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Rate studies on the adsorption of some dyestuffs and *p*-nitrophenol by chitosan and monocarboxymethylated(mcm)-chitosan from aqueous solution

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Abstract

In this study, the effect of temperature on the adsorption of some dyestuffs [orange II (O-II), crystal violet (CV) and reactive blue 5 (RB5)] and *p*-nitrophenol (PNP) by chitosan and of O-II and CV by modified chitosan [monocarboxymethylated(mcm)-chitosan] from aqueous solution was investigated. Kinetical data related to the adsorptions of each dyestuff and PNP by chitosan and of O-II and CV by mcm–chitosan were applied to Lagergren and Weber–Morris equations, and adsorption rate constants (k_{ads}) and pore diffusion rate constants (k_p) were determined, respectively. In addition, Langmuir isotherm constants with experimental data related to the adsorptions of O-II and CV by chitosan and of CV by mcm-chitosan were applied to McKay et al. equation, and external mass transfer coefficients (k_f) were also determined. Lastly, chitosan and mcm-chitosan were compared according to their dyestuffs and PNP uptake capabilities. It was seen that mcm-chitosan removed more O-II (99.2%) and RB5 (34.9%) but less CV (3.1%) and PNP (0.9%).

Keywords: Chitosan; Dyestuff adsorption; Diffusion; Mass transfer

1. Introduction

The effluents of wastewater in some industries such as dyestuff, textiles, leather, paper, plastics, etc. contain various kinds of synthetic dyestuffs. A very small amount of dye in water is highly visible and can be toxic to creatures in water. Because of this reason, the removal of color from process or waste effluents becomes environmentally important. Among several chemical and physical methods, adsorption process is one of the most effective methods to remove dyes from wastewater. Many studies have been undertaken to find suitable adsorbents to lower dye concentrations from aqueous solutions. They included alumina [1], clay [2], chitin [3], peat [4], fly ash [5], activated carbon [6], silica [7], bagasse pith [8], and others [9–12]. For both regenerative and non-regenerative systems, high adsorption capacity is essential for adsorbent selection. However, the amount (g) of dyes adsorbed on the above adsorbents (kg) are not high enough, some have capacities of 200–600 g kg^{-1} and some even lower than 50 g kg^{-1}. To improve adsorption performance, research for finding new adsorbents is still in progress.

Chitosan is the deacetylated form of chitin, which is a linear polymer of acetylamino-D-glucose and contains high contents of amino and hydroxyl functional groups. Chitosan has been reported for the high potentials of the adsorption of dyes [13], proteins [14] and metal ions [15]. Other useful features of chitosan include its abundance, hydrophilicity, biocompatibility, biodegradability, and antibacterial properties [16]. The aim of the present study is to investigate the effect of temperature on the adsorptions of O-II (anionic), CV (cationic), RB5 (reactive), and PNP (ideal adsorbate) by chitosan and of O-II and CV by mcm-chitosan from aqueous solution. For this purpose, Lagergren [17], Weber–Morris [18]

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Nomenclature

b	Langmuir constant related to the energy of adsorption (L mmol^{-1})
C	concentration of adsorbate at time t (mmol L^{-1})
C_e	equilibrium concentration of adsorbate (mmol L^{-1})
C_o	initial concentration of adsorbate (mmol L^{-1})
d_p	particle diameter (cm)
K ($q_m b$)	Langmuir constant (L g^{-1})
k_{ads}	adsorption rate constant (min^{-1})
k_f	external mass transfer coefficient (cm min^{-1})
k_p	pore diffusion rate constant (mg g^{-1} min$^{-1/2}$)
m	mass of adsorbent per unit volume of particle-free slurry (g L^{-1})
q	amount of adsorbate adsorbed at time t (mmol g^{-1})
q_e	amount of adsorbate adsorbed at equilibrium (mmol g^{-1})
q_m	Langmuir constant related to the capacity of adsorption (mmol g^{-1})
S	BET surface area of adsorbent (m^2 g^{-1})
S_s	outer surface of adsorbent particles per unit volume of particle-free slurry (cm^{-1})
t	time (min)
X/M	mass of adsorbate adsorbed per gram adsorbent (mg g^{-1})
ε_p	porosity of adsorbent particles
ρ_p	density of adsorbent particles (g L^{-1})

and McKay et al. [3] rate equations have been used. These substances have toxic property.

2. Experimental

2.1. Chemicals

In this study, chitosan (deacetylation degree: minimum 85%, FW: 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, color: light yellow) (Sigma C 3646, Germany) and mcm-chitosan (FW: 1,101,700 g mol^{-1}, color: light golden) (prepared from chitosan) as adsorbent, and O-II (Sigma, Germany), CV (Merck, Germany), RB5 (Sigma, Germany), and PNP (Fluka, Switzerland) in Fig. 1 as adsorbate were used.

2.2. The preparation of monocarboxymethylated(mcm)-chitosan

Chitosan was modified to increase its adsorption capability. To that end, 45.0 g chitosan (equivalent to 0.275 mol glucosamine units) and 51.57 g monochloroacetic acid (0.55 mol) were stirred together with 75 mL pyridine as the catalyst in 750 mL ethanol and refluxed under nitrogen atmosphere for 3 days. The product gel was washed, sequentially, with 0.5 M sulfuric acid solution and deionized water after filtration, and again stirred in 0.3 M acetic acid solution (Scheme 1). After filtration, it was further washed, sequentially, with water, 1 M aqueous sodium hydroxide solution, water, 0.5 M sulfuric acid solution, and finally with water. It was dried in vacuo to a constant weight before use [19].

2.3. Batch kinetic and isotherm studies

All the kinetic experiments were performed at the natural pHs (6.1 for O-II, 4.7 for CV, 6.2 for RB5 and 4.6 for PNP) of solutions. Acid, base, or buffer solution was not added into the solutions of adsorbates. Kinetic study to investigate the effect of temperature on the adsorptions of O-II, CV, RB5, and PNP by chitosan and of O-II and CV by mcm-chitosan from aqueous solution was firstly carried out. Samples of 0.2 g of adsorbent with samples of 50 mL of adsorbate solution 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 were measured at λ_{max} = 487 nm for O-II, λ_{max} = 590 nm for CV, λ_{max} = 599 nm for RB5 and λ_{max} = 318 nm for PNP. Kinetical data were analyzed using Lagergren (Eq. (1)),

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

$$\frac{X}{M} = k_p t^{1/2} \quad (2)$$

$$\ln\left[\frac{C}{C_o} - \frac{1}{1+mK}\right] = \ln\left[\frac{mK}{1+mK}\right] - \left[\frac{1+mK}{mK} k_f S_s t\right] \quad (3)$$

$$S_s = \frac{6m}{d_p \rho_p (1-\varepsilon_p)} \quad (4)$$

Weber–Morris (Eq. (2)) and McKay et al. (Eq. (3)) equations.

After this kinetic study, the isotherm study for each dyestuff and PNP by chitosan and for O-II and CV by mcm-chitosan from aqueous solution was carried out. Firstly, samples of 0.2 g of adsorbent with samples of 50 mL of solutions having different initial concentration (C_o) prepared from the stock solution of adsorbate were shaken for equilibrium contact time at 293 K and 150 rpm. After this shaking, the absorbance values of solutions were measured. Then, the adsorption isotherms of each dyestuff and PNP by chitosan and of O-II and CV by mcm-chitosan

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

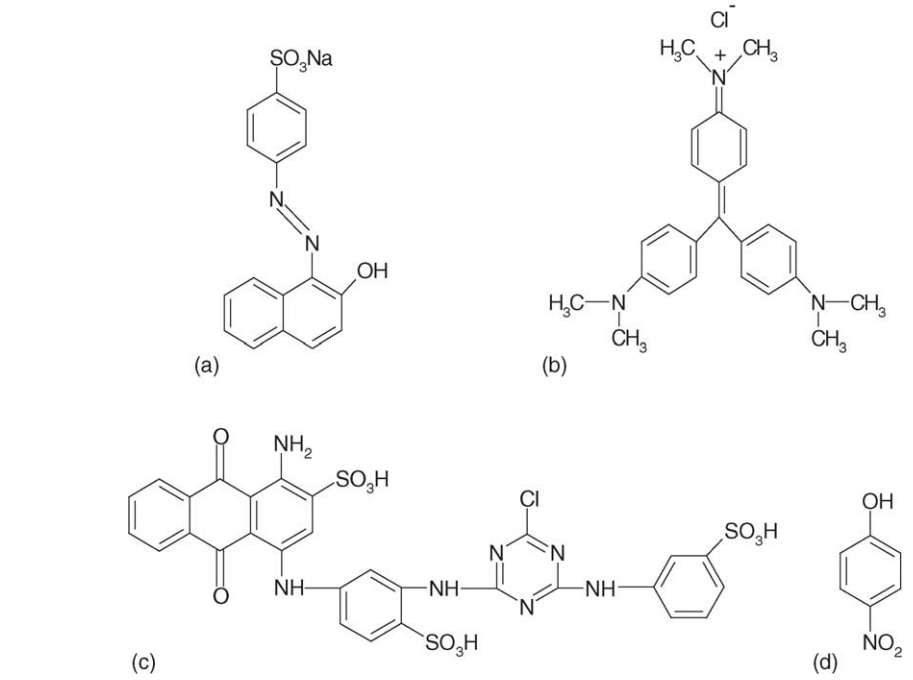
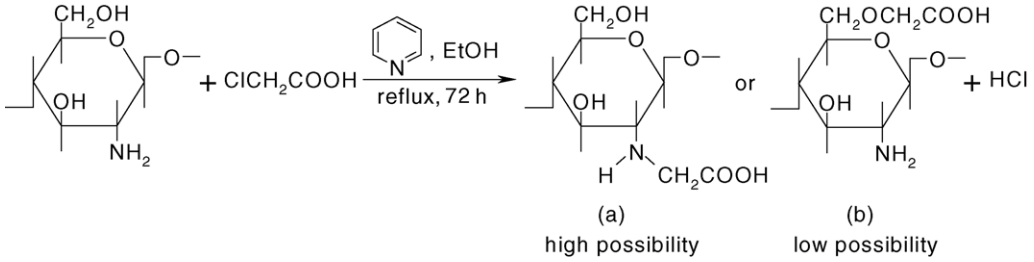


Fig. 1. The molecular structures of some dyestuffs and *p*-nitrophenol: (a) O-II, (b) CV, (c) RB5, and (d) PNP.



Scheme 1. The synthetic route of monocarboxymethylated (mcm)-chitosan.

were similarly investigated at 333 K and 150 rpm. Isotermal data were analyzed using Langmuir linear isotherm equation [20].

2.4. Comparison study the adsorption capabilities of chitosan and mcm-chitosan

In order to compare their adsorption capabilities, samples of 0.2 g of chitosan and mcm-chitosan with samples of 50 mL of each dyestuff and PNP having a known initial concentration (C_o) (1.2845 mM for O-II, 0.3677 mM for CV, 0.5812 mM for RB5 and 1.0783 mM for PNP) were shaken for their equilibrium contact times at 313 K and 150 rpm. Then, the absorbance values of solutions were measured. The percent removal, R (%) amounts of dyestuffs and

$$R(\%) = \frac{C_o - C_e}{C_o} \times 100 \quad (6)$$

PNP were calculated using Eq. (6).

3. Results and discussion

3.1. Effect of temperature

Fig. 2 shows the effect of temperature on the adsorption of some dyestuffs and PNP by chitosan from aqueous solution. O-II is adsorbed faster but less at higher temperature. This result most probably arises from physical and chemical adsorption occurring together between O-II and chitosan. If physical and chemical adsorptions are occurring together, this phenomenon is known as sorption. O-II is adsorbed less due to desorption occurring because of physical adsorption while it is adsorbed faster because of chemical adsorption on chitosan at higher temperature. Such a result was also found by Yoshida et al. [13]. O-II is an anionic dyestuff. The pK_a value of amino group (R–NH_2) in the structure of chitosan is 6.3, and amino group dissociates partly into R–NH_3^+ even at pH = 6.9 [21]. Since aqueous solution of O-II is acidic (pH = 6.1), the amino group in the structure of chitosan is charged positively when it is put into this solution, and a

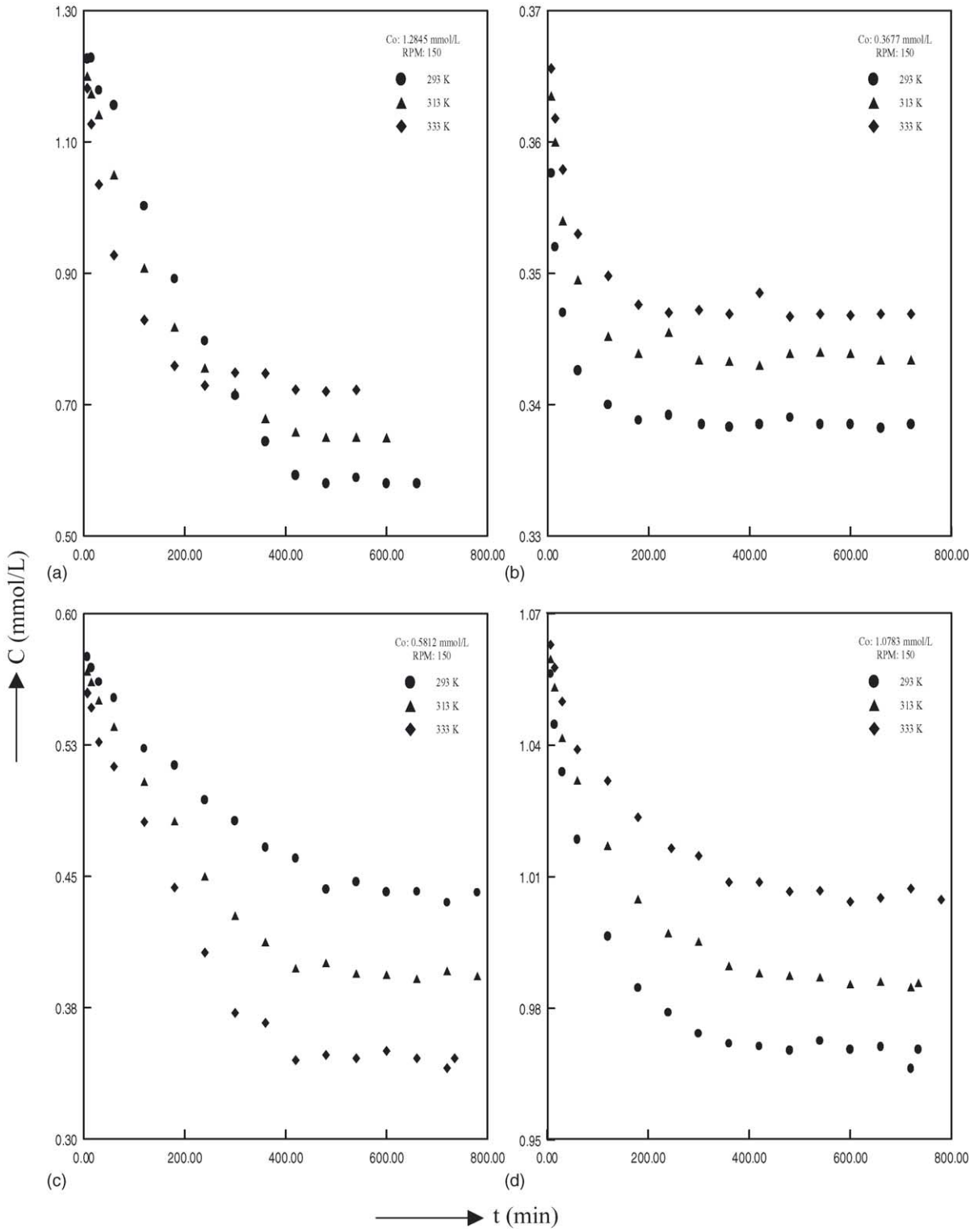


Fig. 2. The effect of temperature on the adsorptions of some dyestuffs and *p*-nitrophenol by chitosan from aqueous solution: (a) O-II, (b) CV, (c) RB5, and (d) PNP.

chemical affinity is formed between this positive charge and negative charge in the structure of O-II.

CV is adsorbed less at higher temperature. This result may be attributed to the physical adsorption occurring between CV and chitosan. Because, CV is a cationic dyestuff, and its aqueous solution is acidic (pH = 4.7). The amino group in the structure of chitosan is charged positively in aqueous solution of CV.

RB5 is adsorbed more at higher temperature. This result is most likely caused by very strong chemical adsorption occurring between RB5 and chitosan. RB5 is a reactive dyestuff. There are three SO_3^- groups per molecule in its structure. These SO_3^- groups render the RB5 acidic (pH = 6.2). Amino group in the structure of chitosan is charged positively when it is put into this solution due to acidity of aqueous solution of RB5, and a very strong chemical affinity is formed between this positive charge and negative charges in the structure of RB5.

PNP is adsorbed less at higher temperature. This result may be explained by the physical adsorption occurring significantly between PNP and chitosan. PNP is an acidic initial substance used in the synthesis of dyestuff. Its pK_a value is 7.15. O–H bond can be broken off easily, and nitro group causes to earn the resonance stability to structure by helping to the delocalization of negative charge [22]. Amino group in the structure of chitosan is charged positively when it is put into this solution because of acidity (pH = 4.6) of aqueous solution of PNP, and a chemical interaction is formed between this positive charge and negative charge existent and delocalized in the anionic structure of PNP. However, adsorption between chitosan and PNP is significantly physical. Because, PNP is a very weak acid and has resonance stability due to its anionic structure.

3.2. Adsorption kinetics

Experimental data related to the adsorptions of O-II, CV, RB5 and PNP on chitosan at different temperatures were applied to Lagergren equation [17] (Fig. 3) and Weber–Morris equation [18] (Fig. 4), and adsorption rate constants (k_{ads}) and pore diffusion rate constants (k_p) in Table 1 were calculated, respectively. The double nature of intraparticle diffusion plots may be explained as: the initial curved portions are attributed to boundary layer diffusion effects [23], while the final linear portions are due to intraparticle diffusion effects [24]. 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 chitosan used as adsorbent in study is very low, physical adsorption kinetics is controlled by surface diffusion. At particularly lower temperatures, surface diffusion is more dominant.

Table 1
Adsorption rate constants (k_{ads}), pore diffusion rate constants (k_p), and external mass transfer coefficients (k_f) related to the adsorptions of some dyestuffs and PNP by chitosan from aqueous solution

T (K)	Rate parameters	O-II	CV	RB5	PNP
293	k_{ads} (min^{-1})	0.0039	0.0295	0.0042	0.0088
	k_p (mg g^{-1} min$^{-1/2}$)	3.92	0.41	1.62	0.24
	$k_f \times 10^3$ S_s (cm min^{-1})	1.91	1.30	–	–
313	k_{ads} (min^{-1})	0.0067	0.0253	0.0054	0.0073
	k_p (mg g^{-1} min$^{-1/2}$)	4.01	0.27	2.29	0.17
	$k_f \times 10^3$ S_s (cm min^{-1})	–	–	–	–
333	k_{ads} (min^{-1})	0.0138	0.0210	0.0060	0.0059
	k_p (mg g^{-1} min$^{-1/2}$)	4.53	0.23	2.72	0.12
	$k_f \times 10^3$ S_s (cm min^{-1})	5.12	0.93	–	–

Table 2
Langmuir constants related to the adsorption isotherms of some dyestuffs by chitosan from aqueous solution

T (K)	O-II		CV	
	q_m (mmol g^{-1})	b (L mmol^{-1})	$q_m \times 10^3$ (mmol g^{-1})	b (L mmol^{-1})
293	0.330	3.96	1.546	74.88
333	0.322	2.99	0.745	70.94

3.3. Langmuir isotherm

Fig. 5 shows the effect of temperature on the adsorption isotherms of some dyestuffs and PNP by chitosan from aqueous solution. Langmuir isotherm [20] constants related to the adsorptions of O-II and CV were determined (Table 2). Langmuir isotherm constants with experimental data related to the adsorptions of O-II and CV were applied to McKay et al. equation [3] (Fig. 6), and external mass transfer coefficients (k_f) in Table 1 were calculated.

As can be seen from k_{ads}, k_p and k_f constants, O-II and RB5 at higher temperature and CV and PNP at lower temperature on chitosan are adsorbed faster.

3.4. Effect of temperature and adsorption kinetics

Fig. 7 shows the effect of temperature on the adsorptions of some dyestuffs by mcm-chitosan from aqueous solution. The introduction of carboxylic groups into the structure of mcm-chitosan being prepared from chitosan was confirmed by its infrared spectrum. The degree of carboxymethylation, as measured by neutralization titration, was greater than 90%. O-II is adsorbed more at higher temperature. This result may be explained on the basis of strong chemical adsorption occurring between O-II and mcm-chitosan. Mcm-chitosan (product having high possibility) resembles an amino acid structurally (Scheme 2). As similar to intramolecule acid–base reactions of amino acids, it gives the intramolecule acid–base reaction as follows. As a result of this, amino group in the structure of mcm-chitosan is charged positively. This amino group

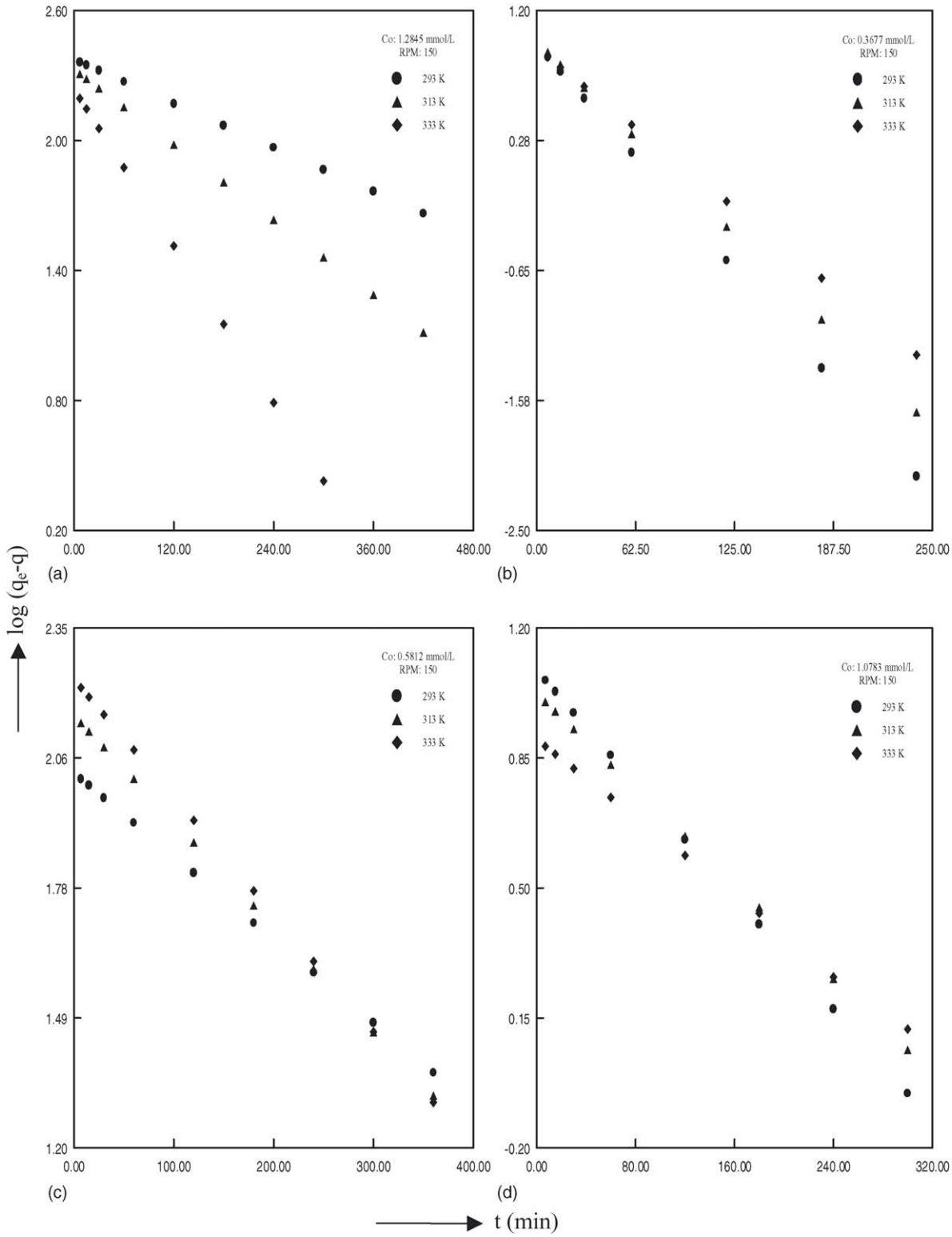


Fig. 3. Lagergren plots of kinetic curves related to the adsorptions of some dyestuffs and *p*-nitrophenol by chitosan from aqueous solution: (a) O-II, (b) CV, (c) RB5, and (d) PNP.

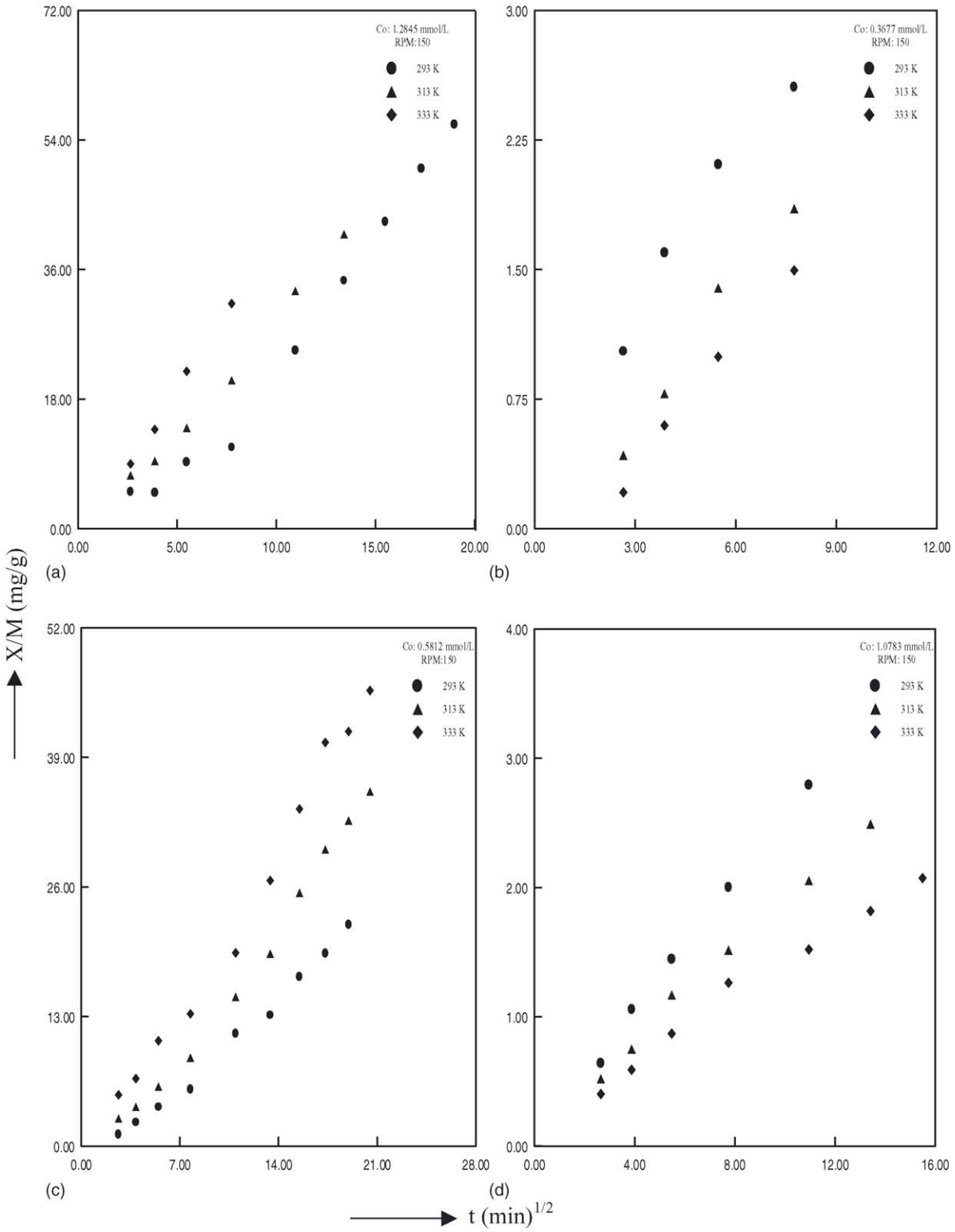


Fig. 4. Weber–Morris plots of kinetic curves related to the adsorptions of some dyestuffs and *p*-nitrophenol by chitosan from aqueous solution: (a) O-II, (b) CV, (c) RB5, and (d) PNP.

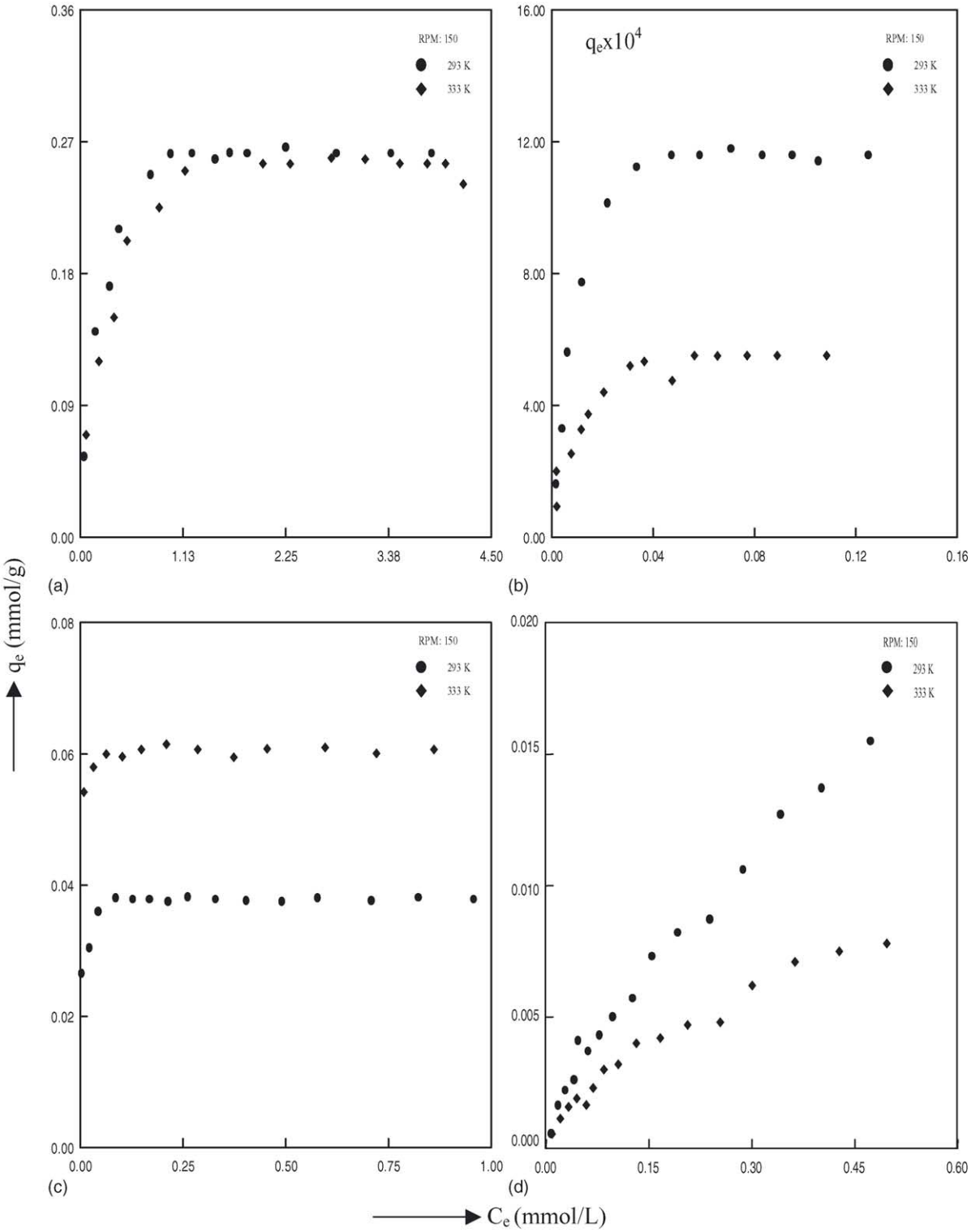


Fig. 5. The effect of temperature on the adsorption isotherms of some dyestuffs and *p*-nitrophenol by chitosan from aqueous solution: (a) O-II, (b) CV, (c) RB5, and (d) PNP.

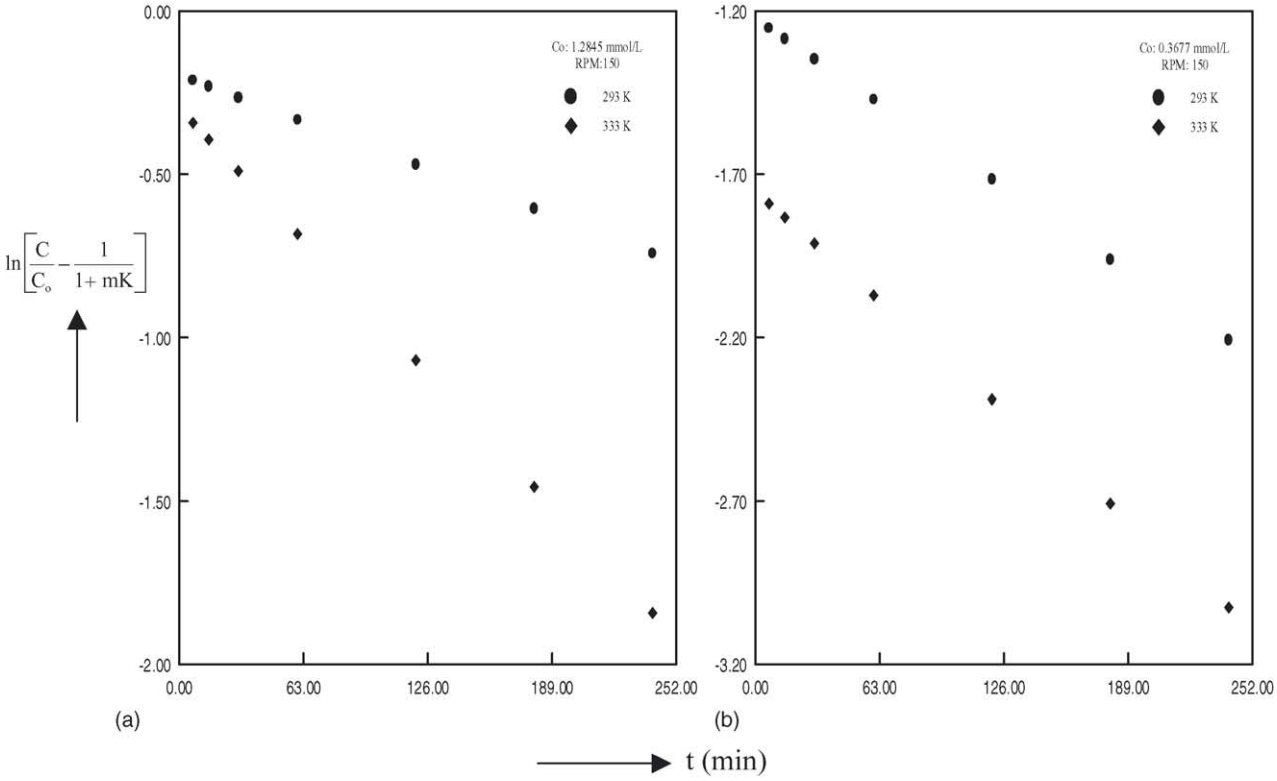


Fig. 6. McKay et al. plots of kinetic curves related to the adsorptions of some dyestuffs by chitosan from aqueous solution: (a) O-II and (b) CV.

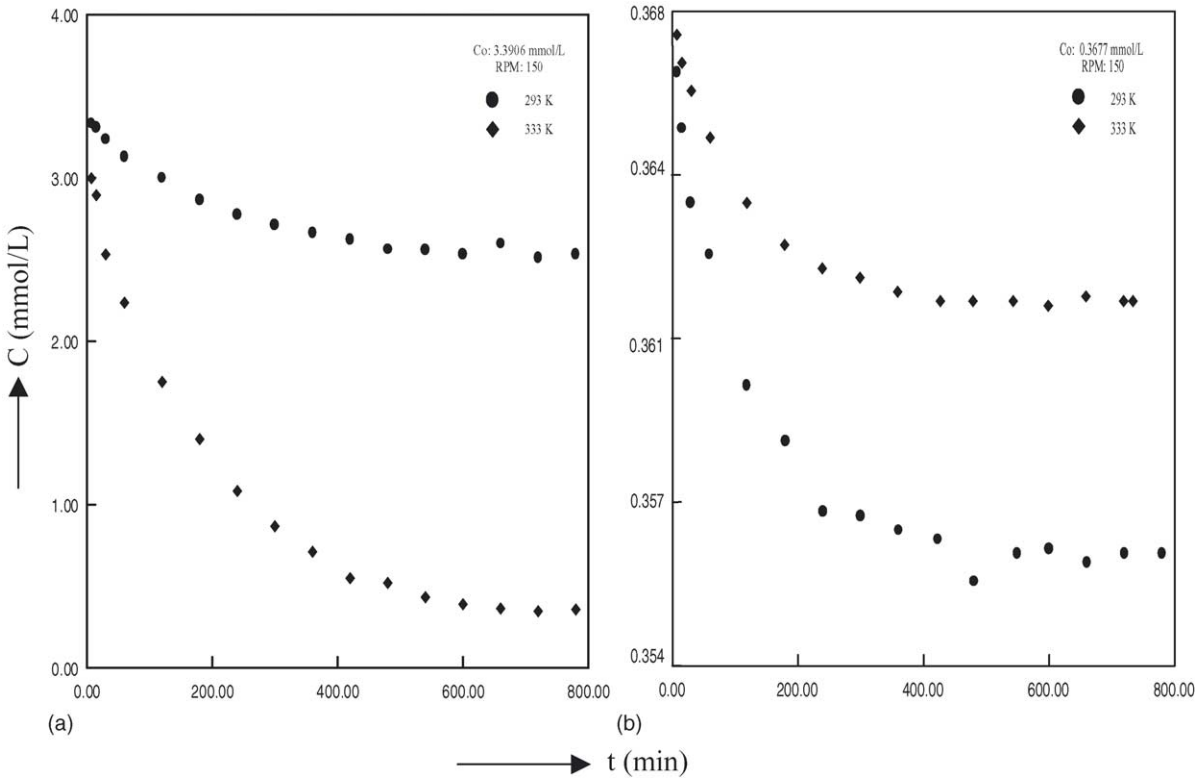
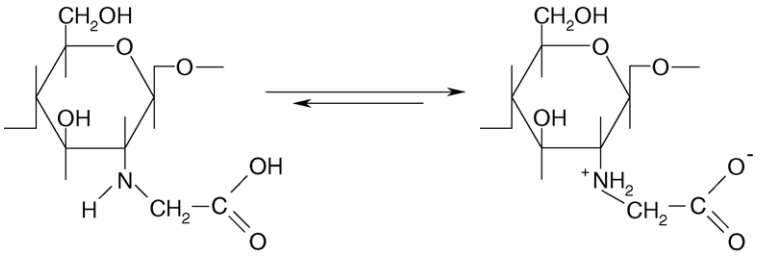


Fig. 7. The effect of temperature on the adsorptions of some dyestuffs by mcm-chitosan from aqueous solution: (a) O-II, (b) CV.



Scheme 2. The zwitterion structures of monocarboxymethylated(mcm)-chitosan.

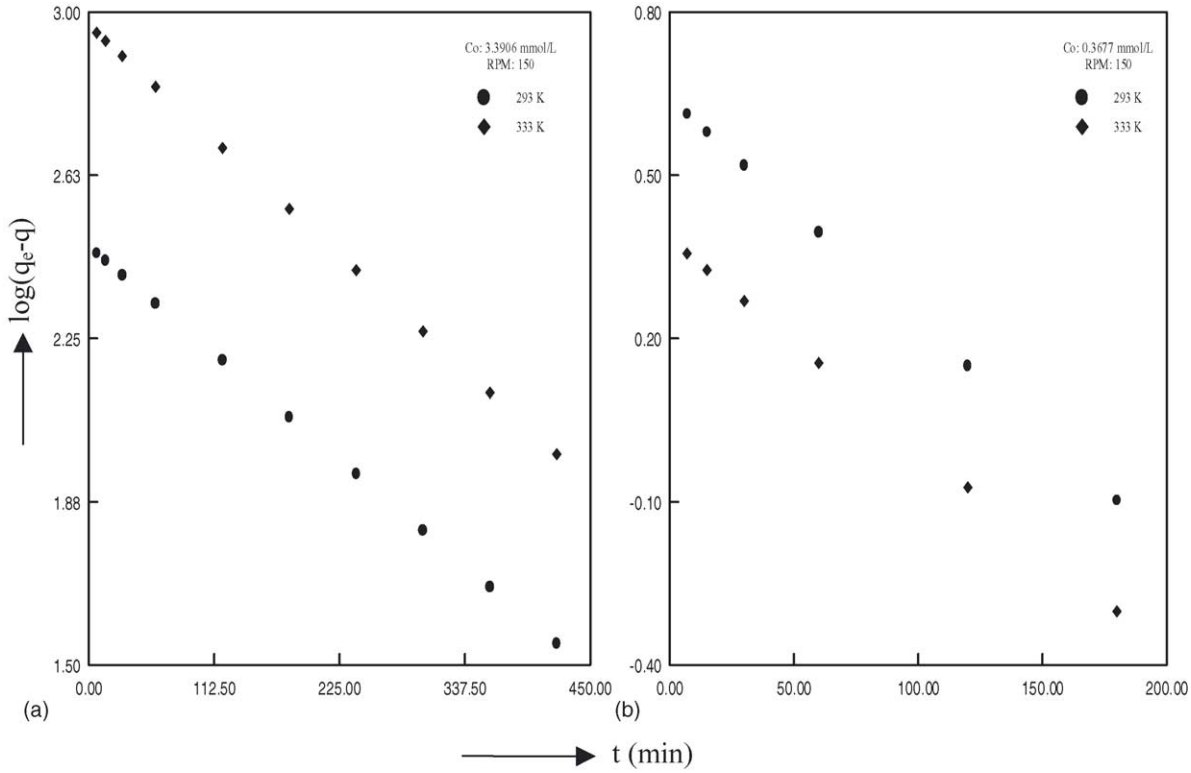


Fig. 8. Legergren plots of kinetic curves related to the adsorptions of some dyestuffs by mcm-chitosan from aqueous solution: (a) O-II, (b) CV.

charged positively because of the effect of zwitter ion has become stronger when it is put into acidic solution of O-II, and a very strong chemical affinity is formed between this amino group charged positively and SO_3^- group in the structure of O-II. Consequently, O-II is adsorbed more on mcm-chitosan at high temperature because of chemical adsorption between O-II and mcm-chitosan. CV is adsorbed more at lower temperature. This result may be attributed to the physical adsorption occurring between CV and mcm-chitosan. Amino group in the structure of mcm-chitosan is charged positively because of intramolecule acid–base reaction as stated above. Consequently, adsorption between CV and mcm-chitosan is a physical adsorption. Experimental data related to the adsorptions of O-II and CV on mcm-chitosan at different temperatures were applied to Lagergren equation [17] (Fig. 8) and Weber–Morris [18] (Fig. 9),

Table 3
Adsorption rate constants (k_{ads}), pore diffusion rate constants (k_p) and external mass transfer coefficients (k_f) related to the adsorptions of O-II and CV by mcm-chitosan from aqueous solution

T (K)	O-II			CV		
	k_{ads} (min^{-1})	k_p ($mg\,g^{-1}\,min^{-1/2}$)	k_f ($cm\,min^{-1}$)	k_{ads} (min^{-1})	k_p ($mg\,g^{-1}\,min^{-1/2}$)	$k_f \times 10^4\ S_s$ ($cm\,min^{-1}$)
293	0.0050	3.992	–	0.0094	0.068	1.034
333	0.0054	13.023	–	0.0088	0.043	0.464

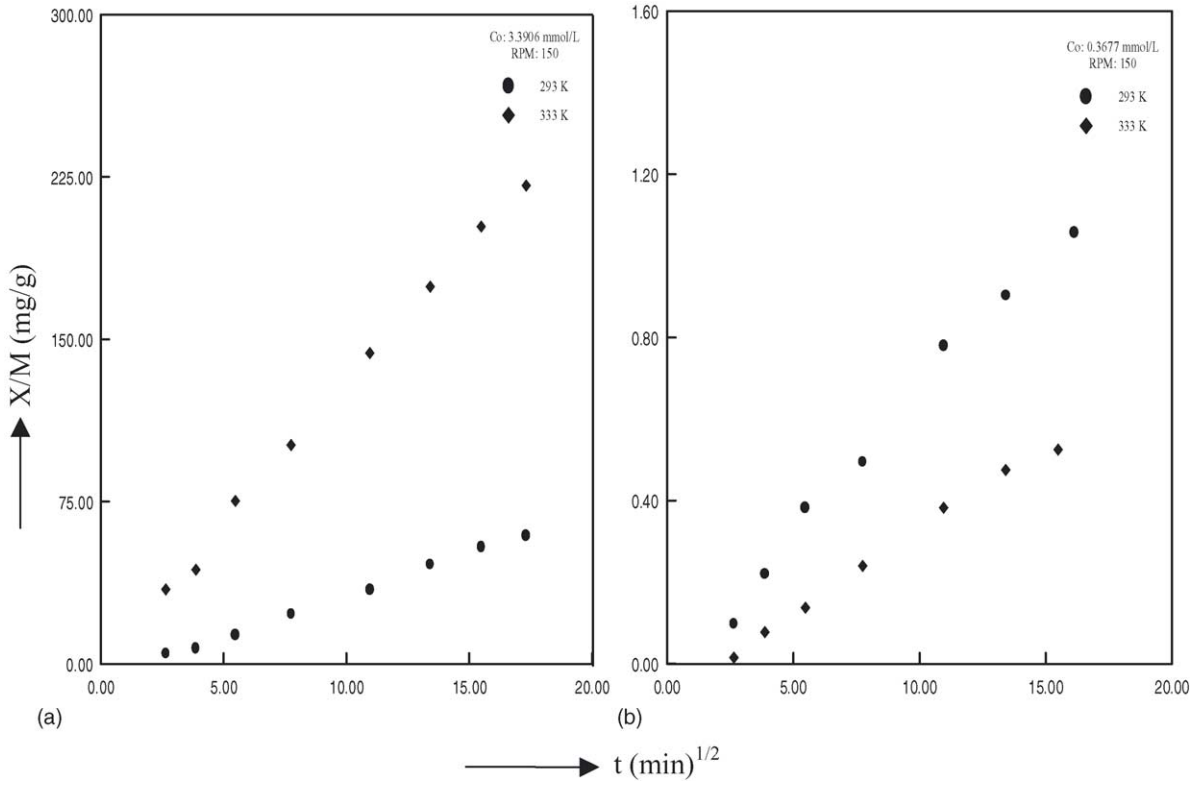


Fig. 9. Weber–Morris plots of kinetic curves related to the adsorptions of some dyestuffs by mcm-chitosan from aqueous solution: (a) O-II, (b) CV.

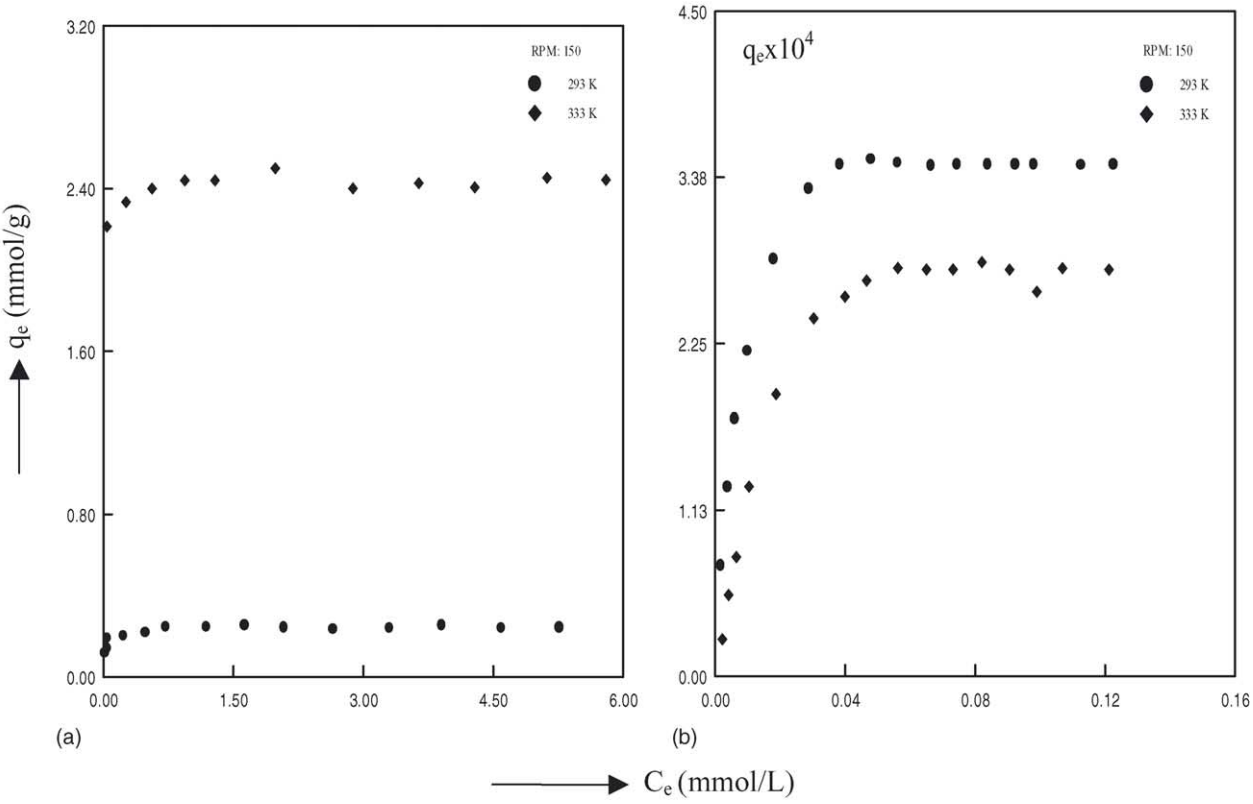


Fig. 10. The effect of temperature on the adsorption isotherms of some dyestuffs by mcm-chitosan from aqueous solution: (a) O-II, (b) CV.

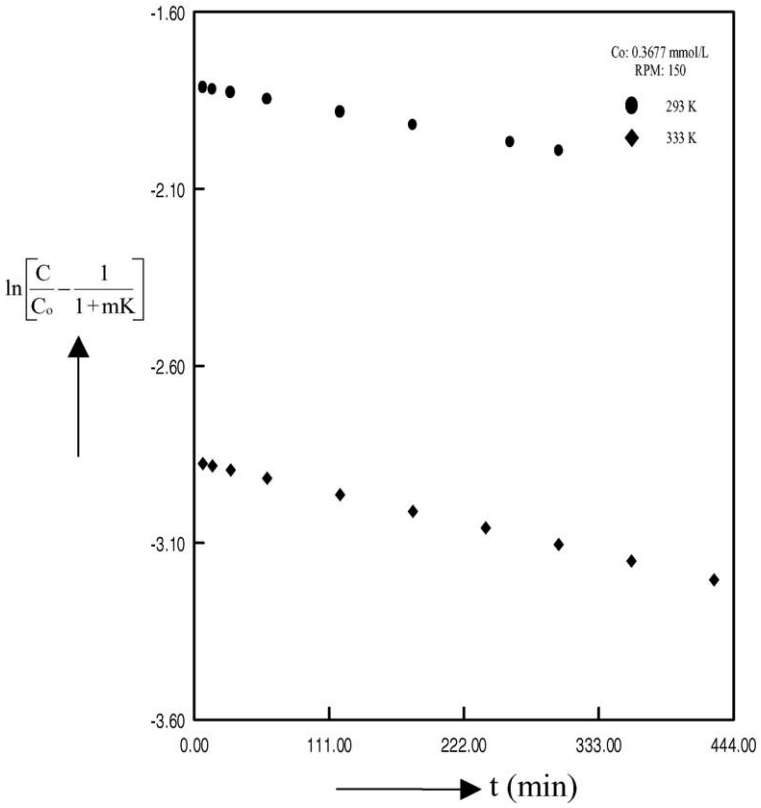


Fig. 11. McKay et al. plots of kinetic curves related to the adsorption of crystal violet by mcm-chitosan from aqueous solution.

and k_{ads} and k_p constants in Table 3 were determined, respectively.

3.5. Adsorption isotherms

Fig. 10 shows the effect of temperature on the adsorption isotherms of some dyestuffs by mcm-chitosan from aqueous solution. The type of isotherms at two temperatures related to the adsorption of O-II is another evidence of strong chemical adsorption between O-II and mcm-chitosan. Langmuir isotherm constants related to the adsorption of CV were determined (Table 4). Langmuir isotherm constants with experimental data related to the adsorption of CV were applied to McKay et al. equation [3] (Fig. 11), and k_f constants in Table 3 were calculated. As can be seen from k_{ads}, k_p and k_f constants, O-II at higher temperature and CV at lower temperature on mcm-chitosan are adsorbed faster.

Table 4
Langmuir constants related to the adsorption isotherms of CV by mcm-chitosan from aqueous solution

T (K)	$q_m \times 10^4$ (mmol g^{-1})	b (L mmol^{-1})
293	4.14	123.03
333	3.99	39.49

3.6. Comparison of chitosan and monocarboxymethylated(mcm)-chitosan

Data obtained in the result of experiments performed to compare the abilities of chitosan and mcm-chitosan to adsorb were applied to Eq. (6), and percent removal, R (%) amounts of O-II, CV, RB5 and PNP were calculated (Table 5).

Fig. 12 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.

Table 5
Percent removal, R (%), results related to some dyestuffs and PNP by chitosan and mcm-chitosan from aqueous solution

Adsorbate	Adsorbent	
	Chitosan	mcm-Chitosan
O-II	12.0	99.2
CV	9.7	3.1
RB5	12.1	34.9
PNP	7.4	0.9

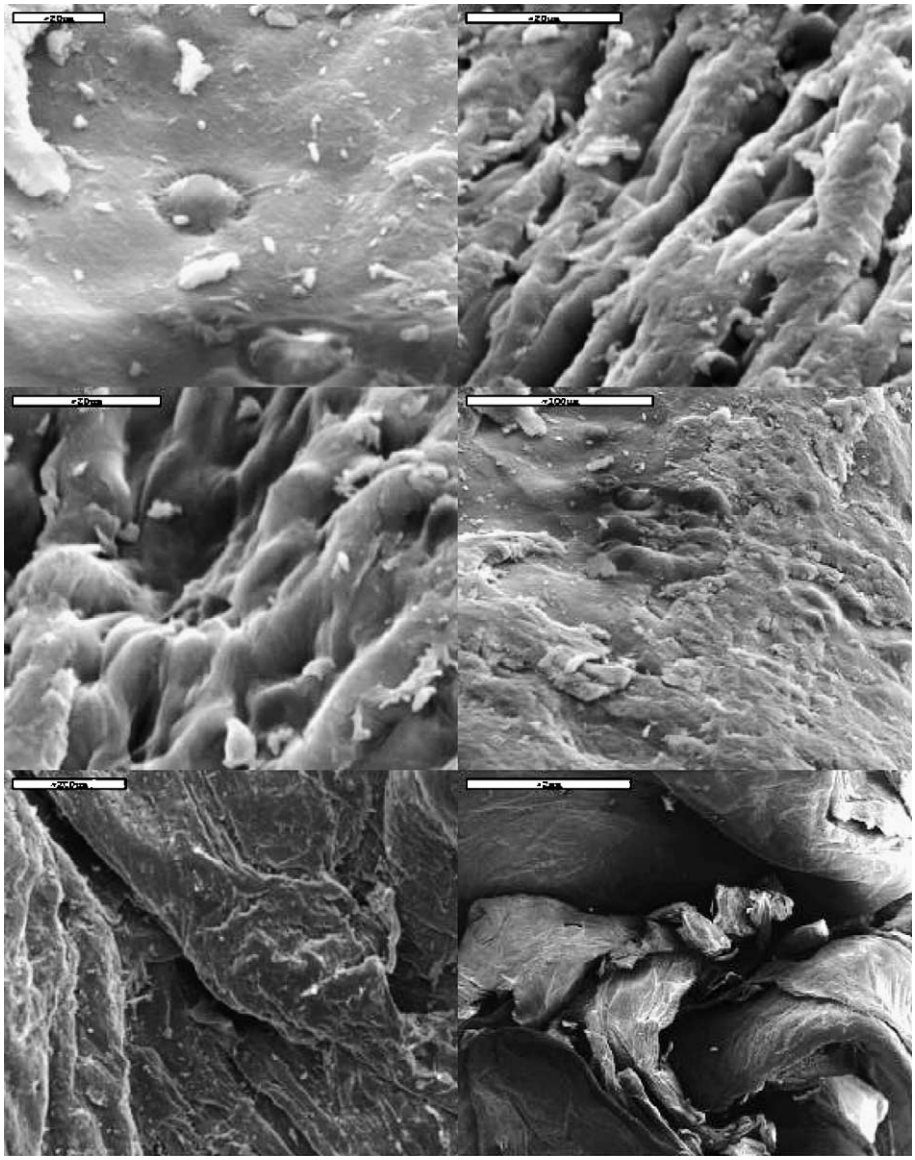


Fig. 12. The SEM micrographs of chitosan (Sigma C 3646).

4. Conclusion

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

1. The adsorptions of O-II, CV, and PNP by chitosan and of CV by mcm-chitosan from aqueous solution must be studied at low temperature. As for the adsorptions of RB5 by chitosan and of O-II by mcm-chitosan from aqueous solution must be studied at high temperature.
2. Since mcm-chitosan removed the O-II and RB5 more than chitosan did, chitosan must be modified with $ClCH_2COOH$ for the adsorptions of these dyestuffs. The modification of chitosan with $ClCH_2COOH$ does not necessitate much cost.

In conclusion, it can easily be said that chitosan and mcm-chitosan can be used together with other adsorbents in the studies of dyestuff adsorption related to environment. Because, chitosan is a very good adsorbent in comparison with most adsorbents in the adsorptions of particularly heavy metals and acidic dyestuffs from aqueous solution, and it is also cheaper compared to most adsorbents and found abundantly in nature. Mcm-chitosan is a rather good adsorbent than chitosan for the adsorptions of acidic dyestuffs from aqueous solution, and its production is not costly.

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