitin from aqueous solution, and to compare the adsorption capability of chitin and chitosan related to these dyestuffs. 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 also cause irritation.

2. Experimental

2.1. Materials

In this study, chitin (Sigma C 9213, Germany) was used as adsorbent, and RY2 (Aldrich, Germany) and RB5 (Aldrich, Germany) were used as adsorbates. Some important properties of chitin are given in Table 1.

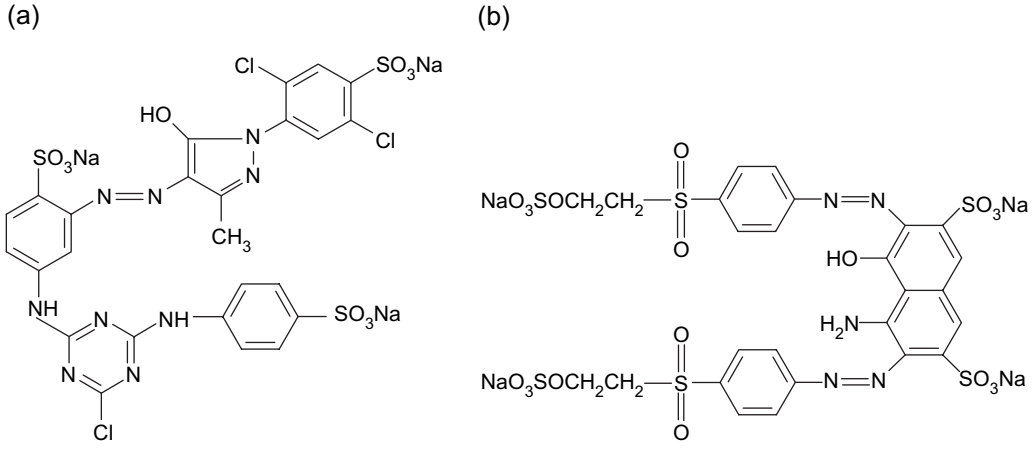


Fig. 2. The molecular structures of: (a) RY2 and (b) RB5.

Table 1
Some important properties of chitin (Sigma C 9213)

Molecular formula	$(C_8H_{13}NO_5)_n$
Formula weight	~400,000 g mol^{-1}
BET surface area	Inadequate for measurement
Density	~0.45 g mL^{-1}
pK_a	6.1
Colour	Light yellow

2.2. Batch kinetic studies

Kinetic experiments related to the effect of initial concentration, temperature and shaking rate were performed at the natural pHs of solutions. Acid, base or buffer solution was not added into the solutions of adsorbates. First, kinetic study to investigate the effect of initial concentration on the adsorption of RY2 and RB5 by chitin from aqueous solution was 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 chitin 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 were measured at $\lambda_{max} = 404$ nm for RY2 and $\lambda_{max} = 597$ nm for RB5 with a SHIMADZU UV-120-02 spectrophotometer after different time intervals. Then the effect 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 chitin from aqueous solution was investigated. In addition, the effect of pH at constant initial concentration, temperature and shaking rate on the adsorption of RY2 and RB5 by chitin from aqueous solution was similarly investigated. The pH of dye solutions was adjusted by buffer solutions of KH_2PO_4/Na_2HPO_4. The pH was adjusted to 6.0 and 8.0 by using 1 M HCl and 1 M NaOH, respectively. Kinetic data related to the effect of temperature were analyzed using the pseudo first-order (Eq. (2)) [26], the pseudo second-order (Eq. (3)) [27] and the intraparticle diffusion (Eq. (4)) [28] equations:

$$\log(q_e - q) = \log q_e - \frac{k_1}{2.303}t \quad (2)$$

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

$$q = k_p t^{1/2} \quad (4)$$

2.3. Batch isotherm studies

Firstly, the samples of 0.2 g of chitin 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 150 rpm and 293 K. 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 150 rpm and 333 K.

3. Results and discussion

3.1. Effect of initial concentration, temperature, shaking rate and pH

Figs. 3–6 show the effect of initial concentration, temperature, shaking rate, and pH, respectively, on the adsorption of

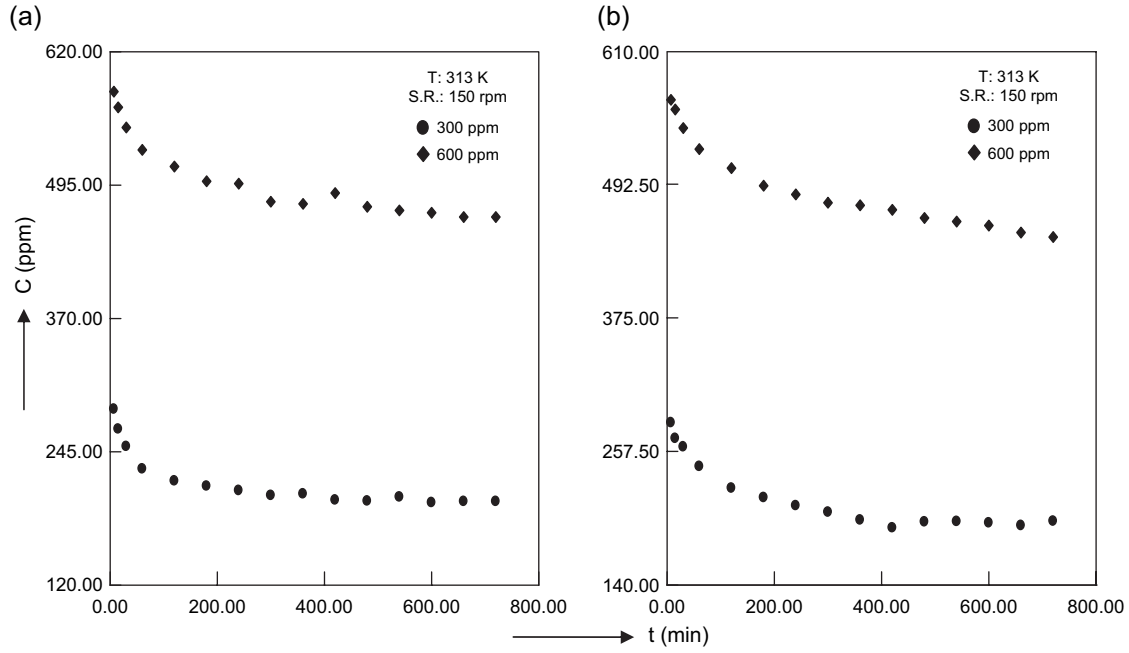


Fig. 3. The effect of initial concentration on the adsorption of two reactive dyestuffs by chitin from aqueous solution: (a) RY2 and (b) RB5.

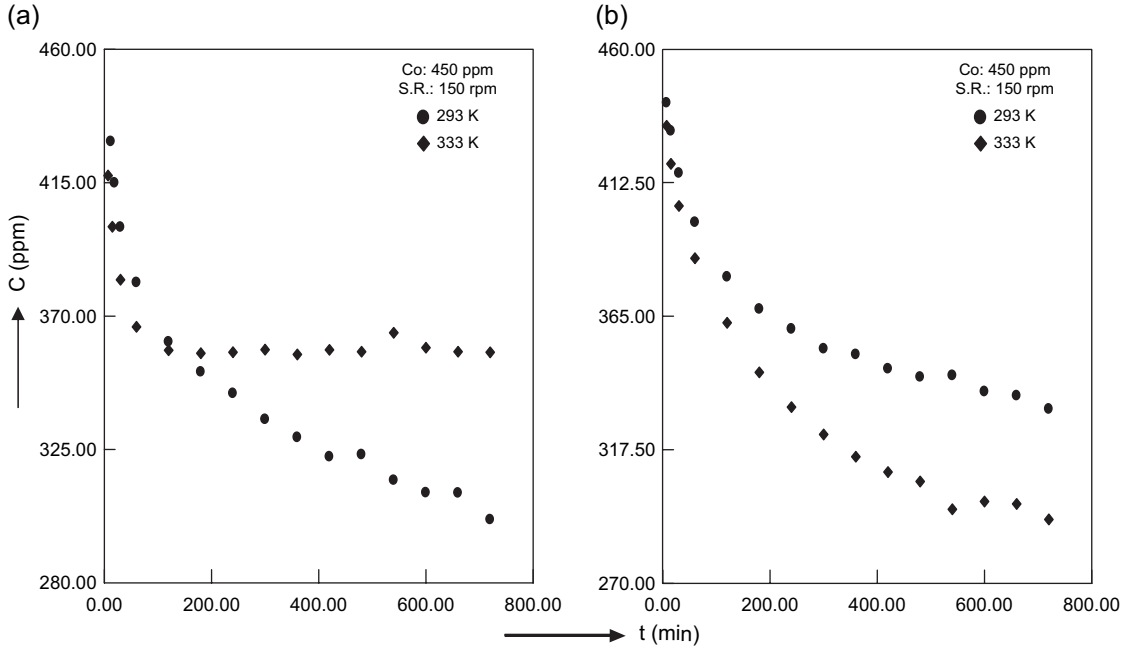


Fig. 4. The effect of temperature on the adsorption of two reactive dyestuffs by chitin from aqueous solution: (a) RY2 and (b) RB5.

RY2 and RB5 by chitin from aqueous solution. As can be seen from Figs. 3–6, the effect of initial concentration and shaking rate is small but the effect of temperature and pH is large on the adsorption of RY2 and RB5 by chitin from aqueous solution. These results most probably arise from the physical and chemical adsorption occurring together between RY2 and chitin, and the chemical adsorption occurring significantly between RB5 and chitin. RY2 is adsorbed less due to desorption occurring because of physical adsorption while it is adsorbed faster because of chemical adsorption on chitin at higher temperature [29]. In addition, RB5 is adsorbed less due to particle attrition while it is adsorbed faster because of chemical interaction occurring between negative groups in its structure and protonated amine group in the structure of chitin at lower pH [30]. These dyestuffs are reactive dyestuffs. There are $-SO_3^-$ groups in their structures.

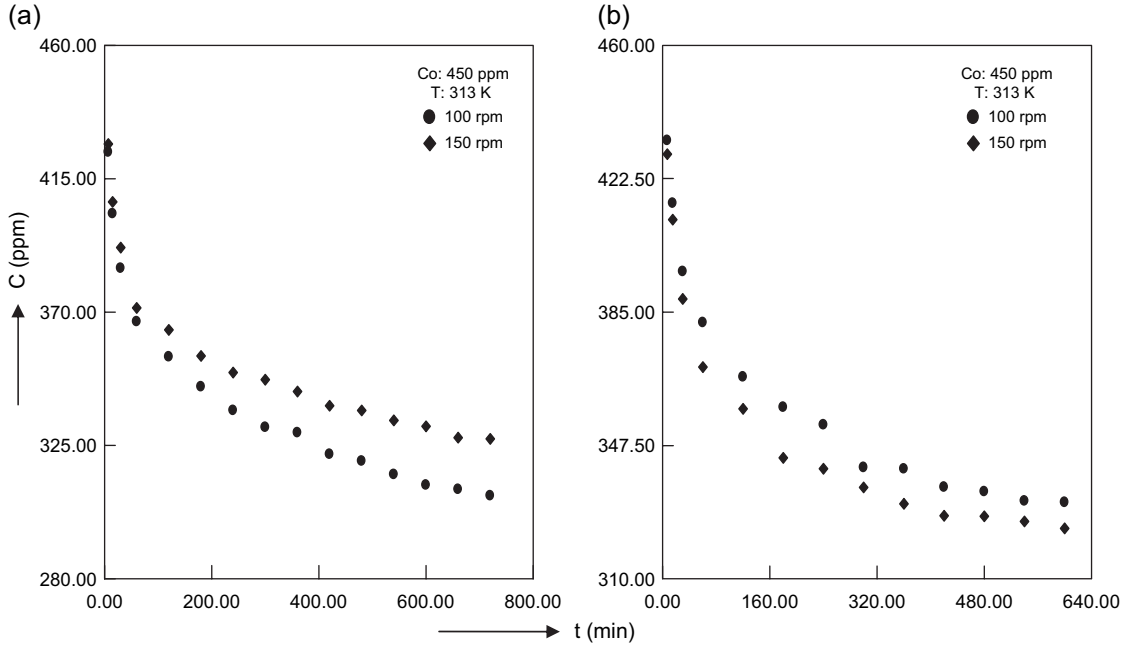


Fig. 5. The effect of shaking rate on the adsorption of two reactive dyestuffs by chitin from aqueous solution: (a) RY2 and (b) RB5.

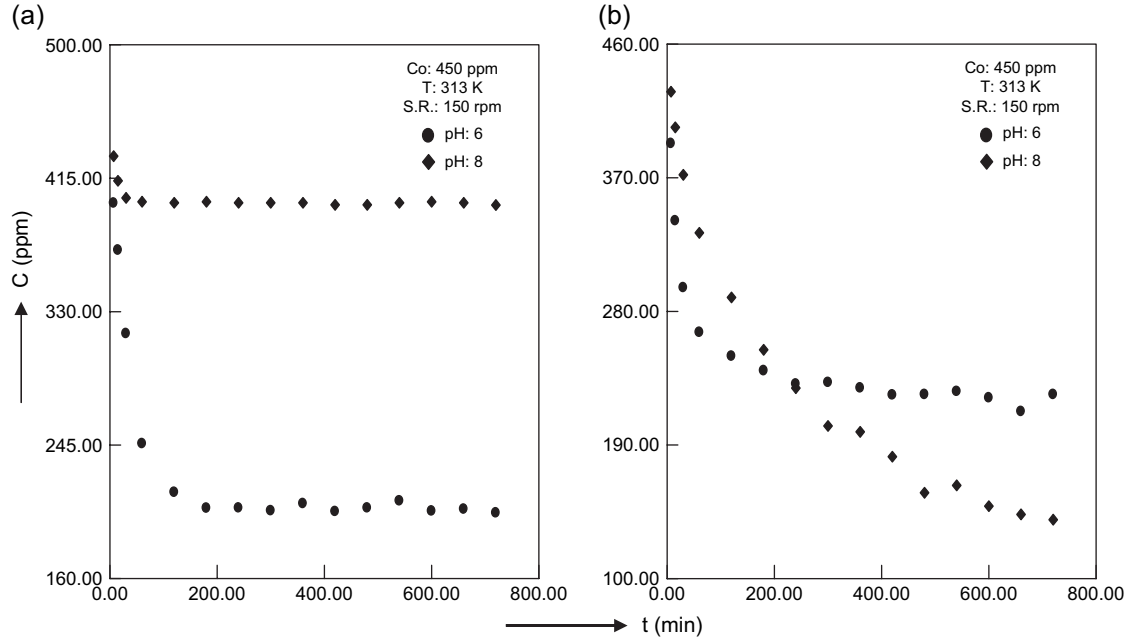


Fig. 6. The effect of pH on the adsorption of two reactive dyestuffs by chitin from aqueous solution: (a) RY2 and (b) RB5.

These groups make the RY2 and RB5 rather acidic. The amino group in the structure of chitin is charged positively when chitin 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 chitin is not much important [13].

3.2. Adsorption kinetics

Experimental data related to the adsorption of RY2 and RB5 on chitin at different temperatures were applied to the pseudo first-order equation (Fig. 7), the pseudo second-order equation (Fig. 8) and the intraparticle diffusion equation (Fig. 9), 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, respectively. It was seen that experimental data fitted pseudo

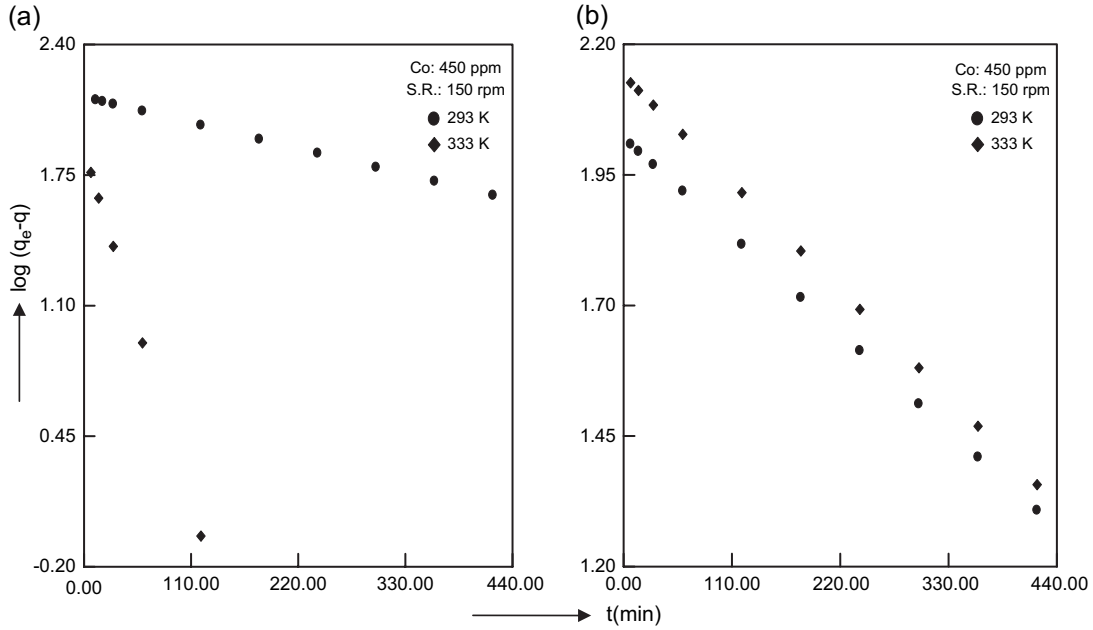


Fig. 7. Lagergren plots of kinetic curves related to the adsorption of two reactive dyestuffs by chitin from aqueous solution: (a) RY2 and (b) RB5.

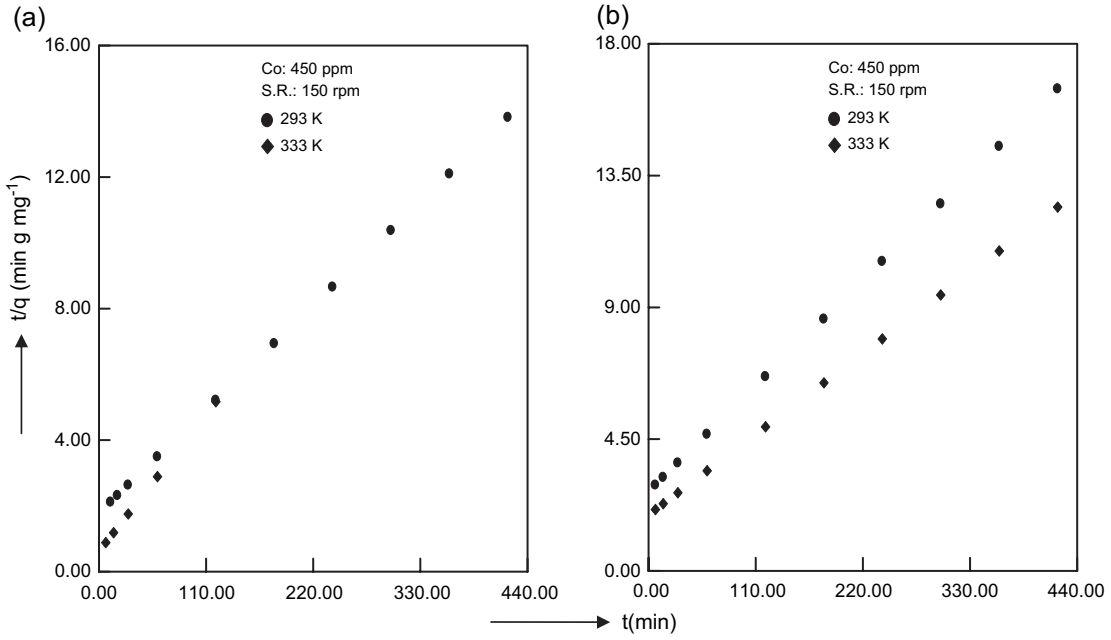


Fig. 8. Plots of the pseudo second-order model of kinetic curves related to the adsorption of two reactive dyestuffs by chitin from aqueous solution: (a) RY2 and (b) RB5.

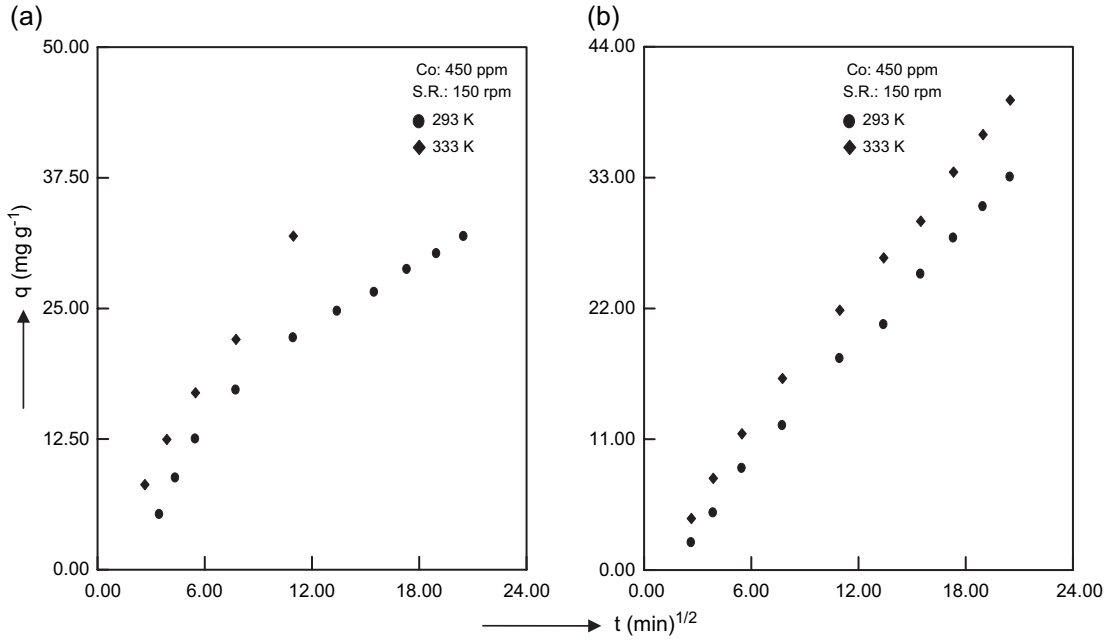


Fig. 9. Weber–Morris plots of kinetic curves related to the adsorption of two reactive dyestuffs by chitin from aqueous solution: (a) RY2 and (b) RB5.

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 chitin from aqueous solution

T (K)	RY2						RB5					
	$k_1 \times 10^3$ (min^{-1})	R^2	$k_2 \times 10^4$ (g mg^{-1} min^{-1})	R^2	k_p (mg g^{-1} $min^{-1/2}$)	R^2	$k_1 \times 10^3$ (min^{-1})	R^2	$k_2 \times 10^4$ (g mg^{-1} min^{-1})	R^2	k_p (mg g^{-1} $min^{-1/2}$)	R^2
293	2.70	0.9503	4.66	0.9948	1.00	0.9988	3.91	0.9588	3.98	0.9839	1.65	0.9984
333	36.9	0.9995	23.4	0.9998	2.83	0.9963	4.29	0.9820	3.26	0.9415	1.88	0.9988

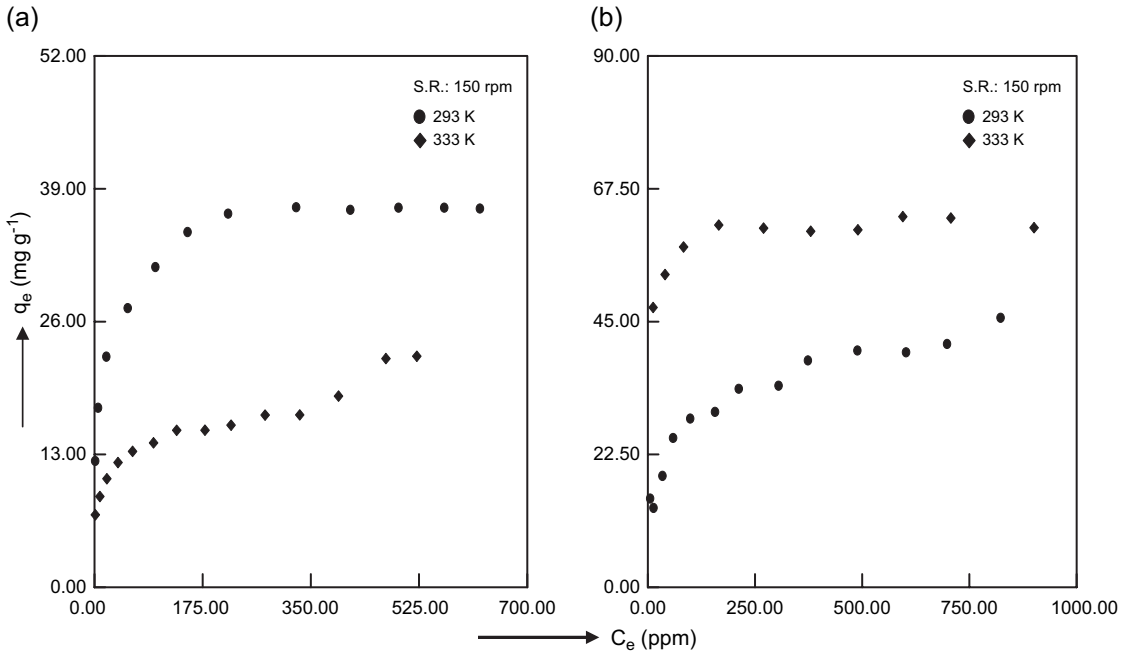


Fig. 10. The effect of temperature on the adsorption isotherm of two reactive dyestuffs by chitin from aqueous solution: (a) RY2 and (b) RB5.

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. According to k_2 constants, RY2 is adsorbed faster at higher temperature but RB5 is adsorbed faster at lower temperature.

3.3. Intraparticle diffusion

The double nature of intraparticle diffusion plots may be explained as follows: the initial curved portions are attributed to boundary layer diffusion effects [31], while the final

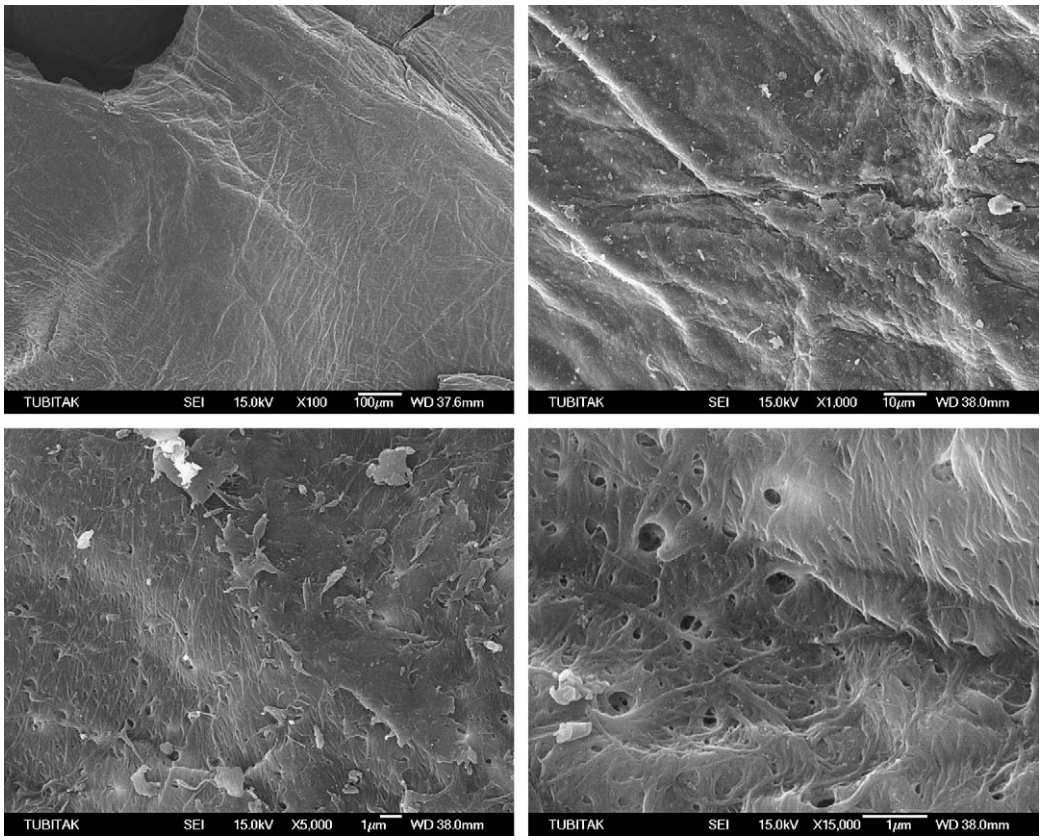


Fig. 11. The SEM micrographs of chitin.

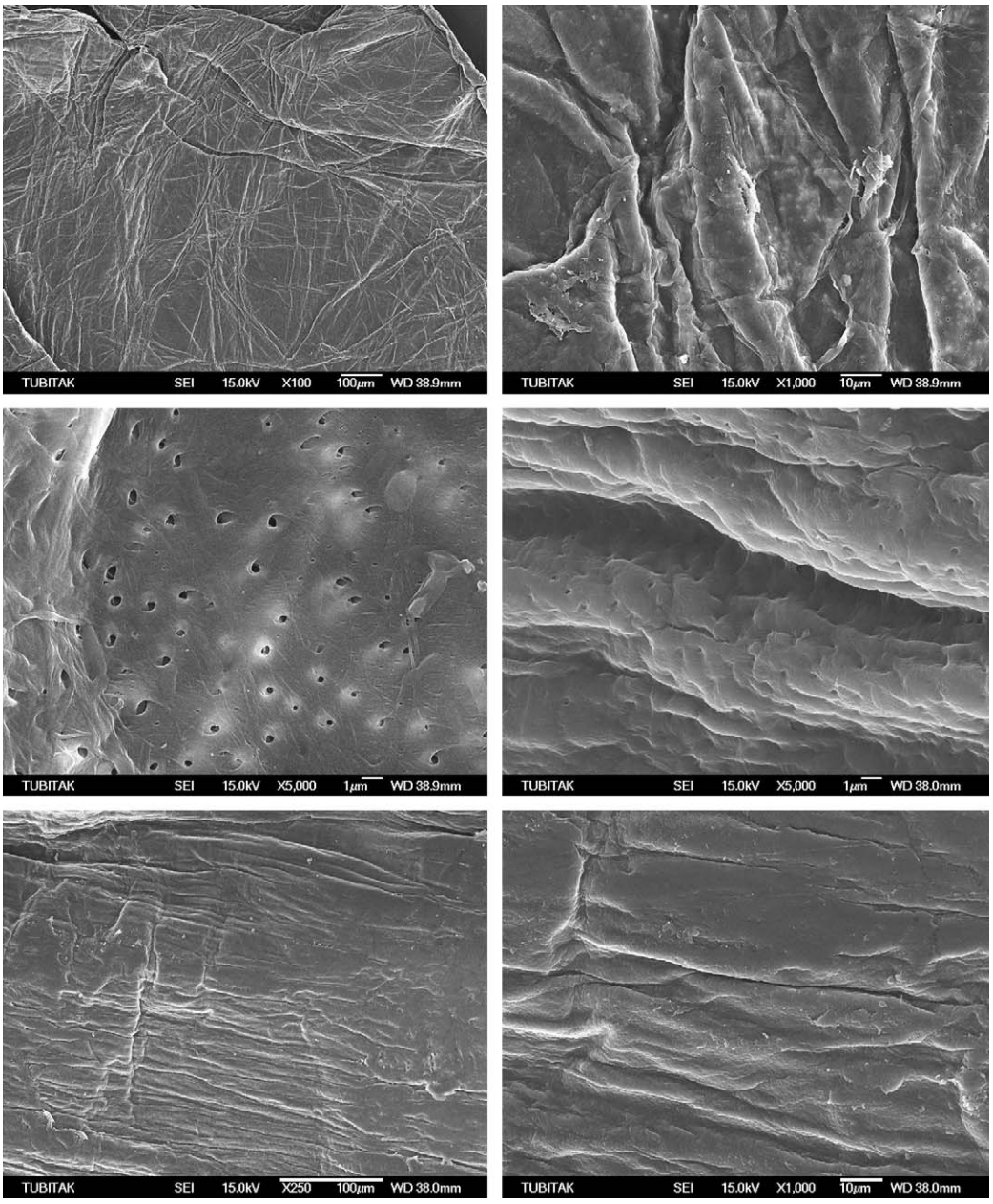


Fig. 12. The SEM micrographs of chitin dyed by RY2.

linear portions are due to intraparticle diffusion effects [32]. 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. But, because the BET surface area of chitin used as adsorbent in the present study is very low (Table 1), adsorption kinetics is controlled by surface diffusion. At particularly lower temperatures, surface diffusion is more dominant.

3.4. Adsorption isotherms

Fig. 10 shows the effect of temperature on the adsorption isotherm of RY2 and RB5 by chitin from aqueous solution. These types of isotherm are known as H-type isotherms (high affinity) according to isotherm classification proposed by Giles et al. [33]. The adsorption isotherm of RY2 at 293 K fits subgroup H-4 while its adsorption isotherm at 333 K fits subgroup H-2. In addition, the adsorption isotherm of RB5 at 293 K fits subgroup H-3 while its adsorption isotherm at 333 K fits subgroup H-4. In the subgroups H-2 and higher 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 [33]. The H-type isotherms are associated 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 [34].

Figs. 11–13 show the SEM (scanning electron microscopy) micrographs of chitin, chitin dyed by RY2, and chitin dyed by RB5, respectively. As it is known, SEM is one of the most widely used surface diagnostic tools. Chitin has heterogeneous surface and macropores as seen from its SEM micrographs. Its low BET surface area is confirming that chitin has macropores. Chitin is a linear homopolymer of β-(1,4)-2-acetamido-2-deoxy-D-glucose, and it is similar to cellulose in morphology. In addition, after chitin adsorbed RY2 and RB5 on its surface it has still heterogeneous surface. This result shows that RY2 and RB5 are significantly adsorbed as chemical on chitin.

4. Conclusions

For maximum adsorption yield on the basis of experimental results obtained, the following conclusions are made:

1. The adsorption of RY2 by chitin from aqueous solution must be studied at low temperature and pH.
2. The adsorption of RB5 by chitin from aqueous solution must be studied at high temperature and pH.
3. It can easily be said that chitin can be used as adsorbent in the studies of dyestuff adsorption as chitin is a better and cheaper adsorbent compared to most adsorbents in the

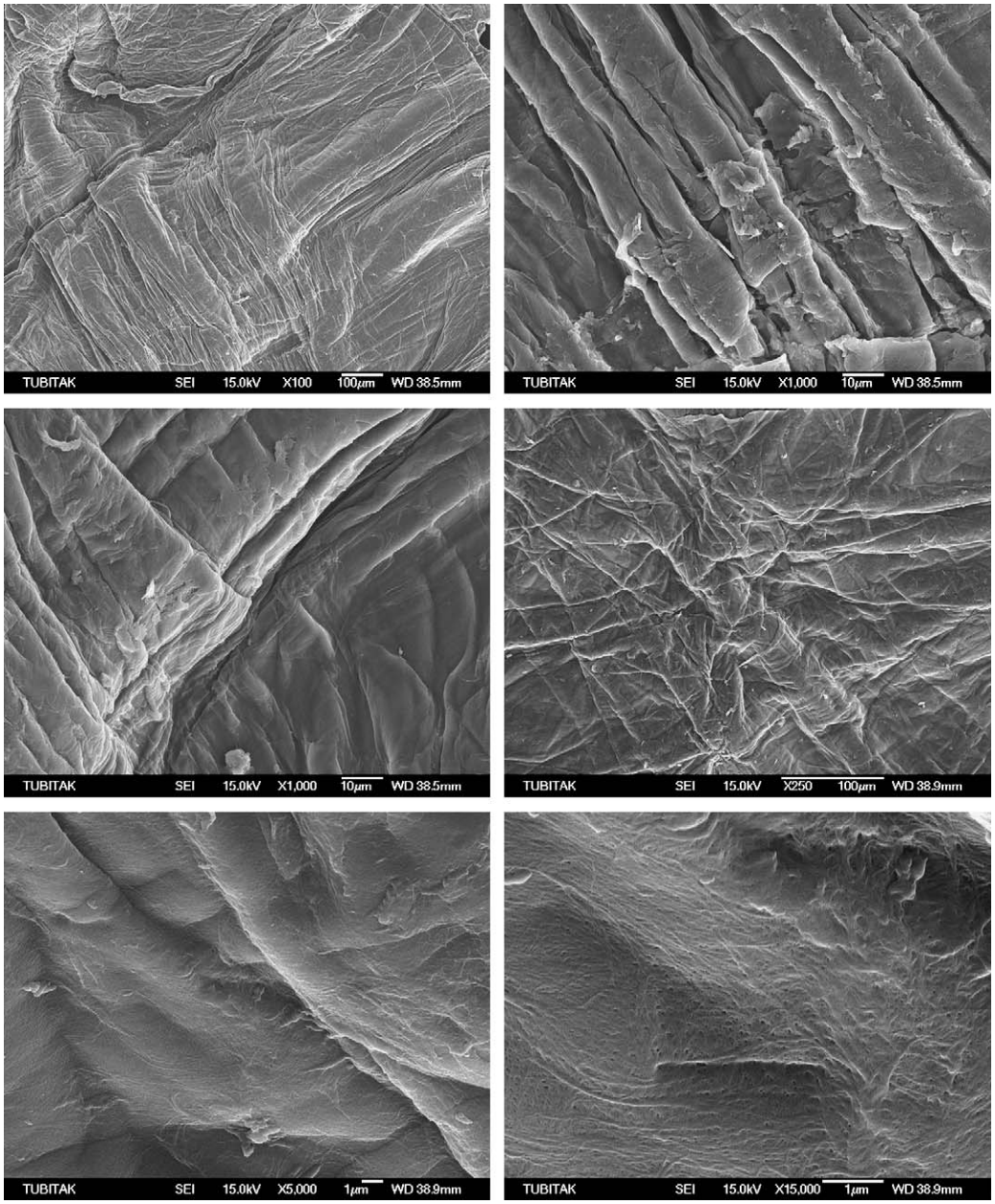


Fig. 13. The SEM micrographs of chitin dyed by RB5.

adsorption of particularly acidic dyestuffs from aqueous solution, and as it is also found abundantly in nature. But, it was seen that chitin adsorbed less RY2 and RB5 than chitosan. In addition, because of the low BET surface area (S) of chitin, the adsorption kinetics in the present study is controlled by surface diffusion.

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