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External Mass Transfer Studies during the Adsorptions of Some Dyestuffs and p-Nitrophenol onto Chitosan from Aqueous Solution

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The effect of temperature on the adsorptions of some dyestuffs [orange II (O-II), crystal violet (CV) and reactive blue 5 (RB5)] and an ideal adsorbate p-nitrophenol (PNP) by chitosan (Sigma C 3646) from aqueous solution was investigated. The experimental data related to adsorption isotherms were applied to linear forms of the equations that they fitted, and isotherm constants were calculated. Since the isotherm curves obtained for the adsorptions of O-II and CV by chitosan fitted the Langmuir adsorption isotherm, the Langmuir constants (q_m and b) related to the adsorption isotherms of these dyestuffs together with their kinetical data at different temperatures were applied to the equation of McKay et al., and external mass transfer coefficients $(k_f)_1$ at these temperatures were calculated. In addition, kinetic data obtained for each dyestuff and PNP at different temperatures were applied to a further equation developed by Weber-Mathews, and $(k_f)_2$ constants at these temperatures were calculated.

Key Words: Chitosan, Dyestuff adsorption, External mass transfer coefficient.

Introduction

Due to the growing demand for the reuse of wastewater in industrialized countries[1,2], it is becoming increasingly necessary to purify polluted waters by physicochemical processes[3−6]. Many dyes and pigments are inert and non-toxic at the concentrations at which they are discharged into receiving waters. However, some are not so innocuous, and, in either case, the colour they impart is very undesirable to the water user. The removal of dyes in an economic fashion remains a major problem, although recently a number of successful systems have been developed using adsorption techniques[7]. The use of agitated vessels containing slurries of adsorbent is growing for pollutant removal. The performance of such vessels is especially dependent on mass transport rates, and it is important to determine the individual and overall mass transport coefficients for such processes[8].

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Adsorption in a slurry of particles involves a mass transfer resistance at the particle surface that may control the adsorption rate. There are many variables involved: geometry of the vessel, nature of the baffles, type of impeller, speed of rotation (or power input) and slurry density all vary with vessel design. The physical variables include liquid density, viscosity and molecular diffusivity of the diffusing solute. The size distribution, shape and density of the particles are also important factors[8]. The adsorption of dyes onto chitosan is assumed to occur by a 3-step process:

(i) mass transfer of solute dyes from the bulk solution to the particle surface,

(ii) intraparticle diffusion in the bulk solution filled pores,

(iii) adsorption from the bulk solution onto an interior site.

The external mass transfer coefficient can be evaluated primarily by assuming step (iii) to be rate-limiting according to McKay et al.[9]. The aim of the present study was to investigate the effect of temperature on the adsorptions of some dyestuffs and PNP (Figure 1) by chitosan (Figure 2) from aqueous solution. For this purpose, the kinetic equations of McKay et al.[9] and Weber-Mathews[10] were used. These substances have toxic properties. In addition, when they come into contact with the eyes or skin, they cause irritation.

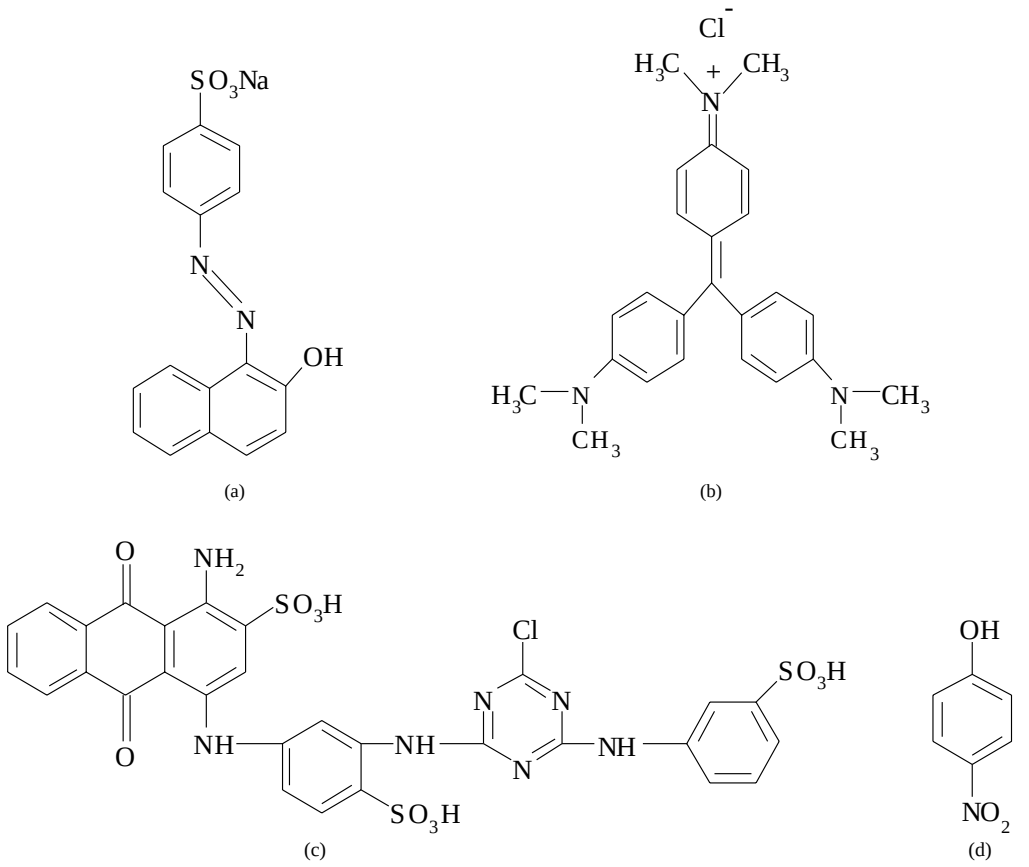

Figure 1. The molecular structures of some dyestuffs and p-nitrophenol: a) O-II, b) CV, c) RB5 and d) PNP.

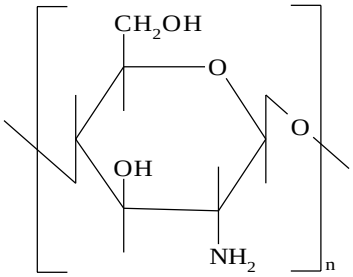

Figure 2. The molecular structure of chitosan.

Experimental

Chitosan (its deacetylation degree was minimum 85%) (Sigma, Germany) as adsorbent and O-II (Sigma, Germany), CV (Merck, Germany), RB5 (Sigma, Germany) and PNP (Fluka, Switzerland) as adsorbate were used. A kinetic study to investigate the effect of temperature on the adsorptions of O-II, CV, RB5 and PNP by chitosan from aqueous solution was firstly carried out. Kinetic experiments were performed at 293 K, 313 K and 333 K. Samples of 0.2 g of chitosan with samples of 50 mL of each dyestuff and PNP having a known initial concentration were shaken. Absorbance values were measured with a Shimadzu UV-120-02 spectrophotometer after different time intervals 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.

Then the isotherm study for each dyestuff and PNP was carried out. Firstly, samples of 0.2 g of chitosan with samples of 50 mL of solutions having different initial concentrations (C_o) prepared from stock solutions of each dyestuff and PNP 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. Then the adsorption isotherms of each dyestuff and PNP were investigated at 333 K and 150 rpm.

Results and Discussion

Figure 3 shows the effect of temperature on the adsorptions of some dyestuffs and PNP by chitosan from aqueous solution. O-II is adsorbed faster but less at high temperatures. CV and PNP are adsorbed less at higher temperatures. RB5 is adsorbed more at higher temperatures. Owing to the adsorption isotherms related to the O-II and CV fitted Langmuir adsorption isotherm[11], experimental data at different temperatures related to the adsorptions of O-II and CV by chitosan were applied to the equation of McKay et al.[9] (Figure 4), and the external mass transfer coefficients (k_f) in Table 1 were calculated: where C_o(mmol

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

$$S_s=\frac{6m}{d_p\rho_p(1-\varepsilon_p)} \tag{2}$$

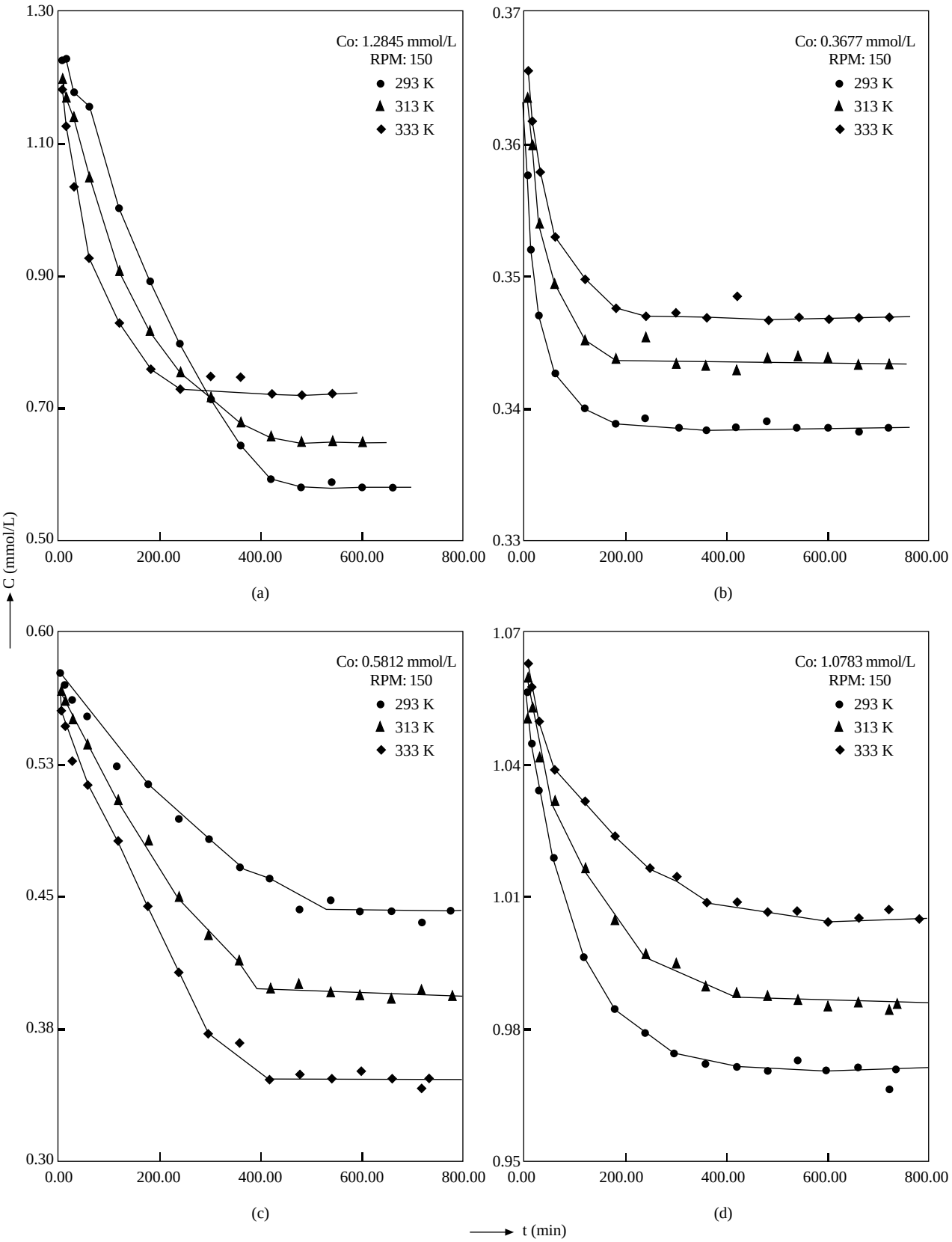

Figure 3. The effect of temperature on the adsorptions of some dyestuffs and p-nitrophenol by chitosan from aqueous solution: a) O-II, b) CV, c) RB5 and d) PNP.

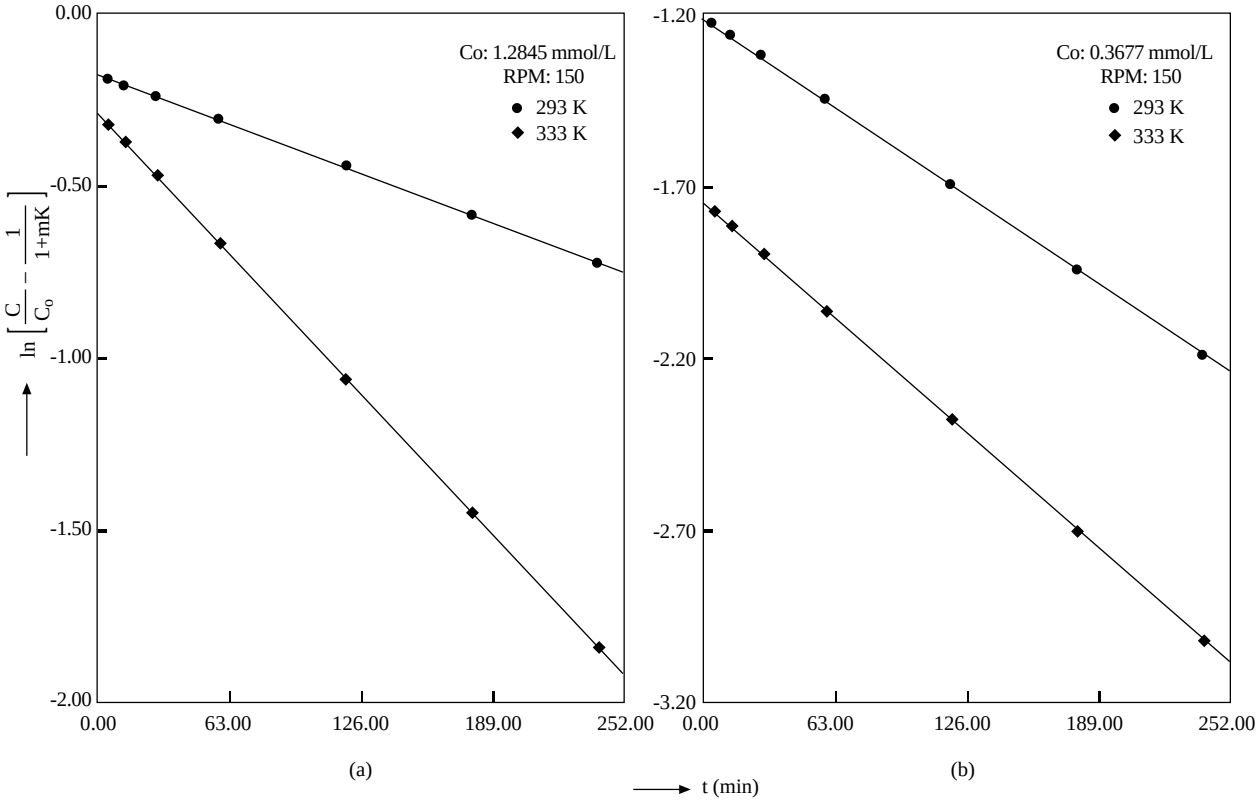

Figure 4. McKay et al. plots of kinetic curves related to the adsorptions of some dyestuffs by chitosan from aqueous solution: a) O-II and b) CV.

C_o(mmol L^{-1}) is the initial concentration of adsorbate, C (mmol L^{-1}) is the concentration of adsorbate at time t, m (g L^{-1}) is the mass of chitosan per unit volume of particle-free slurry, K (q_mb) (L g^{-1}) is the Langmuir constant, S_s (cm^{-1}) is specific particle surface area for mass transfer, d_p (cm) is particle diameter, ρ_p (g L^{-1}) is the density of chitosan particles, and ε_p is the porosity of chitosan particles. Furthermore, experimental data at different temperatures related to the adsorptions of O-II, CV, RB5 and PNP by chitosan were applied to a further equation developed by Weber-Mathews[10] (Figure 5), and the k_f constants in Table 1 were calculated. The Weber-Mathews equation does not consider the effect of isotherm shape at all[8]. C,

$$\frac{d(C/C_o)}{dt} = -k_f S_s \tag{3}$$

C_o and S_s in the Weber-Mathews equation are same as C, C_o and S_s in the equation of McKay et al.. As can be understood from k_f constants calculated from both equations, O-II and RB5 at higher temperatures and CV and PNP at lower temperatures on chitosan are adsorbed faster.

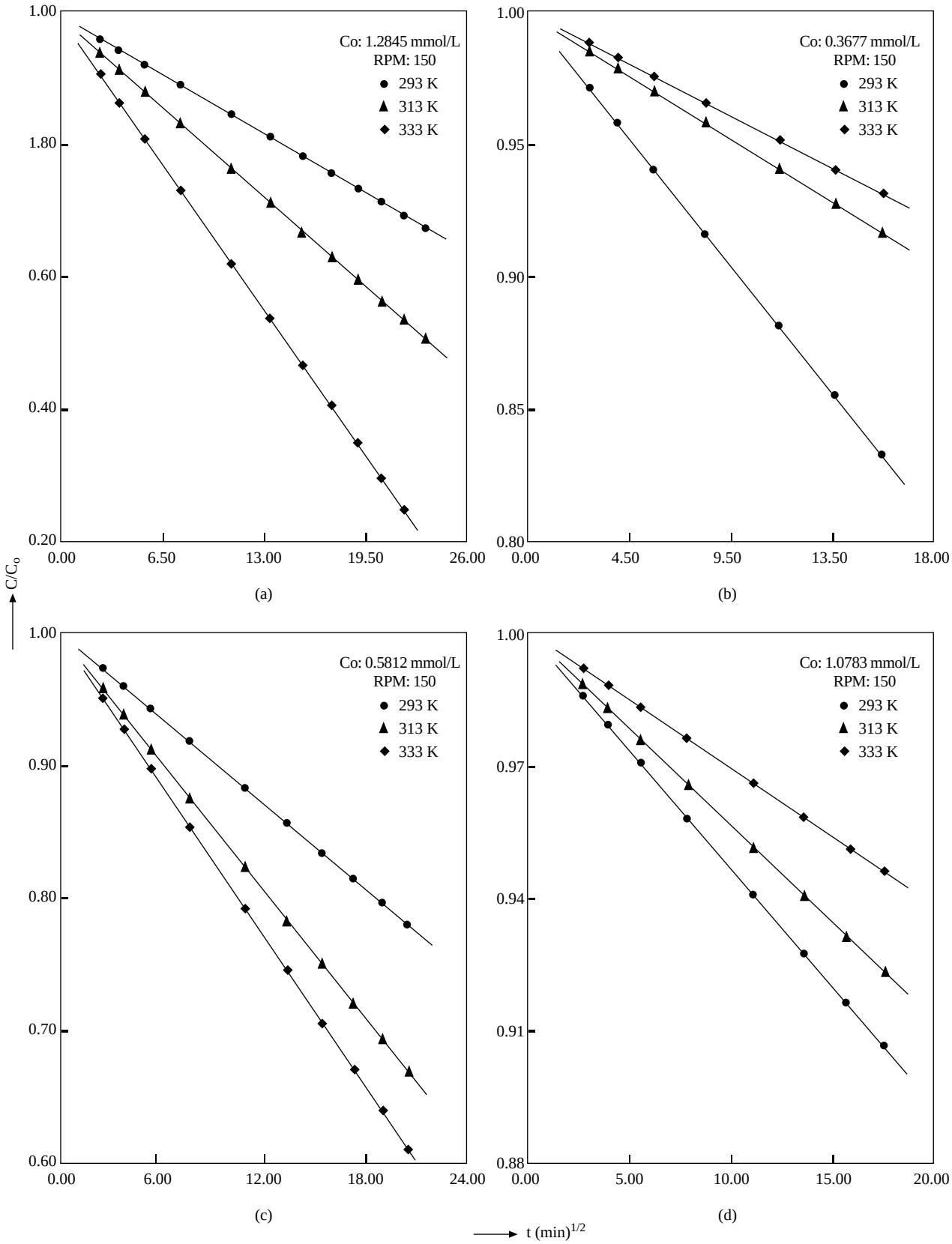

Figure 5. Weber-Mathews plots of kinetic curves related to the adsorptions of some dyestuffs and p-nitrophenol by chitosan from aqueous solution: a) O-II, b) CV, c) RB5 and d) PNP.

Table 1. External mass transfer coefficients (k_f) (cm min^{-1}) calculated from the equations of McKay et al. and Weber-Mathews related to the adsorptions of some dyestuffs and PNP by chitosan from aqueous solution.

T	McKay et al. equation				Weber-Mathews equation			
(K)	O-II $X10^3S_s$	CV $X10^3S_s$	RB5 XS_s	PNP XS_s	O-II $X10^3S_s$	CV $X10^3S_s$	RB5 $X10^3S_s$	PNP $X10^3S_s$
293	1.911	1.299	-	-	1.906	1.350	0.832	2.028
313	-	-	-	-	3.025	1.108	1.385	1.094
333	5.117	0.925	-	-	5.294	0.925	6.256	0.720

Figure 6 shows the effect of temperature on the adsorption isotherms of some dyestuffs and PNP by chitosan from aqueous solution. Owing to the adsorption isotherms related to the O-II and CV fitted Langmuir adsorption isotherm[11], experimental data were applied to the Langmuir linear isotherm equation

$$q_e = q_m \frac{bC_e}{1 + bC_e} \tag{4}$$

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

(Figure 7), and Langmuir constants (q_m and b) were calculated (Table 2): where q_m (mmol g^{-1}) and b (L $mmol^{-1}$) are Langmuir constants related to the capacity and energy of adsorption, respectively. The greater q_m constant at lower temperatures confirmed that O-II and CV are adsorbed more on chitosan at lower temperatures. The type of isotherms at every 2 temperatures related to the adsorption of RB5 is evidence of strong chemical adsorption between RB5 and chitosan. This type of isotherm is known as an H-type isotherm according to Giles' isotherm classification[12]. Due to adsorption isotherms related to PNP fitting the Freundlich adsorption isotherm[13], experimental data were applied to the Freundlich linear isotherm

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

T	O-II		CV	
(K)	q_m(mmol g^{-1})	b(L $mmol^{-1}$)	$q_m x10^3$(mmol g^{-1})	b(L $mmol^{-1}$)
293	0.330	3.962	1.546	74.884
333	0.322	2.994	0.745	70.944

$$q_e = kC_e^{1/n} \tag{6}$$

$$logq_e = logk + \frac{1}{n} logC_e \tag{7}$$

equation (Figure 8), and Freundlich constants (k and n) were calculated (Table 3): where k (L g^{-1}) and n (-) are Freundlich constants related to the capacity of the adsorbent to adsorb and the tendency of the adsorbate to be adsorbed, respectively. The greater k constant at lower temperatures confirmed that PNP is adsorbed more on chitosan at lower temperatures.

Table 3. Freundlich constants related to the adsorption isotherms of PNP by chitosan from aqueous solution.

T (K)	k (L g^{-1})	n (-)
293	0.026	1.417
333	0.013	1.549

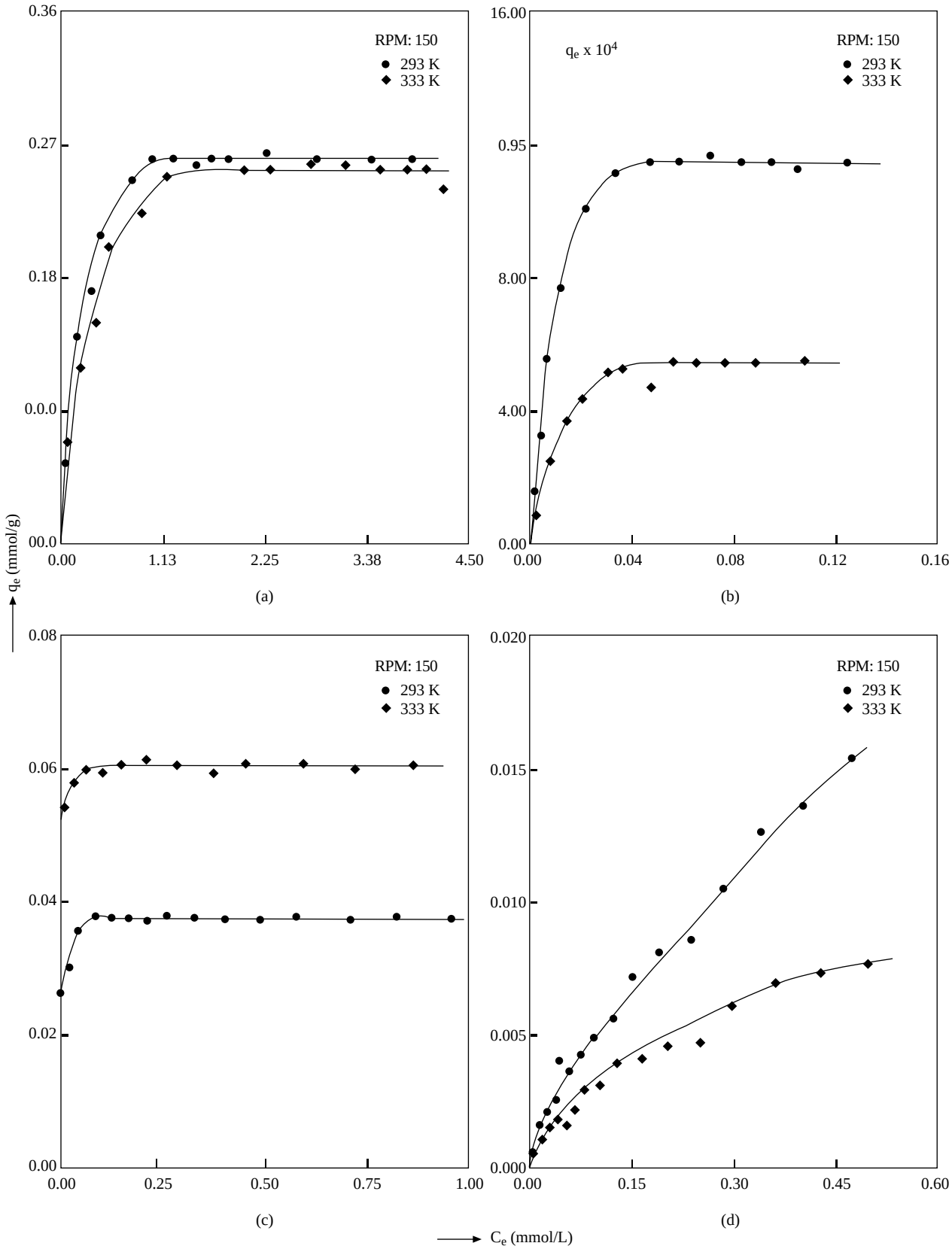

Figure 6. The effect of temperature on the adsorption isotherms of some dyestuffs and p-nitrophenol by chitosan from aqueous solution: a) O-II, b) CV, c) RB5 and d) PNP.

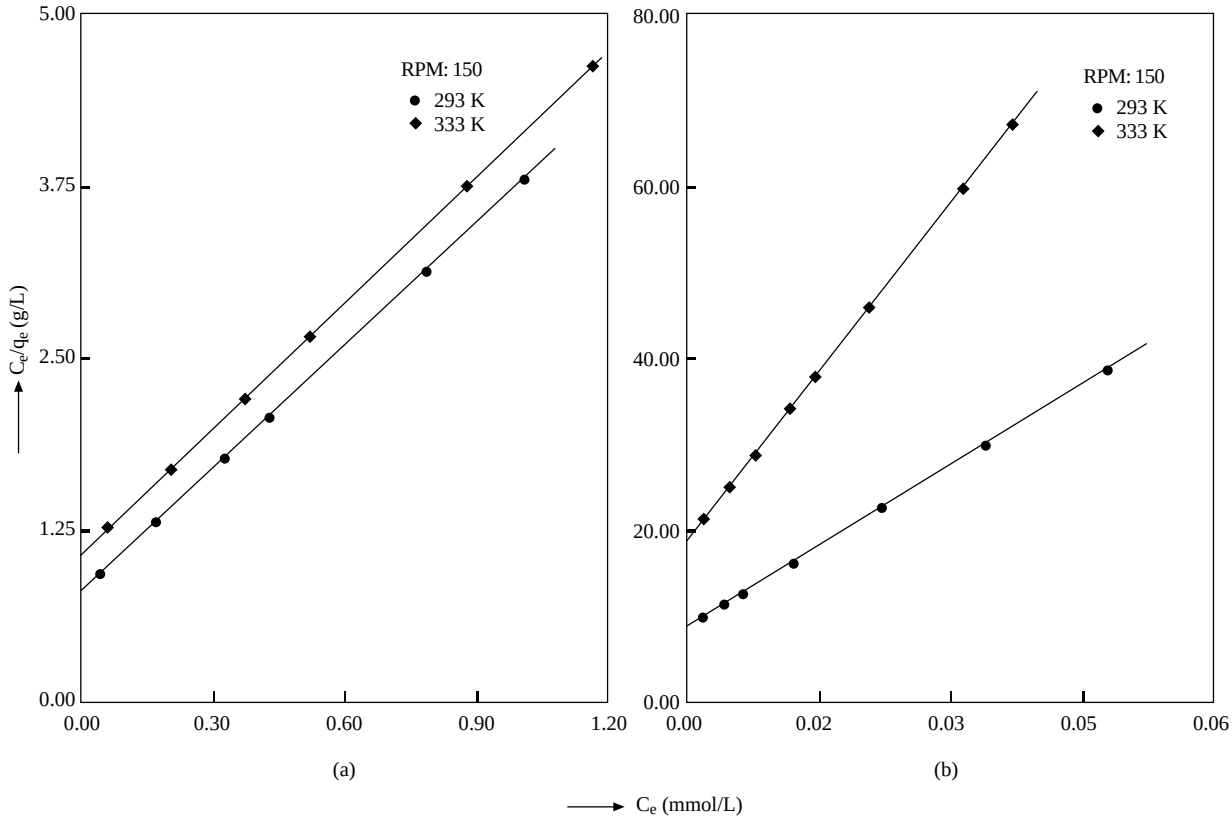

Figure 7. Langmuir linear isotherm plots related to the adsorptions of some dyestuffs by chitosan from aqueous solution: a) O-II, b) CV.

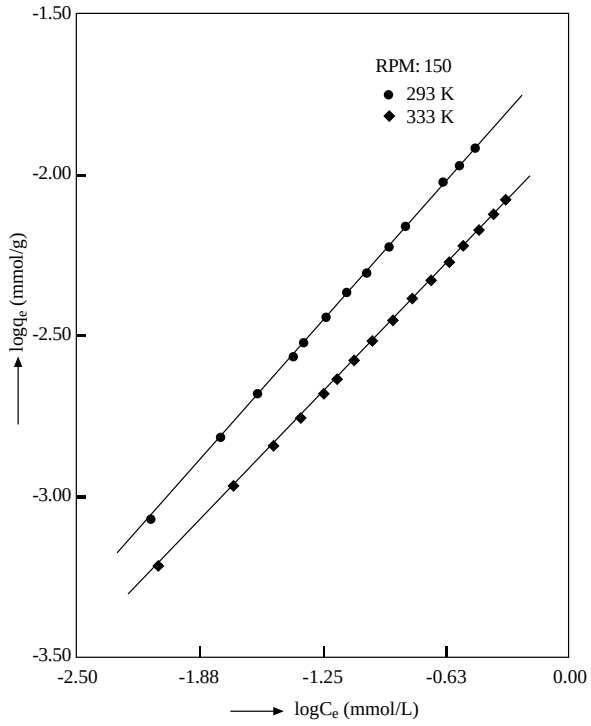

Figure 8. Freundlich linear isotherm plots related to the adsorption of p-nitrophenol by chitosan from aqueous solution.

The BET surface area of chitosan (Sigma C 3646) was measured as 0.65 m^2/g with a Micromeritics Flow Sorb II 2300 (Shimadzu Corporation, Japan). Its density was given as 0.15-0.30 g/mL by the manufacturer. As the pore volume in chitosan was insufficient for precise measurement by Micromeritics Autopore II 9220 Mercury Porosimeter apparatus, the porosity and pore size distribution of the chitosan could not be determined.

Conclusion

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

1. The adsorptions of O-II, CV and PNP by chitosan from aqueous solution must be studied at 20 °C.
2. The adsorption of RB5 by chitosan from aqueous solution must be studied at 60 °C.

Thus, it is clear that chitosan can be used together with other adsorbents in studies of dyestuff adsorption related to the environment, because chitosan is a good adsorbent in comparison with most adsorbents in the adsorption of heavy metals and acidic dyestuffs from aqueous solution in particular[14]. In addition, chitosan is cheaper than most adsorbents and is found abundantly in nature.

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