Desalination and Water Treatment
www.deswater.com

1944-3994/1944-3986 © 2013 Balaban Desalination Publications. All rights reserved
doi: 10.1080/19443994.2012.734967

51 (2013) 2294–2305
February

Taylor & Francis
Taylor & Francis Group

Adsorption of basic dyestuffs from aqueous solution by modified chitosan

Hatice Karaer, İlhan Uzun*

Faculty of Education, Department of Chemistry, Dicle University, Diyarbakir 21280, Turkey
Tel. +90 412 2488030; Fax: +90 412 2488257; email: iuzun@dicle.edu.tr

Received 20 January 2012; Accepted 12 August 2012

ABSTRACT

The capability of chitosan to adsorb the basic dyestuffs is very low. For this purpose, chitosan was modified to increase its adsorption capability with some cyclic acid anhydrides in dimethyl sulfoxide. Then, chitosan and its derivatives, chitosan modified with maleic anhydride (CMA), chitosan modified with phthalic anhydride (CPA), and chitosan modified with trimellitic anhydride (CTA), were compared according to their capabilities to remove brilliant green (BG) and methylene blue (MB) from aqueous solution. It was determined that CTA adsorbed much more BG and MB. The 70.57% of BG (C_o: 50 ppm) and 71.86% of MB (C_o: 50 ppm) in the samples of 50 mL by 0.1 g CTA were adsorbed at room temperature and at a shaking rate of 140 rpm within 24 h. As a result of this, the adsorption of BG and MB by CTA was kinetically investigated as dependent on temperature and pH. Besides, the adsorption isotherms of each dyestuff by CTA were determined at different temperatures. Then, some kinetical and thermodynamical parametres were calculated by using experimental data.

Keywords: Adsorption; Dyestuff; Chitosan; Cyclic anhydride; Modification

1. Introduction

Many industries, particularly textile, paper, rubber, plastic, leather, cosmetic, food, and drug industries, use dyestuffs to make colorful their products. It was reported that there are about 100,000 different commercial dyestuffs and pigments, and over 7×10^5 tons of these are produced annually worldwide [1]. Dyestuffs can be classified as anionic (direct, acid, and reactive dyestuffs), cationic (basic dyestuffs), and nonionic (disperse dyestuffs) [2]. Dyestuff wastewater discharged by various industries, particularly by textile industry, presents certain hazards. From environmental viewpoint, the removal of dyestuffs from wastewater is a great mission since some dyestuffs or their metabolites may be toxic, carcinogenic, mutagenic, and teratogenic [3,4]. It was reported that cationic dyestuffs are more toxic than anionic dyestuffs [5]. The removal of dyestuffs from wastewater before discharging to environment is necessary for the protection of health and environment.

Some techniques used in the treatment of wastewaters containing dyestuff are flocculation, coagulation, precipitation, adsorption, membrane filtration, electrochemical techniques, ozonation, fungal decolorization, and photocatalytic decolorization [6,7]. The advantages and disadvantages of some important techniques are given in [8,9]. Among these techniques, the adsorption technique is one of the most efficient techniques of

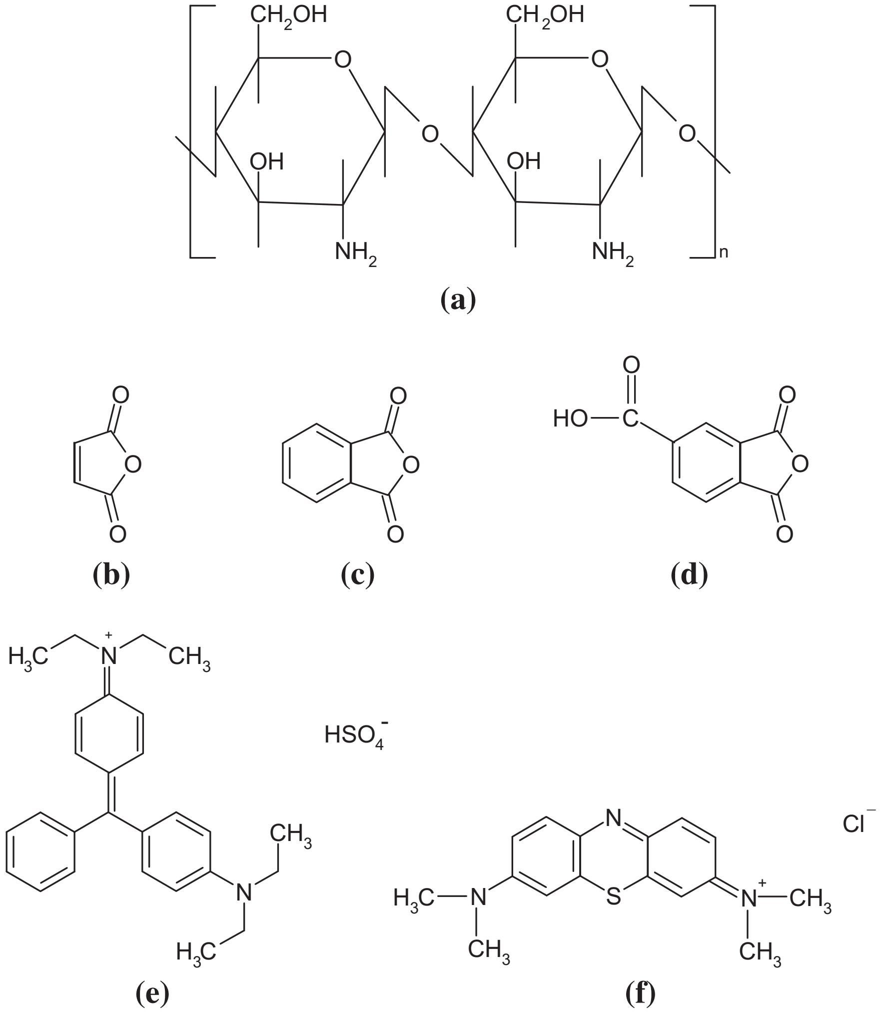
---

*Corresponding author.

Some changes have been made to the original online version of the article (on pp. 3,5,9). Original version published online: 19-Nov-12. Revised version published online: 19-Dec-12.

removing dyestuffs from wastewater. Also, the adsorption technique provides an attractive alternative treatment, especially if the adsorbent is inexpensive and readily available. Granular activated carbon is the most popular adsorbent and has been used with great success [10], but it is expensive. Consequently, many investigators have studied the feasibility of using low-cost substances such as plum kernels [11], chitin [12], chitosan [13], perlite [14], natural clay [15–17], bagasse pith [18–20], coal fly ash [21], boiler bottom ash [22], and bagasse fly ash [23–25] as adsorbent for the removal of dyestuffs from wastewater. The advantages and disadvantages of some important adsorbents are given in [9]. However, new adsorbents, which remove better the dyestuffs from effluent, like new methods are also still under investigation.

Chitin, which is a linear polysaccharide of β-(1-4)-2-acetamido-2-deoxy-D-glucose, is produced from crustacean shells such as prawns, crabs, krill, insects, and shrimps and is the second most abundant biopolymer after cellulose. Chitosan is obtained from chitin by a deacetylation process. The molecular structure of chitosan is shown in (Fig. 1(a)). Chitosan has been reported to have high potential for the adsorption of metal ions [26–28], dyes [29–31], and proteins [32,33]. In addition, chitosan has also many potential applications including the applications in agricultural, food, industrial, and medical fields such as biomedicine, pharmacology, and biotechnology due to its biological activities including biocompatibility, biodegradability, non-toxicity, and bactericidal or bacteriostatic activities [34]. The effect of pH is an important factor on the dye-binding capacity of chitosan because the pK_a value 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 $pH = 6.9$ [35].

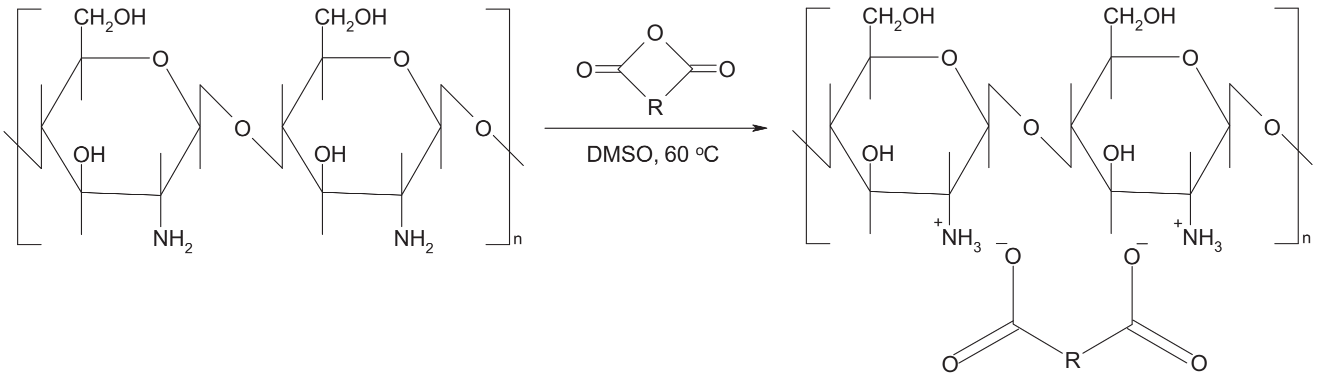


(a)

(b) (c) (d)

(e) (f)

Fig. 1. The molecular structures of: (a) chitosan, (b) maleic anhydride, (c) phthalic anhydride, (d) trimellitic anhydride, (e) BG, and (f) MB.



Scheme 1. Route of the synthesis of modified chitosan.

Basic dyestuffs are cationic. An important change in the structure of chitosan does not occur when it is introduced into the solutions of basic dyestuffs. Due to this reason, chitosan is not a good adsorbent for the adsorption of basic dyestuffs [29]. The aim of the present study was to increase its capability to adsorb the basic dyestuffs by modifying with maleic anhydride (Fig. 1(b)), phthalic anhydride (Fig. 1(c)), and trimellitic anhydride (Fig. 1(d)). In addition, another aim of the present study was also to compare these modified chitosans according to their capabilities to adsorb brilliant green (BG) (Fig. 1(e)) and methylene blue (MB) (Fig. 1(f)) and to investigate the effect of temperature and pH on the adsorption of BG and MB from aqueous solution by modified chitosan which adsorbs more of these dyestuffs. BG and MB are basic dyestuffs and are known to be highly toxic and carcinogenic [9,36,37]. Due to these reasons, the removal of these dyestuffs from wastewater is necessary and indispensable.

2. Materials and methods

2.1. Materials

In this study, chitosan (Sigma C 3646, Germany) was modified with maleic anhydride (Aldrich, Germany), phthalic anhydride (Aldrich, Germany), and trimellitic anhydride (Aldrich, Germany). Some important properties of chitosan used in modification are given in [31]. Dimethyl sulfoxide (Aldrich, Germany), acetic acid (Riedel-de Haën, Germany), acetone (Riedel-de Haën, Germany), and ethanol (Sigma-Aldrich, Germany) were used in modification. BG (Fluka, Switzerland) and MB (Merck, Germany) were used as adsorbate. Na_2HPO_4 (Riedel-de Haën, Germany), NaH_2PO_4 (Riedel-de Haën, Germany), NH_3 (Merck, Germany), NH_4Cl (Merck, Germany), and HCl (Merck, Germany) were used for buffer solution. NaOH (Merck, Germany) was used for both modification and buffer solution.

2.2. Modification of chitosan

The 10 g of chitosan with 100 mL of NaOH (20%) were mixed for 12 h. The mixture was filtered and the precipitate was added into 200 mL dimethyl sulfoxide. Then, 10 g of cyclic acid anhydride was added into the mixture at room temperature with stirring. The mixture in flask was heated in oil bath at 60°C for 7 h. Then, the mixture was poured into a beaker of 250 mL and its pH was adjusted to 7.0 with the addition of 0.1 M acetic acid with stirring. The mixture was filtered and the precipitate was dissolved in distilled water. Then, the mixture was filtered and the precipitate was purified by acetone. Lastly, the mixture was filtered and the product was washed with ethanol (70%) and anhydrous alcohol and was dried (Scheme 1). This process was done eight times and the products obtained were blended.

Table 1
Results related to the percent adsorption of BG (C_o: 50 ppm) and MB (C_o: 50 ppm) from aqueous solution by chitosan, CMA, CPA, and CTA

BG%				MB%			
Chitosan	CMA	CPA	CTA	Chitosan	CMA	CPA	CTA
9.82	19.91	41.07	70.57	41.65	38.24	43.38	71.86

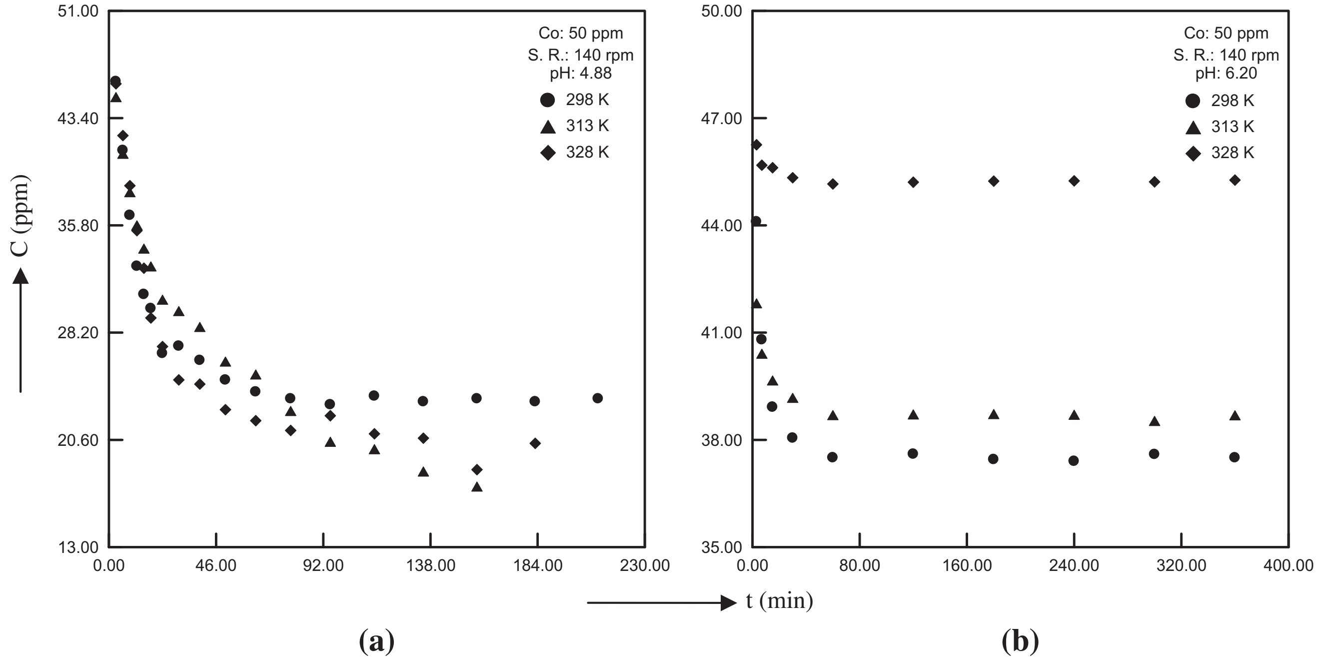


Fig. 2. Effect of temperature on the adsorption of: (a) BG and (b) MB from aqueous solution by CTA.

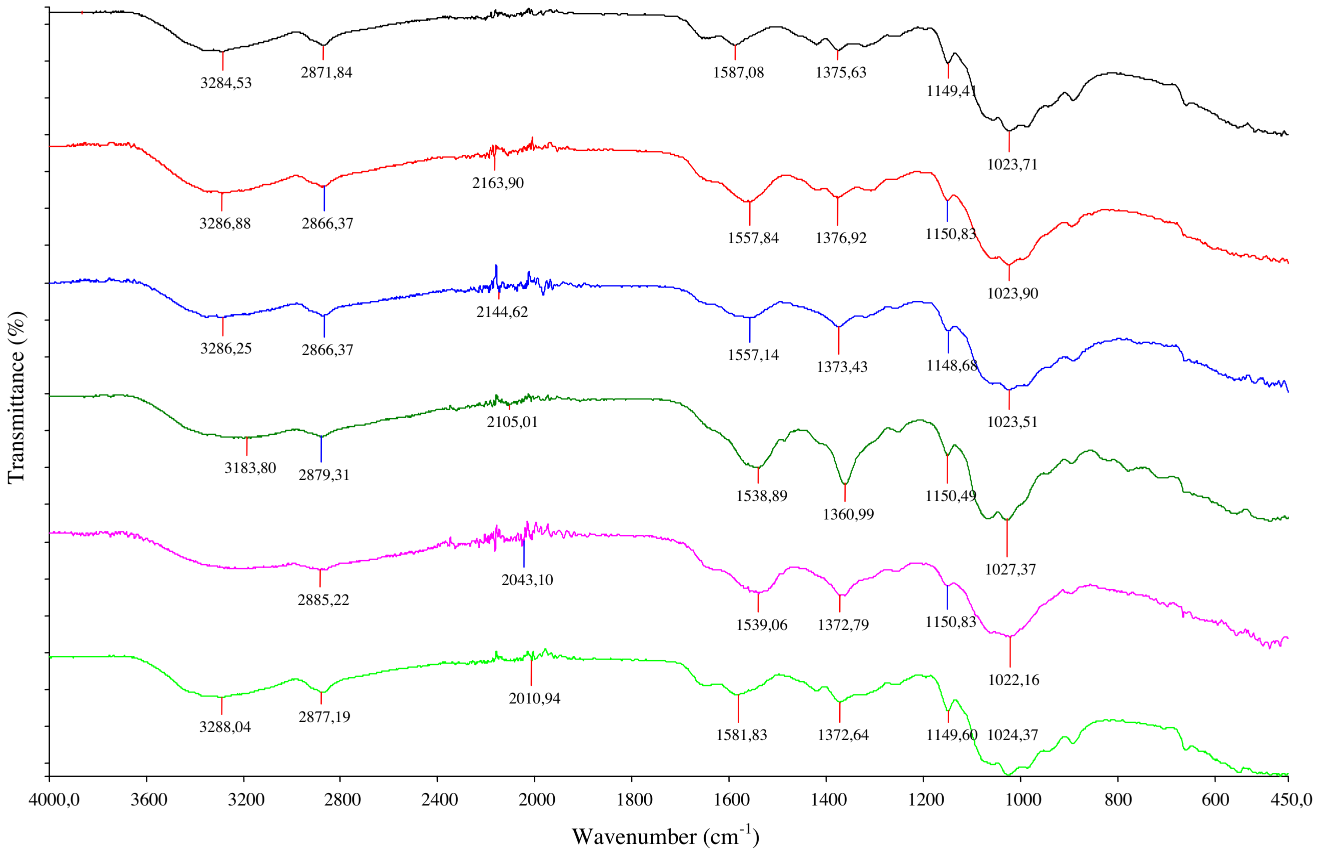


Fig. 3. FTIR spectra of: (—) chitosan, (—) CMA, (—) CPA, (—) CTA, (—) CTA adsorbed BG, and (—) CTA adsorbed MB.

2.3. Comparison of chitosan and modified chitosans

Chitosan, chitosan modified with maleic anhydride (CMA), chitosan modified with phthalic anhydride (CPA) and chitosan modified with trimellitic anhydride (CTA) were compared according to their capabilities to adsorb BG and MB. For this aim, the samples of 0.1 g of adsorbents with the samples of 50 mL of BG (C_o: 50 ppm) and MB (C_o: 50 ppm) were individually shaked at room temperature and at a shaking rate of 140 rpm for 24 h.

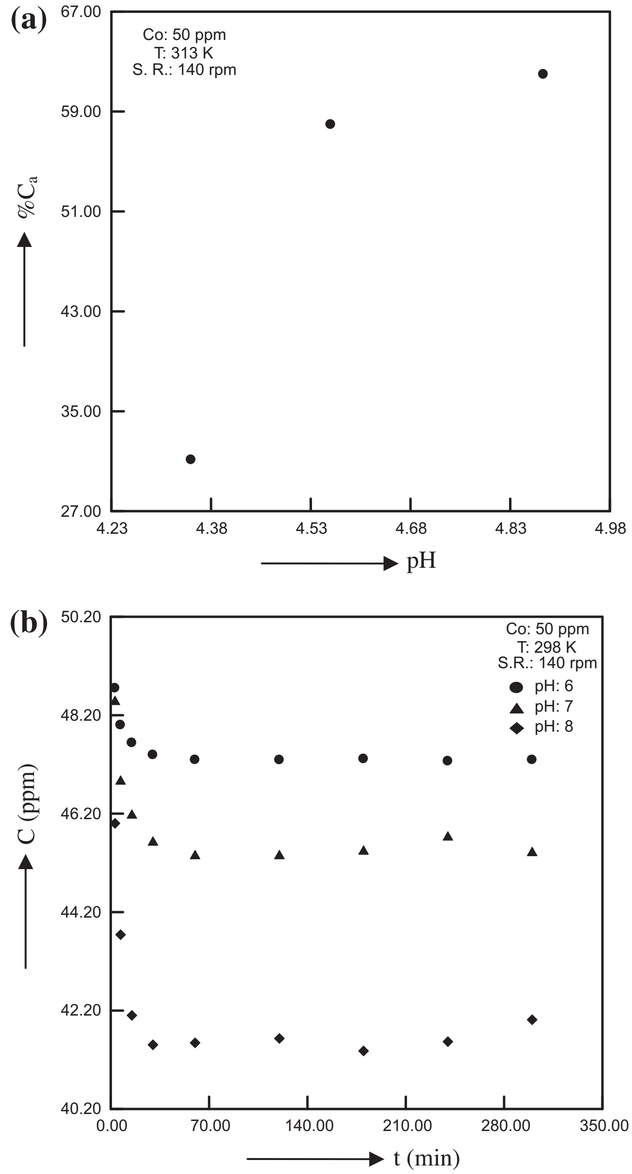


Fig. 4. Effect of pH on the adsorption of: (a) BG and (b) MB from aqueous solution by CTA.

2.4. Kinetic studies

Kinetic experiments related to the effect of temperature on the adsorption of BG and MB from aqueous solution by CTA were performed at natural pHs (4.88 for BG and 6.20 for MB) of solutions. Acid, base, or buffer solution was not added into the solutions of adsorbates. The samples of 0.1 g of CTA with the samples of 50 mL of each dyestuff (C_o: 50 ppm for BG and C_o: 50 ppm for MB) were shaken with a shaker (J.P. SELECTA, S.A., SPAIN) at different time intervals. Absorbance values with a SHIMADZU UV-120-02 spectrophotometer were measured at $\lambda_{max} = 632$ nm for BG and $\lambda_{max} = 669$ nm for MB.

The effect of pH on the adsorption of BG and MB from aqueous solution by CTA was similarly investigated. The pHs of BG solutions were precisely adjusted to 4.35, 4.56, and 4.88 by using 0.1 M HCl, respectively. As for the pHs of MB solutions were roughly adjusted by using NaH_2PO_4/Na_2HPO_4 and NH_3/NH_4Cl buffer solutions, and then they were precisely adjusted to 6.0, 7.0, and 8.0, respectively, by using either 0.1 M HCl or 0.1 M NaOH. Detailed kinetic study related to the effect of pH on the adsorption of BG by CTA could not be done because the color of BG solution was being darkened when acid or acidic buffer solution was added, and it was being cleared when base or basic buffer solution was added. Due to these reasons, the effect of pH on the adsorption of BG by CTA was studied in a narrow pH range and as single point.

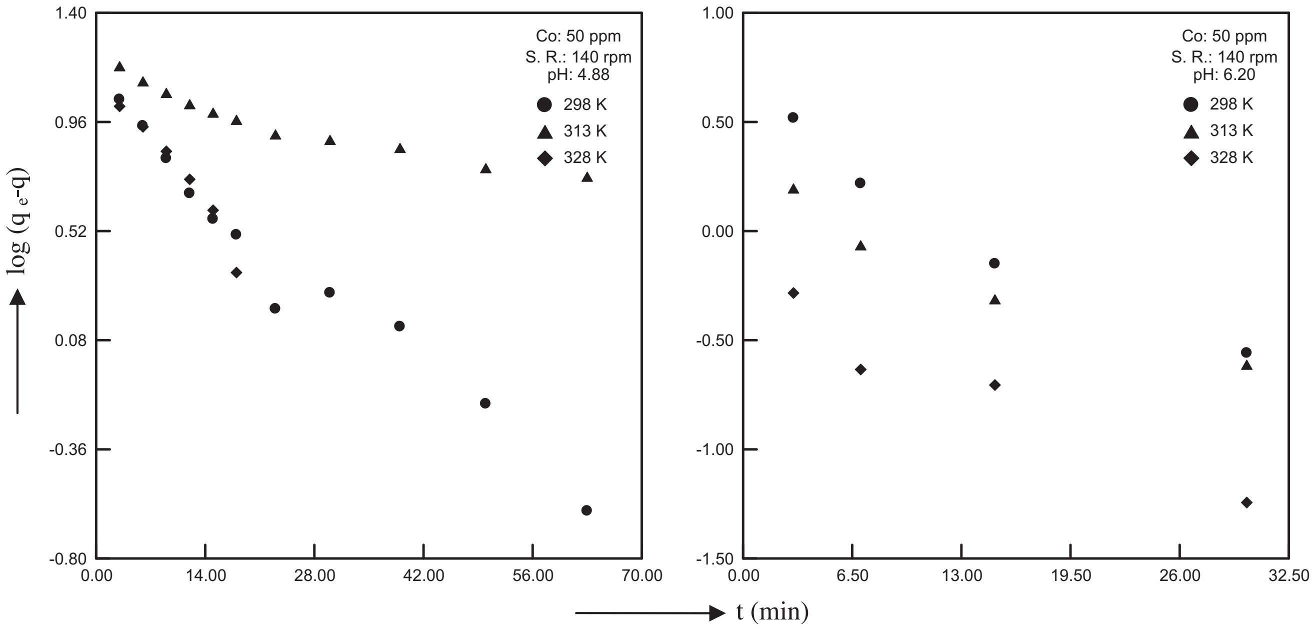
2.5. Isotherm study

Firstly, the adsorption isotherm of each dyestuff at 298 K was determined. For this purpose, the samples of 0.1 g of CTA with the samples of 50 mL of solutions having different initial concentrations (C_o) prepared from the stock solutions of each dyestuff were shaken for their equilibrium contact times at 298 K and 140 rpm. After this shaking, the absorbance values of solutions remaining without adsorption were measured. Then, the adsorption isotherms of each dyestuff were determined at 313 and 328 K at the same shaking rate.

3. Results and discussion

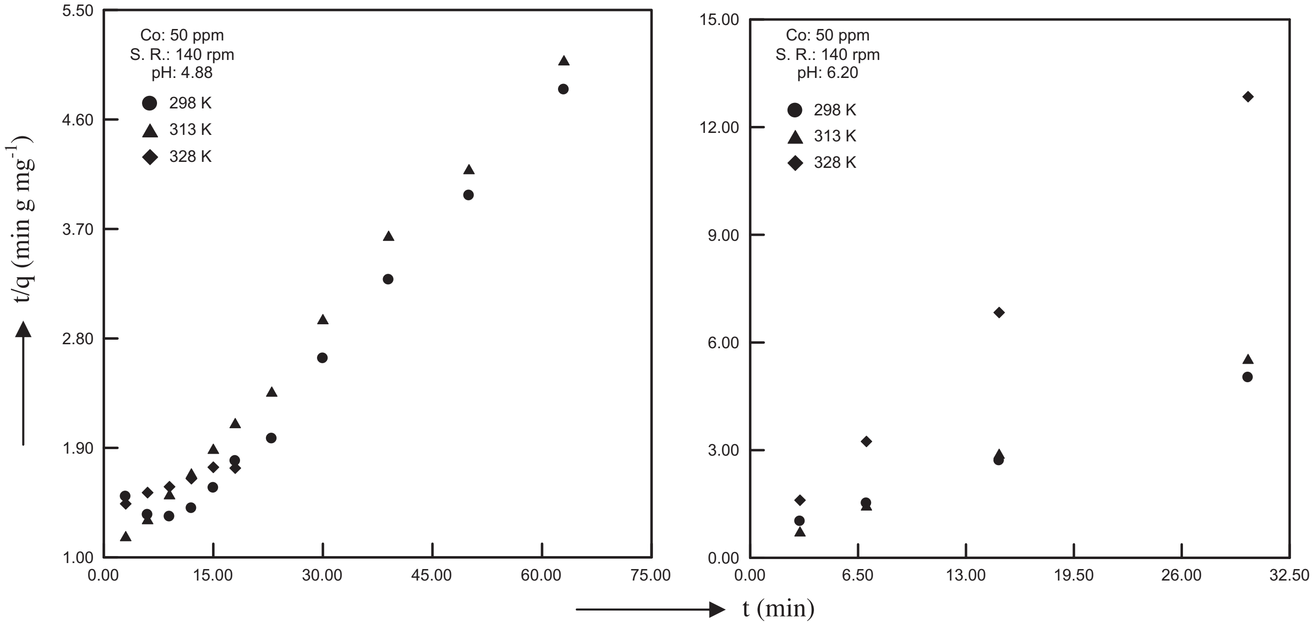
3.1. Results of percent adsorption

Results related to the percent adsorption of BG and MB from aqueous solution by chitosan, CMA,



(a) **(b)**

Fig. 5. Plots of the pseudo-first-order model of kinetic curves related to the adsorption of: (a) BG and (b) MB from aqueous solution by CTA.



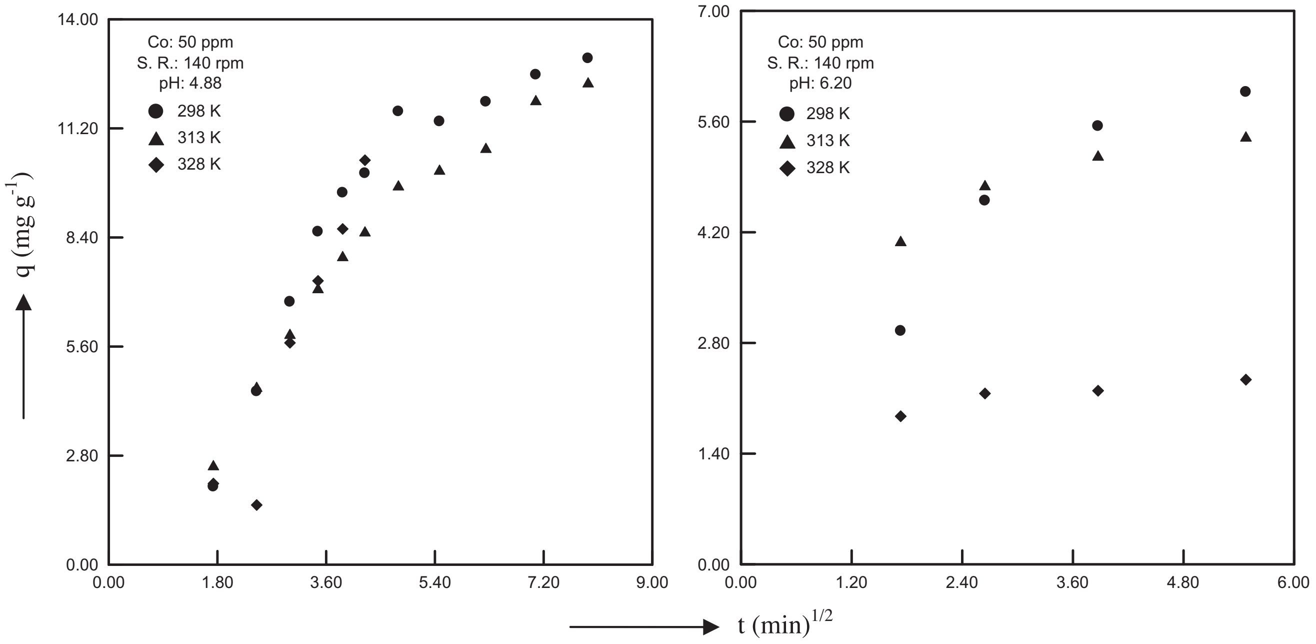
(a) **(b)**

Fig. 6. Plots of the pseudo-second-order model of kinetic curves related to the adsorption of: (a) BG and (b) MB from aqueous solution by CTA.

CPA, and CTA are given in Table 1. Both BG and MB by CTA are much more adsorbed at room temperature.

3.2. *Effect of temperature and pH*

BG by CTA is more adsorbed at 313 K according to other temperatures, whereas MB by CTA is more



(a) **(b)**

Fig. 7. Plots of the intraparticle diffusion model of kinetic curves related to the adsorption of: (a) BG and (b) MB from aqueous solution by CTA.

Table 2
The pseudo-first-order rate constants (k_1), the pseudo-second-order rate constants (k_2), and the intraparticle diffusion rate constants (k_p) related to the adsorption of BG and MB from aqueous solution by CTA

T (K)	BG						MB					
	k_1 (min^{-1})	r^2	$k_2 \times 10^3$ (g mg^{-1} min^{-1})	r^2	k_p (mg g^{-1} min$^{-1/2}$)	r^2	k_1 (min^{-1})	r^2	$k_2 \times 10^2$ (g mg^{-1} min^{-1})	r^2	k_p (mg g^{-1} min$^{-1/2}$)	r^2
298	–	–	7.41	0.9846	3.67	0.9089	–	–	3.64	0.9996	–	–
313	–	–	4.94	0.9989	2.22	0.9675	–	–	7.59	0.9999	–	–
328	–	–	0.45	0.9795	3.03	0.9557	–	–	35.38	0.9997	–	–

adsorbed at 298 K according to other temperatures (Fig. 2). The effect of temperature on the adsorption of BG by CTA is interesting because the amount of BG adsorbed at 313 K is more than the amounts of BG adsorbed at 298 and 328 K. At the first look this situation can be explained with neither physical adsorption nor chemical adsorption. This result was understood after adsorption isotherms were determined. This situation is explained in isotherm section. MB is more adsorbed on CTA at lower temperature. This result shows that the adsorption between MB and CTA is a physical adsorption. FTIR spectrum in Fig. 3 confirms this result because the FTIR spectra of CTA and CTA adsorbed MB are similar. Namely, there is not an important peak related to chemical interaction in the FTIR spectrum of CTA adsorbed MB.

The amounts of BG and MB adsorbed on CTA decreased when pH decreased (Fig. 4). BG and MB are cationic dyestuffs. The number of CTA particles having positively charged amino group increases while pH decreases. Thus, more electrostatical repulsion at lower pHs occurs between cationic BG and MB dyestuffs with positively charged CTA particle, and as a result the amount of BG and MB adsorbed on CTA decreased when pH decreased.

3.3. *Adsorption kinetics*

Kinetical data related to the effect of temperature were analyzed by using the pseudo-first-order Eq. (1) [38], the pseudo-second-order Eq. (2) [39], and the intraparticle diffusion Eq. (3) [40] rate equations (Figs. 5–7). Constants k_2 and k_p related to the adsorption of BG by CTA from Figs. 6 and 7 and constants k_2 related to the adsorption of MB by CTA from Fig. 6

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

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{2}$$

$$q = k_p t^{\frac{1}{2}} \tag{3}$$

$$\log k_2 = \log A - \frac{E_a}{2.303R}\frac{1}{T} \tag{4}$$

were calculated, respectively (Table 2). Constants k_1 related to the adsorption of BG because of linearity was not obtained in Fig. 5 and constants k_1 and k_p related to the adsorption of MB because of linearity was not obtained in Figs. 5 and 7 could not be calculated. It was seen that kinetical data related to the adsorption of BG and MB fitted the pseudo-second-order rate equation. As can be seen from k_2 constants, BG is adsorbed faster at lower temperature, whereas MB is adsorbed faster at higher temperature. Constants k_2 related to the adsorption of MB by CTA were applied to Eq. (4) [41] and the activation energy (E_a) from Fig. 8 was calculated as ~62.1 kJ mol^{-1}. The E_a related to the adsorption of BG by CTA could not be calculated because k_2 constants were decreased with temperature.

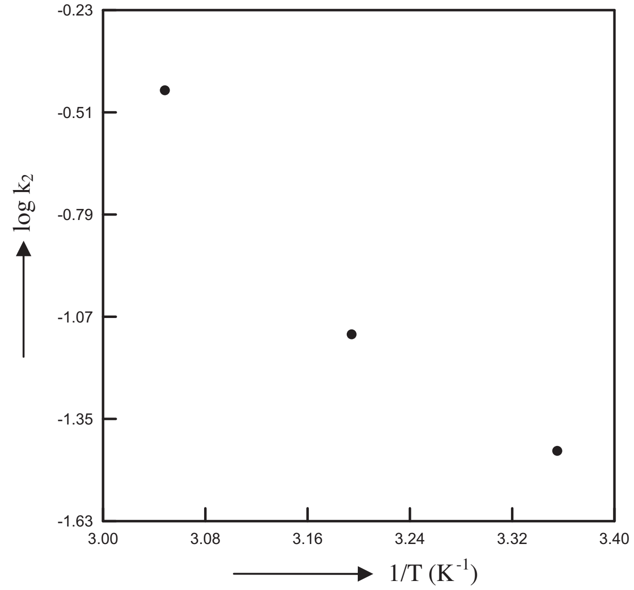
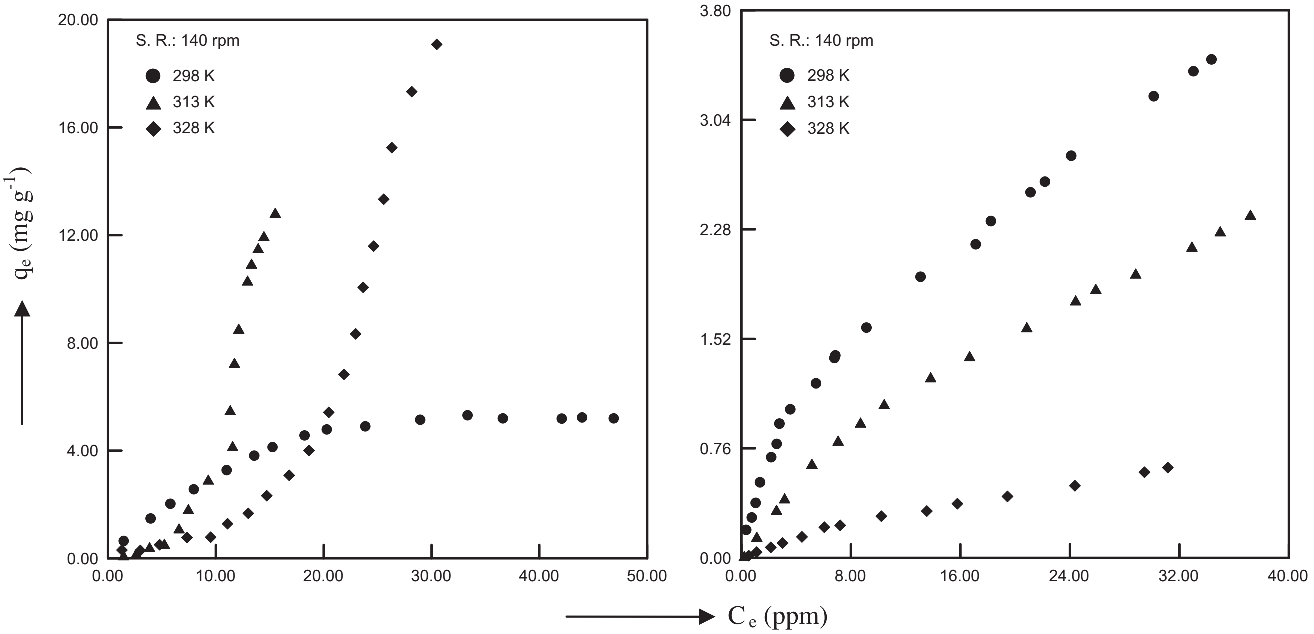


Fig. 8. Plot of $\log k_2$ vs. $1/T$ related to the adsorption of MB from aqueous solution by CTA.



(a) **(b)**

Fig. 9. Effect of temperature on the adsorption isotherm of: (a) BG and (b) MB from aqueous solution by CTA.

3.4. Adsorption isotherms

Fig. 9 shows the isotherms related to the adsorption of BG and MB from aqueous solution by CTA. Adsorption isotherm at 298 K related to BG fitted Langmuir adsorption isotherm Eq. (5) [42], whereas adsorption isotherms at 313 and 328 K related to BG

$$q_e = q_m \frac{bC_e}{1 + bC_e} \tag{5}$$

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \tag{6}$$

$$\Delta G = -\mathrm{RT} \ln b \tag{7}$$

fitted S-b adsorption isotherm according to isotherm classification proposed by Giles et al. [43]. Langmuir adsorption isotherm fits physical adsorption with monolayer, whereas S-b adsorption isotherm fits physical adsorption with multilayer. BG is more adsorbed at 313 K due to its adsorption isotherm changed with temperature. Isothermal data related to the adsorption of BG by CTA at 298 K were applied to Langmuir linear adsorption isotherm (Eq. (6)) (Fig. 10) and the isotherm constants are calculated (Table 3). Then, constant b in Table 3 related to the adsorption of BG by CTA at 298 K was applied to Eq. (7) [41] and Gibbs free energy change (ΔG) was calculated as $-8.04\,\mathrm{kJ\,mol^{-1}}$. This result shows that the adsorption of BG on CTA at 298 K is spontaneous.

Adsorption isotherms related to MB fitted Freundlich adsorption isotherm (Eq. (8)) [44]. As it is known, adsoption isotherm fits Freundlich adsorption isotherm when adsorbent surface is heterogenous. This result indicates that CTA surface shows a heterogenous structure for the adsorption of MB. Isothermal data related to the adsorption of MB by CTA were

$$q_e = kC_e^{1/n} \tag{8}$$

$$\log q_e = \log k + \frac{1}{n} \log C_e \tag{9}$$

applied to Freundlich linear adsorption isotherm (Eq. (9)) (Fig. 11) and the isotherm constants are calculated (Table 3).

Table 3
Isotherm constants related to the adsorption of BG and MB from aqueous solution by CTA

T (K)	BG			MB		
	q_m ($\mathrm{mg\,g^{-1}}$)	b ($\mathrm{L\,mg^{-1}}$)	r^2	k ($\mathrm{L\,g^{-1}}$)	n (–)	r^2
298	10.91	25.69	0.9973	0.46	1.06	0.9936
313	–	–	–	0.21	1.50	0.9807
328	–	–	–	0.05	1.36	0.9915

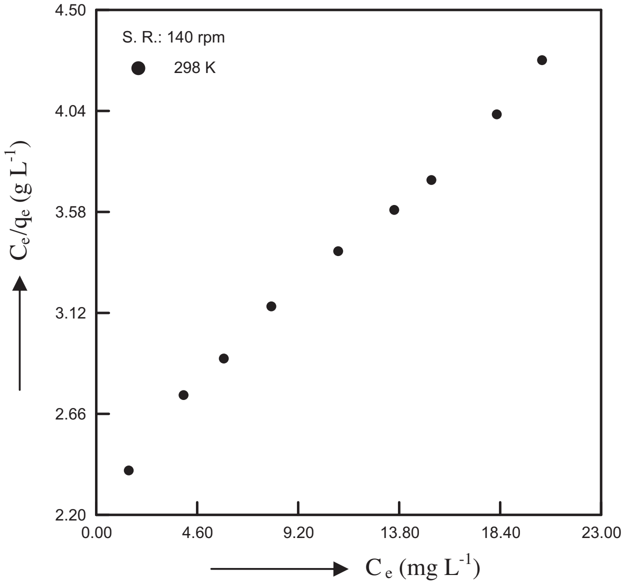


Fig. 10. Langmuir linear plot related to the adsorption isotherm of BG at 298 K from aqueous solution by CTA.

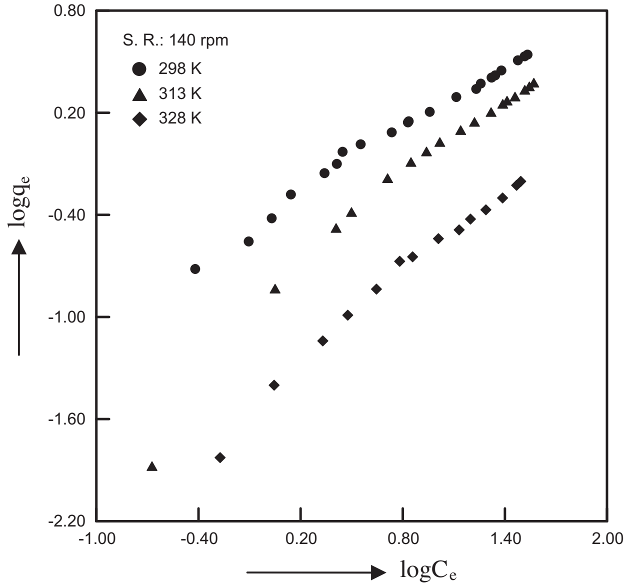


Fig. 11. Freundlich linear plots related to the adsorption isotherms of MB from aqueous solution by CTA.

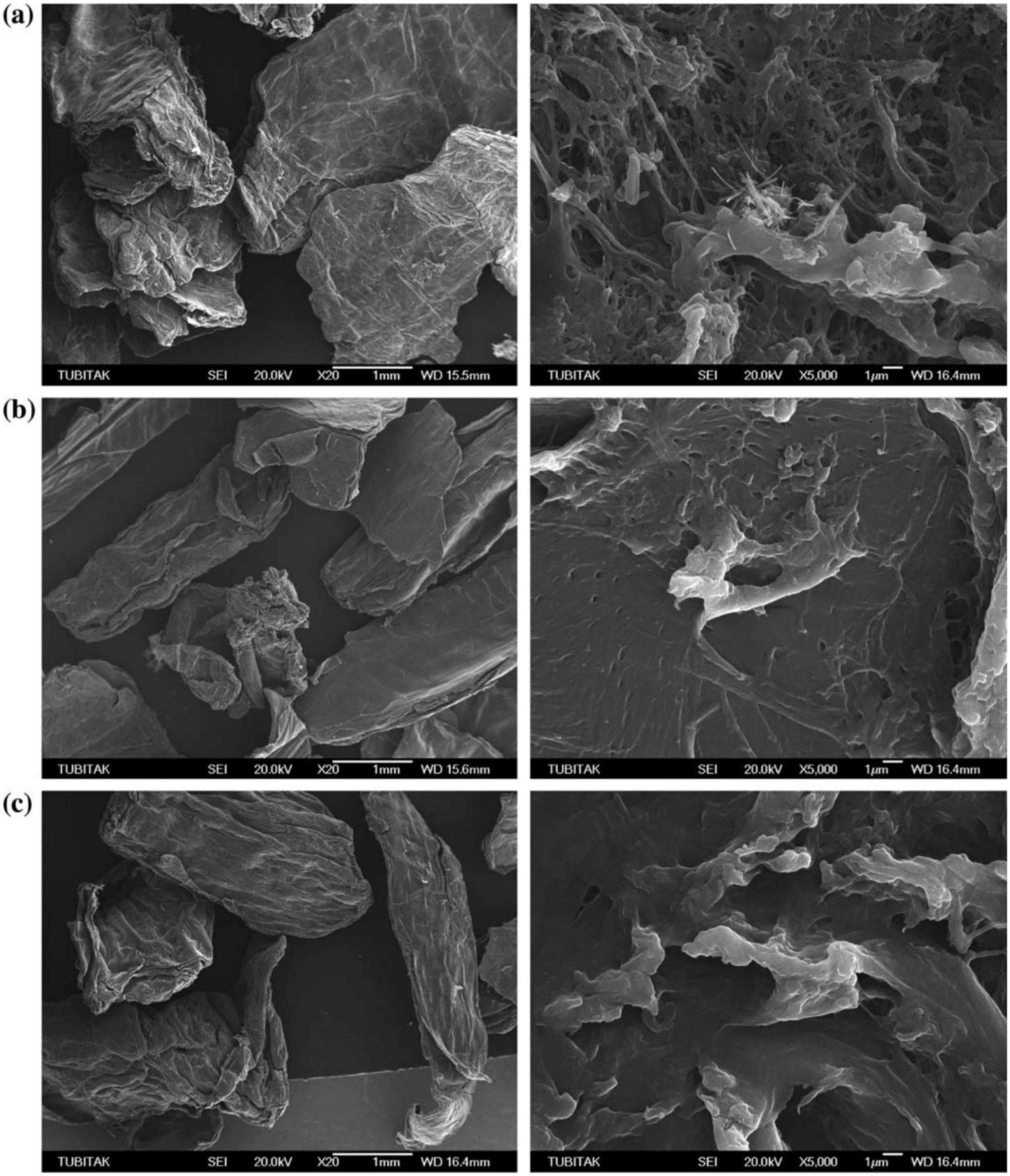


Fig. 12. The SEM micrographs of: (a) CTA, (b) CTA adsorbed BG, and (c) CTA adsorbed MB.

3.5. SEM analysis

Fig. 12 shows the SEM micrographs of CTA, CTA adsorbed BG, and CTA adsorbed MB taken with a JEOL JSM-6335F field emission instrument. As it can be seen from Fig. 12(a), CTA has a heterogenous surface and macropores. The BET surface area (*S*) and pore volume (V_p) of CTA were measured as 1.728 $m^2 g^{-1}$ and 0.003 $cc\,g^{-1}$, respectively, with a NOVA 4000e surface area and pore size analyzer. The BET surface area value confirms that CTA has macropores. CTA has became the owner of a more in order surface after it adsorbed BG and MB (Fig. 12(b,c)). This result shows that BG and MB have been physically adsorbed on CTA.

4. Conclusion

Results related to the percent adsorption of BG and MB from aqueous solution by chitosan, CMA, CPA, and CTA show that both BG and MB by CTA are more adsorbed at room temperature. BG at 313 K and MB at 298 K by CTA are more adsorbed. The amounts of BG and MB adsorbed on CTA decreased when pH decreased. It was seen that kinetical data related to the adsorption of BG and MB fitted the pseudo-second-order rate equation. As can be seen from k_2 constants, BG is adsorbed faster at lower temperature, whereas MB is adsorbed faster at higher temperature. E_a related to the adsorption of MB by CTA was calculated as ~62.1 $kJ\,mol^{-1}$. Adsorption isotherm at 298 K related to BG fitted Langmuir adsorption isotherm, whereas adsorption isotherms at 313 K and 328 K related to BG fitted S-b adsorption isotherm according to isotherm classification proposed by Giles et al. ΔG value ($-8.04\,kJ\,mol^{-1}$) shows that the adsorption of BG on CTA is spontaneous at 298 K. Adsorption isotherms related to MB fitted Freundlich adsorption isotherm.

Symbols

A — Arrhenius constant
b — Langmuir constant related to adsorption energy, $L\,mg^{-1}$
C — concentration of adsorbate at time t, ppm
C_a — adsorbed concentration of adsorbate, ppm
C_e — equilibrium concentration of adsorbate, ppm
C_o — initial concentration of adsorbate, ppm
E_a — activation energy, $kJ\,mol^{-1}$
k — Freundlich constant related to the capacity of adsorbent to adsorb, $L\,g^{-1}$
k_1 — the pseudo-first-order rate constant, min^{-1}
k_2 — the pseudo-second-order rate constant, $g\,mg^{-1}\,min^{-1}$
k_p — the intraparticle diffusion rate constant, $mg\,g^{-1}\,min^{-1/2}$
n — Freundlich constant related to the tendency of the adsorbate to be adsorbed, –
q — amount of adsorbate adsorbed at time t, $mg\,g^{-1}$
q_e — amount of adsorbate adsorbed at equilibrium, $mg\,g^{-1}$
q_m — Langmuir constant related to the adsorption capacity of adsorbent, $mmol\,g^{-1}$
r — correlation coefficient
R — universal gas constant, $J\,mol^{-1}\,K^{-1}$
S — BET surface area, $m^2\,g^{-1}$
T — absolute temperature, K
t — time, min
V_p — pore volume, $cc\,g^{-1}$
ΔG — Gibbs free energy change, $J\,mol^{-1}$

Acknowledgment

This study was financially supported by Dicle University Research Foundation (Project No. DUAPK-08-EF-37).

References

[1] H. Zollinger, Color Chemistry-Synthesis, Properties, and Applications of Organic Dyes and Pigments, Wiley-VCH, Weinheim-Federal Republic of Germany, 2001.
[2] G. Mishra, M. Tripathy, A critical review of the treatments for decolourization of textile effluent, Colourage 40 (1993) 35–38.
[3] G. McKay, M.S. Otterburn, J.A. Aga, Fullers earth and fired clay as adsorbents for dyestuffs-equilibrium and rate studies, Water Air Soil Pollut. 24 (1985) 307–322.
[4] A.R. Gregory, J. Elliott, P. Kluge, Ames testing of direct black 38 parallels carcinogenicity testing, J. Appl. Toxicol. 1 (1981) 308–313.
[5] O.J. Hao, H. Kim, P.C. Chiang, Decolorization of wastewater, Crit. Rev. Environ. Sci. Technol. 30 (2000) 449–505.
[6] A. Dąbrowski, Adsorption-from theory to practice, Adv. Colloid Interface Sci. 93 (2001) 135–224.
[7] Q. Xiao, Q. Zhou, J. Zhang, L. Ouyang, Photocatalytic decolorization of methylene blue over monoclinic pyrochlore-type $Pb_2Nb_2O_7$ under visible light irradiation, J. Alloy. Compd. 468 (2009) L9–L12.
[8] A.S. Mahmoud, A.E. Ghaly, M.S. Brooks, Removal of dye from textile wastewater using plant oils under different pH and temperature conditions, Am. J. Environ. Sci. 3 (2007) 205–218.
[9] H. Pekkuz, İ. Uzun, F. Güzel, Kinetics and thermodynamics of the adsorption of some dyestuffs from aqueous solution by poplar sawdust, Bioresour. Technol. 99 (2008) 2009–2017.
[10] G. McKay, Adsorption of dyestuffs from aqueous solutions with activated carbon. 1. equilibrium and batch contact-time studies, J. Chem. Technol. Biotechnol. 32 (1982) 759–772.
[11] G. McKay, M.S. Otterburn, A.G. Sweeney, Removal of color from effluent using various adsorbents: 3. Silica-rate processes, Water Res. 14 (1980) 15–20.
[12] G. McKay, H.S. Blair, J.R. Gardner, Adsorption of dyes on chitin. 1. Equilibrium studies, J. Appl. Polym. Sci. 27 (1982) 3043–3057.
[13] D. Knorr, Dye binding properties of chitin and chitosan, J. Food Sci. 48 (1983) 36–41.
[14] M. Doğan, M. Alkan, Adsorption kinetics of methyl violet onto perlite, Chemosphere 50 (2003) 517–528.
[15] M.S. El-Geundi, Homogeneous surface diffusion model for the adsorption of basic dyestuffs onto natural clay in batch adsorbers, Adsor. Sci. Technol. 8 (1991) 217–225.

[16] M.S. El-Geundi, Branched-pore kinetic model for basic dyestuff adsorption onto natural clay, Adsor. Sci. Technol. 9 (1993) 199–211.

[17] M.S. El-Geundi, Pore diffusion model for the adsorption of basic dyestuffs onto natural clay in batch adsorbers, Adsor. Sci. Technol. 9 (1993) 109–120.

[18] G. McKay, M. El-Geundi, M.M. Nassar, Equilibrium studies during the removal of dyestuffs from aqueous solutions using bagasse pith, Water Res. 21 (1987) 1513–1520.

[19] G. McKay, M. El-Geundi, M.M. Nassar, External mass transport processes during the adsorption of dyes onto bagasse pith, Water Res. 22 (1988) 1527–1533.

[20] M.M. Nassar, E.A. Ashour, Y.H. Magdy, Dye adsorbent bagasse, a new potential source for energy conversion. in: Proceedings of the Fifth International Conference on Energy and Environment, Cairo, Egypt, 1996, pp. 993–1001.

[21] I.D. Mall, S.N. Upadhyay, Studies on treatment of basic dyes bearing wastewater by adsorptive treatment using flyash, Ind. J. Environ. Health 40 (1998) 177–188.

[22] I.D. Mall, S.N. Upadhyay, Removal of basic dyes from wastewater using boiler bottom ash, Ind. J. Environ. Health 37 (1995) 1–10.

[23] I.D. Mall, S.N. Upadhyay, Treatment of methyl violet bearing wastewater from paper mill effluent using low cost adsorbents, J. Indian Pulp Paper Technol. Assoc. 7 (1995) 51–57.

[24] M.M. Swamy, I.D. Mall, B. Prasad, I.M. Mishra, Sorption characteristics of O-cresol on bagasse fly ash and activated carbon, Ind. J. Environ. Health 40 (1998) 67–78.

[25] I.D. Mall, V.C. Srivastava, N.K. Agarwal, Removal of orange-G and methyl violet dyes by adsorption onto bagasse fly ash-kinetic study and equilibrium isotherm analyses, Dyes Pigments 69 (2006) 210–223.

[26] C. Peniche-Covas, L.W. Alvarez, W. Argüelles-Monal, The adsorption of mercuric ions by chitosan, J. Appl. Polym. Sci. 46 (1992) 1147–1150.

[27] E. Guibal, C. Milot, J.M. Tobin, Metal-anion sorption by chitosan beads: Equilibrium and kinetic studies, Ind. Eng. Chem. Res. 37 (1998) 1454–1463.

[28] R.-S. Juang, H.-J. Shao, A simplified equilibrium model for sorption of heavy metal ions from aqueous solutions on chitosan, Water Res. 36 (2002) 2999–3008.

[29] İ. Uzun, F. Güzel, Kinetics and thermodynamics of the adsorption of some dyestuffs and p-nitrophenol by chitosan and MCM-chitosan from aqueous solution, J. Colloid Interface Sci. 274 (2004) 398–412.

[30] W.H. Cheung, Y.S. Szeto, G. McKay, Enhancing the adsorption capacities of acid dyes by chitosan nano particles, Bioresource Technol. 100 (2009) 1143–1148.

[31] İ. Uzun, Kinetics of the adsorption of reactive dyes by chitosan, Dyes Pigments 70 (2006) 76–83.

[32] X.F. Zeng, E. Ruckenstein, Cross-linked macroporous chitosan anion-exchange membranes for protein separations, J. Membr. Sci. 148 (1998) 195–205.

[33] J. Benesch, P. Tengvall, Blood protein adsorption onto chitosan, Biomaterials 23 (2002) 2561–2568.

[34] M.N.V. Ravi Kumar, A review of chitin and chitosan applications, React. Funct. Polym. 46 (2000) 1–27.

[35] R.A.A. Muzzarelli, Chitin, Pergamon Press, Great Britain, 1977.

[36] K.G. Bhattacharyya, A. Sarma, Adsorption characteristics of the dye, Brilliant Green, on Neem leaf powder, Dyes Pigments 57 (2003) 211–222.

[37] A. Gücek, S. Şener, S. Bilgen, M.A. Mazmancı, Adsorption and kinetic studies of cationic and anionic dyes on pyrophyllite from aqueous solutions, J. Colloid Interface Sci. 286 (2005) 53–60.

[38] S. Lagergren, Zur theorie der sogenannten adsorption gelöster stoffe, Kungliga Svenska Vetenskapsakademiens, Handlingar 24 (1898) 1–39.

[39] Y.S. Ho, G. McKay, Sorption of dye from aqueous solution by peat, Chem. Eng. J. 70 (1998) 115–124.

[40] W.J. Weber, Jr., J.C. Morris, Kinetics of adsorption on carbon from solutions, J. Sanit. Engng. Div. Am. Soc. Civ. Engrs. 89 (1963) 31–59.

[41] R.H. Petrucci, W.S. Harwood, General Chemistry, Macmillan, New York, NY, 1993.

[42] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, J. Amer. Chem. Soc. 40 (1918) 1361–1403.

[43] C.H. Giles, A.P. D'silva, I.A. Easton, A general treatment and classification of the solute adsorption isotherm: II. Experimental interpretation, J. Colloid Interface Sci. 47 (1974) 766–778.

[44] H.M.F. Freundlich, Über die adsorption in lösungen, Z. Phys. Chem. 57 (1906) 385–470.