

Sorption Kinetics for the Removal of Dyes from Effluents onto Chitosan

Y. C. Wong,¹ Y. S. Szeto,¹ W. H. Cheung,² G. McKay²

¹*Institute of Textiles and Clothing, Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong*

²*Department of Chemical Engineering, Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong*

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ABSTRACT: The ability of chitosan, a biosorbent obtained by the processing of waste seafood shells, to remove five acid dyes from effluents has been studied. Chitosan is a deacetylated bio-polymer of chitin. The effect of varying initial dye concentration on the rate of adsorption has been investigated. The rate data have been analyzed using three kinetic models, namely, a pseudosecond order, the Ritchie modified second order, and the Elovich models. The sorption kinetics of Acid Green 25, Acid Orange 10, Acid Orange 12, Acid Red 18, and Acid Red 73 onto chitosan can be best correlated by the Elovich equation. The kinetic model was determined in accordance

with the agreement between the rate equations and the differentiation of kinetic equations. The values of rate constants for the three models are in the range of 0.003–2.230, 0.004–0.237, and 0.0173–405 for the pseudosecond order, the Ritchie modified second order and the Elovich models, respectively. The sensitivity analysis, by plotting the reciprocal of the rate, $Z_L = (d_q/d_t)^{-1}$ against time, is used to identify the true kinetic model. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 2232–2242, 2008

Key words: adsorption; chitosan; dyes; Elovich model; kinetic modeling

INTRODUCTION

In the textile sector, an estimated 10–20% of dyes (active substance) used is lost in residual liquors through exhaustion and washing operations. For pigments, the rate of loss is about 1–2%, and 10% for paper and leather dyes. All of these, make up to a total of about 30% out of 1.0 billion kg dye consumption as reported in 1994.^{1,2} However, available effluent treatment processes for dye containing effluents are currently only capable of removing about half the dyes lost in residual liquors to the environment. Therefore, about 40,000 tons finds its way into the environment, primarily dissolved, or suspended in water.³

Liquid phase adsorption has been shown to be an effective method for the removal of suspended solids, odors, organic matters, metal ions, and dyestuffs by the application of activated carbon,^{4–6} peat,⁷ chitosan,^{8,9} bentonite clay, rice husk, teakwood bark, cotton waste, hair,^{10,11} and maize cob¹² as adsorbents. There may be several mechanisms by which

dyestuffs can be removed from a solution and attach to a sorbent particle surface. The mechanism may be due to ion exchange, physical sorption, chemisorption, chemical reaction, lone pair electron sharing or donating, plus a number of other mechanistic processes. The present research investigates the application of chitosan for the removal of acid dyes from effluents.

Chitosan (Fig. 1) is a partially deacetylated polymer of acetylglucosamine (2-acetamido-2-deoxy-D-glucose-(*N*-acetylglucan)), and it is usually prepared by deacetylation of chitin (2-acetamido-2-deoxy-D-glucose-(*N*-acetylglucosamine)). Chitin has been found in a wide range of natural sources, such as crustaceans, fungi, insects, annelids, mollusks, coelenterata, etc.¹³ However, chitosan is only commercially manufactured from crustaceans (crab, krill, and crayfish) primarily because a large amount of the crustacean's exoskeleton is available as a waste by-product of food processing. It is more chemically versatile than cellulose and chitin due to the presence of free amino groups. The amino group in chitosan has a pKa value of 6.5, hence, chitosan is positively charged and readily binds to negative charged surfaces. In addition, it is widely used in different industries due to its useful features, such as its hydrophilicity, biocompatibility, biodegradability, antibacterial properties and high affinity to dyes and some metal ions.

Michelsen et al.¹⁴ showed that for the removal of Navy 106 from stack wash water discharge was due

Correspondence to: McKay (kemckayg@ust.hk).

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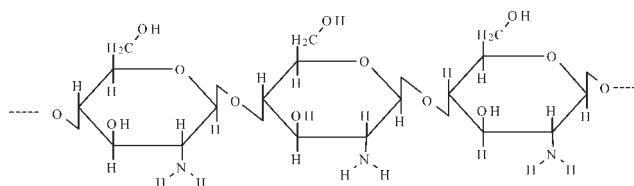


Figure 1 Chemical structure of chitosan.

to the influence of the intraparticle diffusion rate constant. Stefancich et al.¹⁵ reported that no interaction was observed between cationic dyes (Neocuproin hydrochloride, Ethidium bromide, Ruthenium Red, 1-(2-pyridilazo)-2-naphthol), and chitosan in the pH range of 5–6. Smith et al.¹⁶ and Shimizu et al.¹⁷ showed that sorption of anionic dyes onto chitosan was related to the protonation of the chitosan's free amino groups at low pH. According to Knorr¹⁸ and Kumar et al.,¹⁹ the dye binding capacity of chitin was stable within a pH range of 2.0–7.0.

Initial dye concentrations ranging from 0.2 to 1.6 mg/g have been shown to significantly affect the dye-binding capacity of chitin and chitosan performed by Knorr¹⁸ and Kumar et al.¹⁹ The treatment performance showed that the dye-binding capacity of chitosan was 25–30% greater than chitin at the same initial dye concentration level. Besides, they also found that an increase in dosage of chitin or chitosan, i.e., four times, to the system would result in a decrease in the dye-binding capacity of about 50%. The dye-binding capacity of chitin and chitosan was being enhanced about 25 and nine times, respectively, if the initial dye concentration increases from 0.2 mg/g of chitin to 1.6 mg/g of chitin. According to McKay et al.,²⁰ the film mass transfer coefficients appeared to be independent of initial dye concentration for the adsorption of Mordant Yellow 5 on chitin because there was no apparent difference in the initial gradients. However, the rate of adsorption at the lower initial dye concentration was about 20–50% higher than the rate at the high initial dye concentration. The adsorption of Acid Orange II and Brilliant Yellow on chitosan fiber using a column study showed that the amount of the dye adsorbed increased with increase in initial dye concentration due to the increase of the intrafiber effective diffusivity with concentration according to Yoshida and coworkers.^{21–23} Safarik²⁴ showed that the adsorption of organic polycyclic molecules (Acridine Orange, Congo Red, Safranin O, Neutral Red, and Crystal Violet) was a chemical, equilibrated and saturatable mechanism, and therefore, adsorption increased with the initial dye concentration, as long as binding sites were not saturated.

In the present research, the ability of chitosan to adsorb five acid dyes, namely, Acid Green 25 (AG25), Acid Orange 10 (AO10), Acid Orange 12

(AO12), Acid Red 18 (AR18), and Acid Red 73 (AR73) from aqueous effluents has been investigated. These dyes are widely used in China. Equilibrium studies have been carried out previously²⁵ to determine the adsorption capacities. In this study, an analysis of these kinetic models has been performed; pseudosecond order, modified Ritchie second order and Elovich model to determine which kinetics best describe the experimental results.

MATERIALS AND METHODS

Materials

The adsorbent used in this research is a powdered form of chitin purchased from Sigma Chemical Company. All raw chitin was dried at 75°C in an oven for 6 h and then was sieved into discrete particle size range from 355 to 500 μm. The sieved chitin was deacetylated to chitosan by using 48% sodium hydroxide solution (w/w) at 100°C under nitrogen atmosphere for 1-h periods. Then, the products were washed with deionized water completely, dried at 70°C in an oven overnight and sieved again into several particle size ranges from 125 to 250, 250 to 355, and 355 to 500 μm. The fractions were further dried in a vacuum oven for 1 day and stored in a desiccator. The degree of deacetylation of this chitosan was found to be 53% by ¹H-NMR.

Five different commercially available textile dyestuffs were used in the study including four azo dyes (AO10, AO12, AR18, and AR73) and one anthraquinone dye (AG25). All dyestuffs were purchased from Aldrich Chemical Co. and used without any further purification process. The characteristics and chemical structures of the selected dyestuffs are shown in Table I and Figure 2.

Kinetic experiments on various dyes

The effect of initial dye concentration on the adsorption rate was studied by contacting a fixed mass of chitosan (1.700 g) at a fixed particle size (355–500 μm) with fixed temperature (room temperature, 25°C) and pH (4.00) using a range of initial concentrations of dye solution (from a minimum of 0.25 mM up to a maximum of 2.125 mM, depending on the dye being studied). At time = 0 and at selected time intervals (up to a maximum of 6 h), adequate volume of samples were extracted using a Hamilton 2.50 mL syringe. The sample concentration was determined by UV-Vis spectrophotometer.

The concentration of dye adsorbed at time t , q_t (mmol/g), was calculated as follows:

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (1)$$

TABLE I
The Physical and Chemical Properties of Selected Dyestuffs

Generic Name	Commercial Name	Purity (%)	Chromophore	F.W.	λ_{\max} (nm)
C.I. Acid Green 25 (AG25)	Acid Green 25	75	Anthraquinone	622.5	642
C.I. Acid Orange 10 (AO10)	Orange G	80	Monoazo	452.4	475
C.I. Acid Orange 12 (AO12)	Crocein Orange G	70	Monoazo	350.3	482
C.I. Acid Red 18 (AR18)	New Coccine	75	Monoazo	604.5	506
C.I. Acid Red 73 (AR73)	Brilliant Crocein MOO	70	Diazo	566.5	510

Where C_0 and C_t are the initial dye concentration and concentration at time t (mmol/L), respectively, V is the volume of the sample (L), and m is the mass of sorbent (g), and at equilibrium, $q_t = q_e$.

THEORY

Kinetic modeling

The use of kinetic equations in acid dye sorption has been studied for many years. The mechanism of acid dye sorption onto various sorbents has been subjected to extensive research, debate and controversy for decades. Numerous researches are based on a reaction kinetic sorption process in which reaction rate constants are determined as key parameters describing the process. In the present work, three kinetic models will be tested to determine the reaction order of the sorption process of acid dyes onto chitosan; the models are:

- i. Elovich Equation,
- ii. Modified Ritchie Second Order Equation,
- iii. Pseudo-Second Order Equation.

The Elovich equation

The Elovich equation has general application to chemisorption kinetics. The equation has been proved satisfactorily applicable to most chemisorption data and will cover a large range of slow adsorption. A detailed report to interpret the use of this equation in the kinetics of chemisorption of gases on solids was demonstrated by Low.²⁶ The Elovich equation is formulated as:

$$\frac{dq_t}{dt} = a \exp(-bq_t) \quad (2)$$

where q_t is solid phase sorbate concentration, (mmol/g), at time t , a , and b are kinetic rate constants. Integration of eq. (2) with boundary conditions $q = 0$ at $t = 0$ and $q = q_t$ at $t = t$, gives

$$q_t = \frac{1}{b} \ln(1 + abt) \quad (3)$$

Then, rearrange eq. (3) to form a linear transformation of the Elovich kinetic equation:

$$q_t = \frac{1}{b} \ln ab + \frac{1}{b} \ln \left(t + \frac{1}{ab} \right) \quad (4)$$

Thus, a linear plot of eq. (4) q_t versus $\ln(t + \frac{1}{ab})$, yields both constants a and b from the intercept and the slope. Determination of constants a and b is based on the trial and error optimization method.

The modified Ritchie second order model

Ritchie²⁷ found that the Elovich plot gives curved lines or sharp changes in the gradient in some cases. The sharp changes in gradient are sometimes interpreted as indicating a change in adsorption mechanism. As a result, an alternative method for the kinetic study was proposed by assuming that the rate

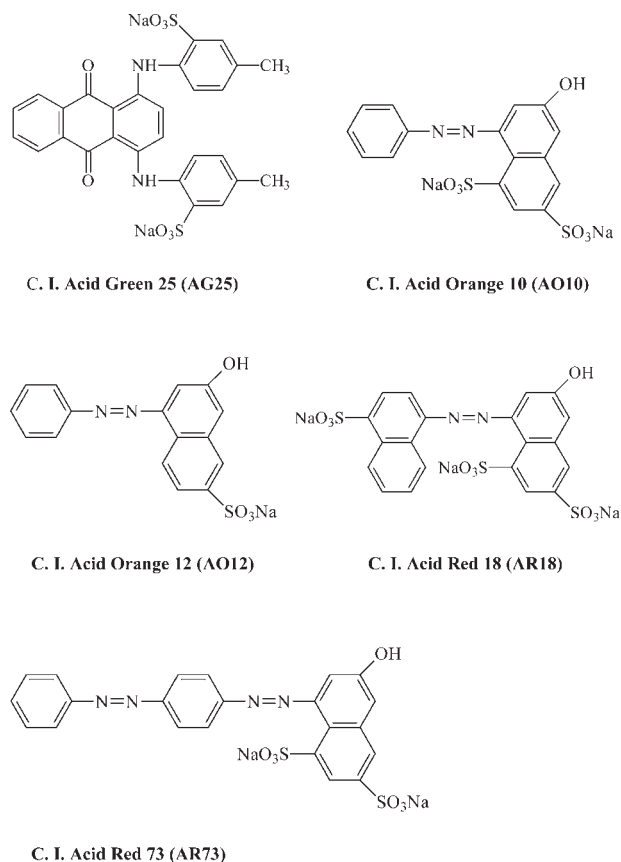


Figure 2 The molecular structures of the five selected dyestuffs.

of adsorption depends solely on the fraction of sites, which are not occupied at time t :

$$\frac{d\theta}{dt} = k'_2(1-\theta)^n \quad (5)$$

where θ is surface coverage of sorbent, q_t/q_e (dimensionless), k'_2 is the kinetic rate constant (min^{-1}).

Integration of eq. (5) yields,

For $n \neq 1$

$$\frac{1}{(1-\theta)^{n-1}} = (n-1)k'_2t + 1 \quad (6)$$

For $n = 1$,

$$\theta = 1 - e^{-k'_2t} \quad (7)$$

It is assumed that no site is occupied at $t = 0$, and the amount of adsorption, q_t , occurs at time t .

Then, eq. (6) becomes:

$$\frac{q_e^{n-1}}{(q_e - q_t)^{n-1}} = (n-1)k'_2t + 1 \quad (8)$$

Similarly, eq. (7) becomes:

$$q_t = q_e(1 - e^{-k'_2t}) \quad (9)$$

For $n = 2$, eq. (9) becomes:

$$\frac{q_e}{(q_e - q_t)} = k'_2t + 1 \quad (10)$$

Rearranging eq. (10) yields the linear forms of Ritchie equation (11 or 12)

$$\frac{1}{q_t} = \frac{1}{k'_2q_e t} + \frac{1}{q_e} \quad (11)$$

or

$$\frac{t}{q_t} = \frac{1}{k'_2q_e} + \frac{t}{q_e} \quad (12)$$

A plot of $\frac{t}{q_t}$ versus t yields the constants q_e and k'_2 from the slope and intercept. If the results were plotted with eq. (10), a reasonable straight line is obtained. The intercept, however, at $t = 0$ may not equal to 1.0, which indicates that some adsorption was shown at time $t = 0$. A possible solution to the situation can be attributed to the redefinition of the boundary conditions of eq. (5), in which at $t = 0$, and at $q = q_0 \neq 0$. Then, it is assumed that the pseudo-second order reaction occurs very rapidly at $t \approx 0$:

$$\int_{\theta_0}^{\theta} \frac{d\theta}{(1-\theta)^n} = k'_2 \int_0^t dt \quad (13)$$

where $\theta_0 = q_0/q_e$, at $t = 0$,

$$\frac{1}{(1-\theta)^{n-1}} \Big|_{\theta_0}^{\theta} = (n-1)k'_2t \quad (14)$$

$$\frac{1}{(1-\theta)^{n-1}} = (n-1)k'_2t + \frac{1}{(1-\theta_0)^{n-1}} \quad (15)$$

For $n = 2$ and $\theta = q_t/q_e$, eq. (15) becomes:

$$\frac{q_e}{(q_e - q_t)} = k'_2t + \frac{1}{1-\theta_0} \quad (16)$$

Assume $\beta = \frac{1}{1-\theta_0}$,

$$\frac{q_e}{(q_e - q_t)} = k'_2t + \beta \quad (17)$$

Rearranging eq. (17) gives the nonlinear form:

$$q_t = q_e \left[1 - \frac{1}{\beta + k'_2t} \right] \quad (18)$$

The linear form becomes:

$$\frac{1}{q_t} = \frac{1}{q_e[(\beta - 1) + k'_2t]} + \frac{1}{q_e} \quad (19)$$

When $\theta_0 = 0$, i.e., no surface coverage at $t = 0$, then, $\beta = 1$, eq. (18) becomes eq. (11). Since, eq. (18) contains three unknown parameters, which cannot be solved by the linear plot of the equation. Therefore, the trial and error method is used to minimize the sum of error squares.

Pseudo-second order equation

If the rate of sorption is a second order mechanism,²⁸ the pseudosecond order chemisorption kinetic rate equation may be expressed as:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (20)$$

where q_e and q_t are the sorption capacity (mmol/g) at equilibrium and at time t , respectively, and k_2 is the rate constant of pseudo-second order sorption, (g/mmol/min). For the boundary conditions $t = 0$ to $t = t$ and $q = q_i$; the integrated form of eq. (20) becomes:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2t \quad (21)$$

which is the integrated rate law for a pseudo-second order reaction. Equation (21) can be rearranged to obtain:

$$q_t = \frac{t}{\frac{1}{k_2q_e} + \frac{t}{q_e}} \quad (22)$$

which has a linear form:

$$\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (23)$$

Equation (23) does not have the problem of assigning an effective q_e . If pseudo second-order kinetics is applicable, the plot of t/q_t against t of eq. (23) should give a linear relationship, from which q_e and k_2 can be determined from the intercept and slope respectively, of the plot and there is no need to know any parameter beforehand.

Determination of the kinetic model

Three kinetic models have been used to determine the best fitting equation, which correlates the theoretically predicted data with the experimental data. The best fitting kinetic model will be determined by choosing the equation resulting in the lowest sum of error squares (SSE). If the differences between the square of correlation coefficient among the three kinetic models are too close to determine the true kinetic reaction: Ungarish and Aharoni²⁹ reported that the applicability of the Elovichian kinetics could be compared directly by plotting the reciprocal of the rate $Z = (dq/dt)^{-1}$ against t . Therefore, a sensitivity analysis-plotting $Z = (dq/dt)^{-1}$ against t will be used to identify a true kinetic model.

For the Elovich Equation, by rearranging eq. (2), then:

$$Z_p = \frac{1}{a \exp(-bq_t)} \quad (24)$$

Differentiating eq. (4) gives:

$$Z_L = b \left(t + \frac{1}{ab} \right) \quad (25)$$

For the Modified Ritchie Second Order Equation

Equation (5) is rearranged in terms of q_t and q_e ,

$$\frac{dq_t}{dt} = \left(\frac{k'_2}{q_e} \right) (q_e - q_t)^2 \quad (26)$$

Rearrange:

$$Z_p = \left(\frac{q_e}{k'_2 (q_e - q_t)^2} \right) \quad (27)$$

Differentiating eq. (18) gives eq. (28)

$$Z_L = \frac{(\beta + k'_2 t)^2}{q_e k'_2} \quad (28)$$

For the pseudo-second order equation, rearranging eq. (20), gives,

$$Z_p = \frac{1}{k_2 (q_e - q_t)} \quad (29)$$

By differentiating eq. (21), we obtain:

$$Z_L = \frac{(1 + k_2 q_e t)^2}{q_e^2 k_2} \quad (30)$$

Equations (25), (28), and (30) are expressed in terms of parameters and q_t . Therefore, the Z_L versus t plot can be obtained and used for a sensitivity analysis. Identical results of the differential form of the kinetic model, in terms of parameters and t , will be obtained for the fitted kinetic model.

RESULTS AND DISCUSSION

Batch kinetic systems

Sorption systems have been investigated to assess the applicability of chitosan as a suitable sorbent for the removal of acid dyes in dye wastewater. An equilibrium analysis is one of the most important fundamental pieces of information required for evaluating the affinity or capacity of a sorbent. However, an ideal sorbent for wastewater pollution control must not only have a large sorbate capacity, but also the sorption rate must be fast. Therefore, the sorption rate is the other important factor for the selection of the sorbent and sorption kinetics which must be taken into account.

In this research, three kinetic models have been applied to the sorption of acid dyes on chitosan. The kinetic models are the pseudo-second order equation, the modified Ritchie second order equation and the Elovich equation. The parameters of the modified Ritchie second order equation were determined by the Solver "add-in" for Microsoft Excel to minimize the sum of error squares. However, the parameters of the pseudo-second order equation and the Elovich equation were determined by the linear regression analysis of those equations to obtain the highest value of the square of correlation coefficient (R^2), such that:

$$R^2 = 1 - \frac{SSE}{SST} \quad (31)$$

Where, $SSE = \sum (q_{\text{exp}} - q_{\text{cal}})^2 =$ Sum of error square

$SST = \sum (q_{\text{exp}})^2 - \frac{(\sum q_{\text{exp}})^2}{n} =$ Sum of total error square

Furthermore, pseudo kinetic models are based on the solid phase adsorbent loading, q_e and q_t , and these are dependent on the initial dye concentration, C_0 . Consequently, the pseudo rate constants are dependent on C_0 as well. Each kinetic model is now analyzed.

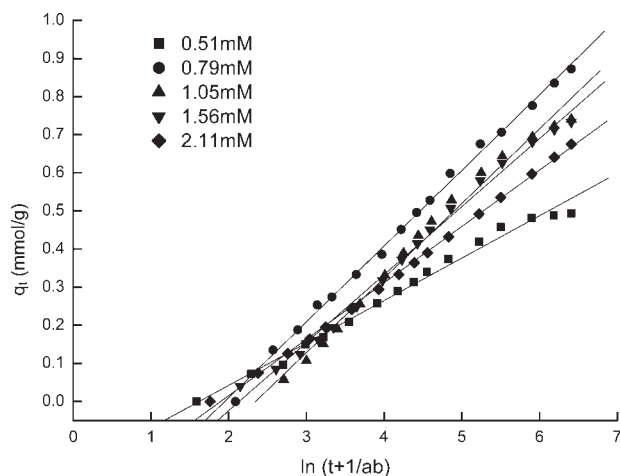


Figure 3 Linear Plot for the Elovich equation for the sorption of acid green 25 onto chitosan with different initial concentrations at room temperature, mass = 1.7000 g, degree of deacetylation (DD = 53%), pH = 4.00, dp = 355–500 μm .

The Elovich equation

The linear form of Elovich equation is given by eq. (4). Figure 3 shows the linear plots of Elovich equation for the sorption of AG25 onto chitosan with the change of initial concentrations. Similar results were obtained for other dyes. The values of a and b were estimated by an iterative procedure from a linear plot of q_t against $\ln(t + \frac{1}{ab})$. The parameters a and b are calculated from the intercept and the slopes of the lines. The Elovich constants, a , b , and $\frac{1}{ab}$, the SSE and the square of correlation coefficient, R^2 , were reported in Table II. The squares of correlation coefficients are very high in these five systems. The experimental data points could also be plotted as q_t versus t graphs such as Figure 4, the curves for different concentrations of Acid Orange 12 were completely separated and similar results, which were obtained for other acid dyes were not shown. The values in Table II demonstrate that increase the concentration of acid dyes will lead to a decrease in constant b . In this study, the Elovich constants a and b were plotted against initial concentration, C_0 , and the best correlating equation for the data shown in Figure 5 is the power equation:

$$a = A_E [C_0]^{B_E} \quad (32)$$

$$b = A_1 [C_0]^{B_1} \quad (33)$$

The values of A_E , B_E , A_1 , B_1 and the square of correlation coefficient, R^2 , are shown in Table III. As can be seen from Table IV, all the dyes except AO10 correlate well with eq. (32) and (33).

The pseudo-second order equation

The experimental results were substituted into the linear form of the pseudo-second order equation to evaluate the fitness of the model on the sorption of acid dyes to chitosan for different initial dye concentrations. The linear plot of the pseudo-second order equation for AO10 is shown in Figure 6. As can be seen that the distance between each line is clearly separated and the experimental data were almost perfectly fitted with an extremely high square of correlation coefficient. Similar results were observed for other dyes. The parameters of the pseudo-second order equation for the effect of different initial concentration and the effect of change of sorbent mass are listed in Table IV.

Equation (24) is the linear form of the equation and the equilibrium capacity can be determined from the slope of the linear plot and the rate constant k_2 can be calculated from the intercepting point of the line. Figure 7 shows the effect of initial concentration of Acid Red 73 on the rate constant, k_2 ,

TABLE II
Parameters of the Elovich Equation for the Sorption of AG25, AO10, AO12, AR18, and AR73 onto Chitosan with Different Initial Concentration at Room Temperature

Concentration (mM)	a	b	$1/ab$	SSE	R^2
AG25					
0.51	0.023	9.069	4.906	0.004	0.9998
0.79	0.019	6.400	8.071	0.002	0.9999
1.05	0.0173	5.765	10.007	0.004	0.9999
1.56	0.0209	5.563	8.593	0.001	1.0000
2.11	0.0324	5.290	5.837	0.002	1.0000
AO10					
0.57	4.072	49.139	0.005	0.002	0.9997
0.86	2.931	26.988	0.013	0.005	0.9997
1.14	405.065	31.523	8×10^{-5}	0.007	0.9998
1.61	128.636	20.000	0.0004	0.018	0.9997
2.32	9.078	10.756	0.010	0.032	0.9997
AO12					
0.36	1.572	29.502	0.022	0.015	0.9992
0.77	0.128	8.561	0.910	0.063	0.9993
1.05	0.079	5.778	2.193	0.091	0.9997
1.55	0.032	3.135	10.002	0.053	0.9999
2.05	0.021	2.270	20.613	0.020	1.0000
AR18					
0.26	3.232	68.399	0.005	0.002	0.9996
0.51	0.292	25.652	0.134	0.013	0.9992
1.01	0.049	11.360	1.783	0.018	0.9992
1.55	0.031	8.710	3.662	0.006	0.9999
2.06	0.031	7.529	4.274	0.003	1.0000
AR73					
0.51	0.087	10.828	1.057	0.014	0.9997
0.76	0.042	6.058	3.914	0.008	0.9999
1.03	0.028	4.501	8.025	0.002	1.0000
1.51	0.023	3.771	11.658	0.002	1.0000
2.04	0.020	2.983	17.093	0.011	1.0000

Mass = 1.7000 g, degree of deacetylation (DD = 53%), pH = 4.00, dp = 355–500 μm .

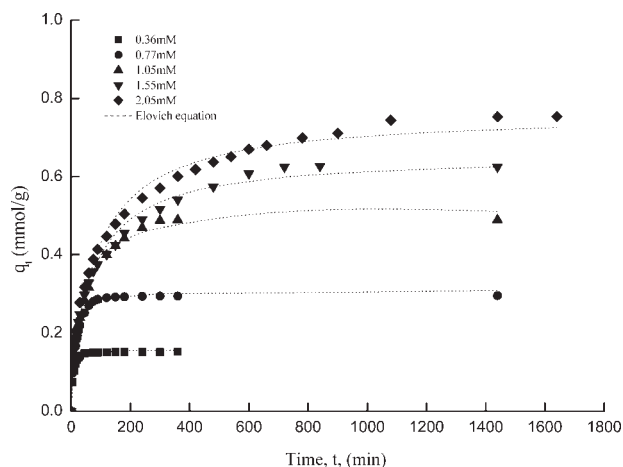


Figure 4 The Elovich Equation for the Sorption of Acid Orange 12 onto Chitosan with Different Initial Concentrations at Room Temperature, Mass = 1.7000 g, degree of deacetylation (DD = 53%), pH = 4.00, dp = 355–500 μm .

and the equilibrium capacity, q_e . Similar results obtained for AG 25, AO10, AO12, and AR18 are not presented. The parameters were best fitted to the following equations and are listed in Table V.

$$k_2 = A_3[C_0]^{B_3} \quad (34)$$

$$q_e = A_4 \ln[C_0] + B_4 \quad (35)$$

The modified Ritchie second order equation

The results for the pseudo-second order equation show that the acid dyes were adsorbed faster during the first hour of the experimental studies than the removal rate predicted. Therefore, the modified Ritchie second order equation was obtained by incorporating the boundary condition of Ritchie reaction ki-

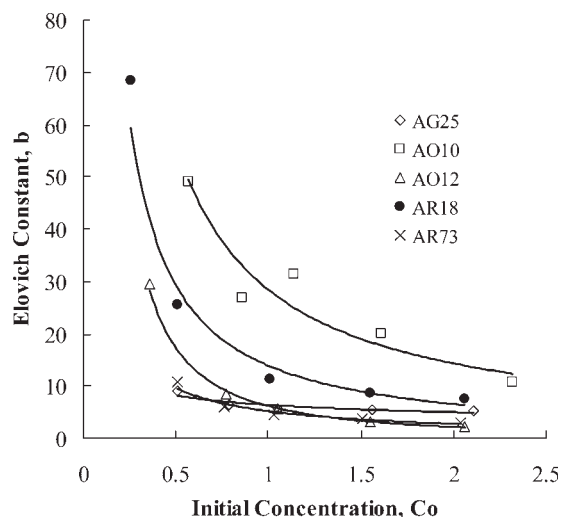


Figure 5 The relationship of the Elovich Rate Constant, b against Initial Concentration, C_0 , for AG25, AO10, AO12, AR18, and AR73.

TABLE III
The Parameters and the Square of Correlation Coefficient for the Elovich Rate Constant Expression for Various Initial Dye Concentrations

Dye	Elovich Constants					
	a			b		
	A_E	B_E	R^2	A_1	B_1	R^2
AG25	5.93×10^{-5}	8.500	0.876	6.439	-0.352	0.827
AO10	2.30×10^{-4}	12.733	0.106	28.428	-0.985	0.899
AO12	6.43×10^{-2}	-3.129	0.999	6.221	-1.480	0.997
AR18	2.75×10^{-2}	-3.539	0.999	13.929	-1.075	0.971
AR73	3.33×10^{-2}	-1.372	0.958	5.250	-0.887	0.951

netic model, in which the boundary condition was modified such that, at $t = 0$, $q = q_0$. As a result, a better fit to the experimental data points would be obtained. The modified Ritchie second order equation contains three parameters and they were determined by trial and error. Table VI lists the equation parameters of the modified Ritchie second order, i.e.,

TABLE IV
Parameters of Pseudo-second Order Equation for the sorption of AG25, AO10, AO12, AR18, and AR73 onto chitosan with the Effect of different Initial Concentration at Room Temperature

Concentration (mM)	k_2	q_e	SSE	R^2
AG25				
0.51	0.042	0.533	0.002	0.9999
0.79	0.020	0.732	0.017	0.9994
1.05	0.018	0.780	0.024	0.9992
1.56	0.018	0.823	0.013	0.9996
2.11	0.020	0.923	0.020	0.9996
AO10				
0.57	1.600	0.210	0.001	0.9999
0.86	0.739	0.351	0.001	1.0000
1.14	0.671	0.477	0.003	0.9999
1.61	0.843	0.653	0.026	0.9996
2.32	0.163	0.960	0.008	0.9999
AO12				
0.36	0.864	0.316	0.010	0.9995
0.77	0.069	0.737	0.012	1.0000
1.05	0.024	1.042	0.024	0.9999
1.55	0.006	1.598	0.045	0.9999
2.05	0.003	2.013	0.156	0.9997
AR18				
0.26	2.230	0.153	0.001	1.0000
0.51	0.480	0.297	0.006	1.0000
1.01	0.079	0.500	0.007	1.0000
1.55	0.027	0.652	0.020	1.0000
2.06	0.015	0.780	0.027	1.0000
AR73				
0.51	0.126	0.511	0.003	1.0000
0.76	0.036	0.786	0.006	1.0000
1.03	0.015	1.032	0.026	1.0000
1.51	0.007	1.290	0.045	1.0000
2.04	0.004	1.585	0.113	1.0000

Mass = 1.7000 g, degree of deacetylation (DD = 53%), pH = 4.00, dp = 355–500 μm .

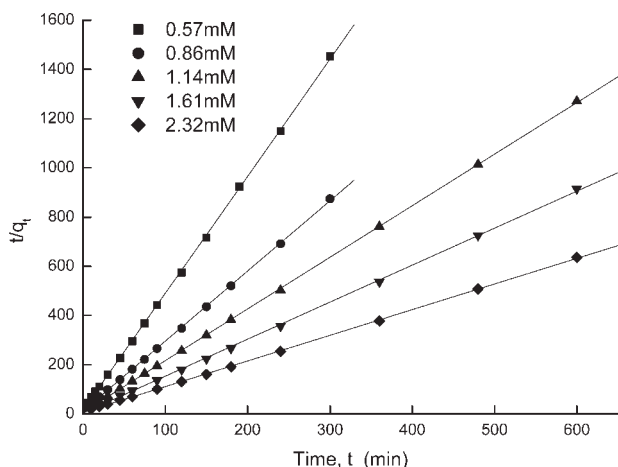


Figure 6 Linear Plot of The Pseudo-second Equation of the Sorption of Acid Orange 10 onto Chitosan with Different Initial Concentrations at Room Temperature, Mass = 1.7000 g, degree of deacetylation (DD = 53%), pH = 4.00, dp = 355–500 μm.

rate constant, k'_2 and β , equilibrium capacity, q_e , SSE and the square of correlation coefficient, R^2 . The plot of modified Ritchie second order equation for AR18 is shown in Figure 8.

By comparing the SSE and the square of correlation coefficient of the pseudo-second order equation, the modified Ritchie second order equation provides a closer fit to the experimental data of both the effect of initial concentration and the effect of sorbent mass. However, the values of rate constants and equilibrium capacities of both equations are very close to each other for some dyes and a better correlation of rate constants and equilibrium with the effect of initial concentration and sorbent mass were obtained for the pseudo-second order model. The rate constants can be expressed in term of initial concentration:

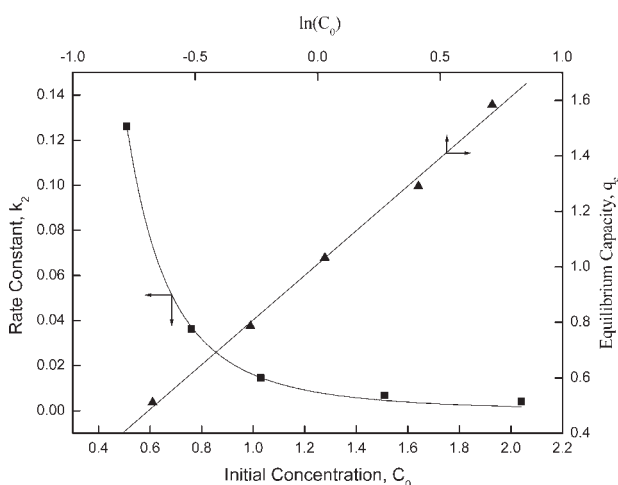


Figure 7 The relationship of Rate Constants and Equilibrium Capacities against Initial Concentration of Acid Red 73.

TABLE V
The Parameters and the Square of Correlation Coefficient for the Pseudo-Second Order Rate Constant Expression for Various Initial Dye Concentrations

Dye	k_2			q_e		
	A_3	B_3	R^2	A_4	B_4	R^2
AG25	0.0229	-0.4700	0.5422	0.7289	0.3495	0.8946
AO10	0.7788	-1.3125	0.7258	0.3986	1.0666	0.9965
AO12	0.0293	-3.2781	0.9984	0.9666	1.0765	0.9982
AR18	0.0847	-2.4511	0.9989	0.4681	0.7792	0.9909
AR73	0.02	-2.4584	0.9808	0.936	0.7997	0.9822

$$k'_2 = A_5[C_0]^{B_5} \tag{36}$$

The parameters for eq. (36) are listed in Table VII.

Determination of sorption kinetics

Figure 9 shows that the pseudosecond order, the modified Ritchie second order and Elovich equation can be used effectively to describe the sorption of

TABLE VI
Parameters of the Ritchie Modified Second Order Equation for the sorption of AG25, AO10, AO12, AR18, and AR73 onto chitosan with the Effect of Initial Concentration at Room Temperature

Concentration (mM)	k'_2	q_e	β	SSE	R^2
AG25					
0.51	0.020	0.540	1.032	0.001	0.9999
0.79	0.012	0.744	1.070	0.010	0.9996
1.05	0.009	0.830	1.086	0.010	0.9997
1.56	0.013	0.829	1.051	0.008	0.9998
2.11	0.015	0.934	1.073	0.010	0.9998
AO10					
0.57	0.237	0.214	0.997	9×10^{-5}	1.0000
0.86	0.208	0.356	0.999	9×10^{-5}	1.0000
1.14	0.201	0.484	0.999	0.0002	1.0000
1.61	0.172	0.687	0.999	0.002	1.0000
2.32	0.120	0.973	1.000	0.001	1.0000
AO12					
0.36	0.132	0.329	0.984	0.001	0.9999
0.77	0.041	0.758	1.005	0.006	0.9999
1.05	0.020	1.070	1.018	0.012	1.0000
1.55	0.008	1.636	1.059	0.023	1.0000
2.05	0.004	2.123	1.090	0.062	1.0000
AR18					
0.26	0.212	0.158	0.990	0.0002	1.0000
0.51	0.084	0.312	0.998	0.001	1.0000
1.01	0.028	0.523	1.050	0.003	1.0000
1.55	0.014	0.654	1.105	0.010	1.0000
2.06	0.012	0.762	1.093	0.014	1.0000
AR73					
0.51	0.055	0.525	1.007	0.002	1.0000
0.76	0.025	0.799	1.042	0.004	1.0000
1.03	0.012	1.051	1.077	0.011	1.0000
1.51	0.007	1.305	1.080	0.024	1.0000
2.04	0.005	1.641	1.095	0.053	1.0000

Mass = 1.7000 g, degree of deacetylation (DD = 53%), pH = 4.00, dp = 355–500 μm.

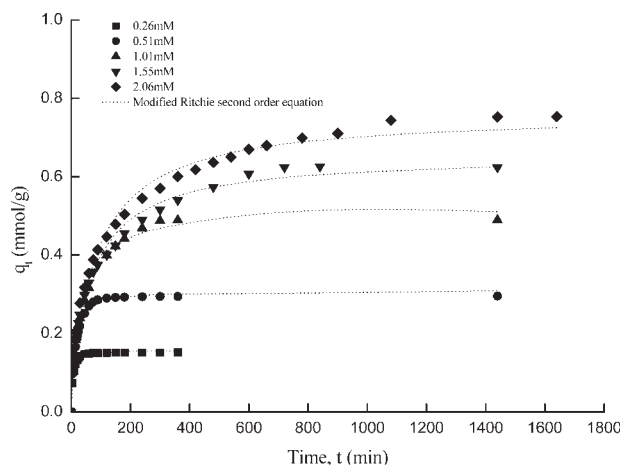


Figure 8 Plot of The Modified Ritchie second order Equation of the Sorption of Acid Red 18 onto Chitosan with Different Initial Concentrations at Room Temperature, Mass = 1.7000 g, degree of deacetylation (DD = 53%), pH = 4.00, dp = 355–500 μm .

Acid Red 73 onto chitosan with various initial concentrations. In this research, similar results were obtained for different acid dyes studied at different initial concentration and the mass of chitosan for each of the experimental runs. Since the sums of error squares and the square of correlation coefficients of the equations are the different methods to evaluate the fitness of model to the experimental data, the direct comparison of different error methods cannot be used in this research. Alternatively, the applicability of kinetic models can be directly comparing by plotting the reciprocal of the rate $Z = (dq/dt)^{-1}$ against t . The equations are expressed in terms of kinetic models' parameters and q_t . Therefore, the Z_L - t plot can be obtained and used for a visual sensitivity analysis. Therefore, by differentiating the kinetic equation, the correlation between Z and t can be fitted into the differential form and the linearity of the Z versus t plots represented the true kinetics of sorption of acid dyes onto chitosan. The reciprocal values of the rates of the different kinetic equations are as follows:

TABLE VII
The Parameters and the Square of Correlation Coefficient for the Modified Ritchie Second Order Rate Constant Expression for Various Initial Dye Concentrations

Dye	k'_2		R^2
	A_5	B_5	
AG25	0.0133	-0.1555	0.0919
AO10	0.1955	-0.4519	0.8875
AO12	0.0199	-1.9879	0.9889
AR18	0.0302	-1.4435	0.9954
AR73	0.0152	-1.7543	0.9847

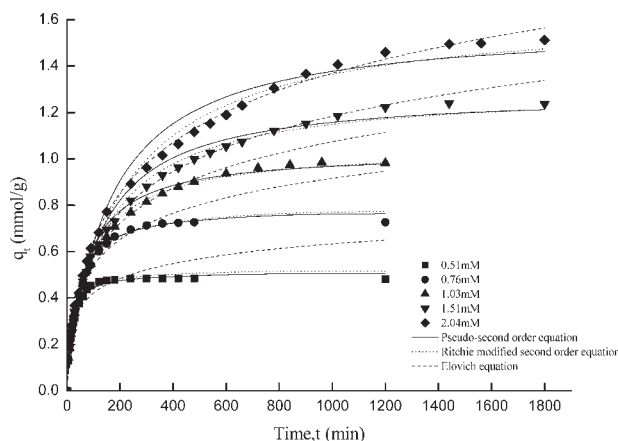


Figure 9 Plots of Different Kinetic Models for the Sorption of Acid Red 73 onto Chitosan at Room Temperature, $C_0 = 2.04 \text{ mM}$, degree of deacetylation = 53%, pH = 4.00, dp = 355–500 μm .

The Elovich kinetic model:

$$Z_L = b(t + t_0) \quad (25)$$

The modified second order kinetic model:

$$Z_L = \frac{(\beta + k'_2 t)^2}{q_e^2 k'_2} \quad (28)$$

The pseudosecond order kinetic model:

$$Z_L = \frac{(1 + k_2 q_e t)^2}{q_e^2 k_2} \quad (30)$$

The plot in Figure 10 shows a perfect fit of the experimental data to the theoretical line of Elovichian kinetics for the effect of changing initial concentrations of AO12. The corresponding the squares of correlation coefficients for each model are presented in Table VIII, the Elovich equation provides the best

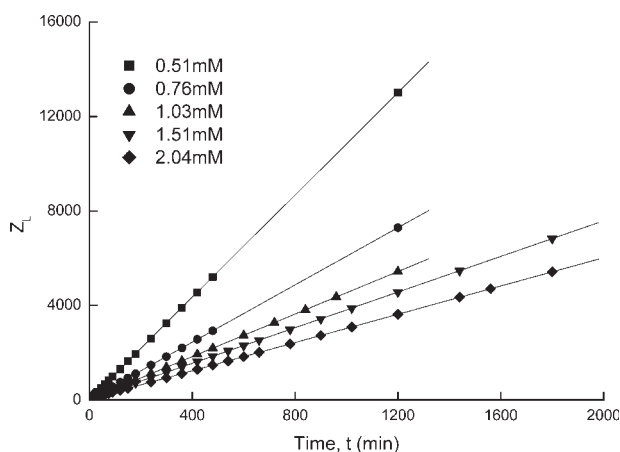


Figure 10 The sensitivity analysis, Z_L - t plot of the Elovich equation for Acid Red 73 for different initial concentration.

TABLE VIII
The Square of Correlation Coefficients of the Sensitivity Analysis Plots, Z_L-t , for Different Kinetic Models for Various Dyes Sorption on Chitosan at 25°C

Concentration (mM)	Correlation	Coefficient,	R^2
	Pseudo-second order	Modified Ritchie second order	
AG25			
0.51	0.9709	0.9721	1.0000
0.79	0.9745	0.9775	1.0000
1.05	0.9752	0.9807	1.0000
1.56	0.9744	0.9766	1.0000
2.11	0.9725	0.9752	1.0000
AO10			
0.57	0.9752	0.9579	1.0000
0.86	0.9563	0.9568	1.0000
1.14	0.9613	0.9618	1.0000
1.61	0.9602	0.9613	1.0000
2.32	0.9614	0.9619	1.0000
A012			
0.36	0.9534	0.9550	1.0000
0.77	0.9680	0.9687	1.0000
1.05	0.9656	0.9668	1.0000
1.55	0.9710	0.9733	1.0000
2.05	0.9750	0.9799	1.0000
AR18			
0.26	0.9588	0.9597	1.0000
0.51	0.9682	0.9628	1.0000
1.01	0.9694	0.9703	1.0000
1.55	0.9443	0.9473	1.0000
2.06	0.9560	0.9569	1.0000
AR73			
0.51	0.9393	0.9399	1.0000
0.76	0.9431	0.9444	1.0000
1.03	0.9609	0.9638	1.0000
1.51	0.9565	0.9595	1.0000
2.04	0.9657	0.9704	1.0000

correlation of the experimental kinetic data. However, the correlation parameter, Z_L , for the other two models, namely, the pseudo-second order and the modified Ritchie second order, showed that the data points deviate from the theoretical line, which proved that these are not fully representative reaction kinetic models for the sorption of acid dyes onto chitosan.

This demonstrates that the acid dye-chitosan sorption systems studied belong to the Elovich kinetic model, based on the assumption that the rate limiting step may be chemical sorption or chemisorption involving valency forces through sharing or exchange of electrons between sorbent and sorbate. In general, Elovich model involves a variation of the energetics of chemisorption with the active sites are heterogeneous and therefore, exhibit different activation energies for chemisorption.³⁰

CONCLUSIONS

Kinetic data have been measured for the sorption process of five acid dyes, namely, Acid Green 25,

Acid Orange 10, Acid Orange 12, Acid Red 18, and Acid Red 73 on to chitosan. The experimental data were substituted to three kinetic models, which were the pseudo-second order, the modified second order and the Elovich equation. The sorption kinetics of all five acid dyes onto chitosan can be best correlated by the Elovich equation. This indicates the sorption process is heterogeneous chemisorption. The kinetic model was determined in accordance with the agreement between the rate equations and the differentiation of kinetic equations. The sensitivity analysis, by plotting the reciprocal of the rate, $Z_L = (d_q/d_t)^{-1}$ against time, can be used to identify a true kinetic model.

NOMENCLATURE

a	mmol/min/g	Elovich rate constant
b	g/mmol	Elovich rate constant
C_0	mmol/L	Initial concentration of solute in aqueous phase
C_t	mmol/L	Concentration of solute at time t , in aqueous phase
k_2	g/mmol/min	Pseudo-second order rate constant
k_2'	/min	Modified Ritchie second order rate constant
m	g	Mass of sorbent
q_e	mmol/g	Equilibrium sorption capacity
q_0	mmol/g	Solid phase initial concentration at equilibrium
q_t	mmol/g	Solid phase concentration at time t
t	min	Time
V	L	Volume of sample
Z	min g/mmol	d_t/d_q , invert of rate equation

Greek Alphabet

β	Dimensionless	Modified Ritchie second order rate constant
θ	Dimensionless	Surface coverage of sorbent
θ_0	Dimensionless	Initial surface coverage of sorbent

References

- Marc, R. C&EN 1996, 73, 10.
- Robinson, T.; McMullan, G.; Marchant, R.; Nigam, P. Bioresour Technol 2001, 77, 247.
- Marsh, H.; Rodriguez-Reinoso, F. Activated Carbon; Elsevier: Oxford, 2006.
- Allen, S.; Brown, P.; McKay, G.; Flynn, O. J Chem Technol Biotechnol 1992, 54, 271.
- Namasivayam, C.; Kavitha, D. Dyes Pigment 2002, 54, 47.
- Malik, P. K. Dyes Pigment 2003, 56, 239.
- McKay, G.; Allen, S. J. Low-Cost Adsorbents in Continuous Processes; Taylor and Francis: UK, 1997.
- Chiou, M. S.; Ho, P. Y.; Li, H. Y. Dyes Pigment 2004, 60, 69.

9. Smith, B.; Koonce, T.; Hudson, S. *Am Dyestuff Reporter* 1993, 82, 18.
10. McKay, G.; Otterburn, M. S.; Aga, J. A. *Water Air Soil Pollut* 1985, 24, 307.
11. McKay, G.; Ramprasad, G.; Mowli, P. P. *Water Air Soil Pollut* 1986, 29, 273.
12. El-Geundi, M. S. *Water Res* 1991, 25, 271.
13. Muzzarelli, R. A. A. *Chitin*; Pergamon Press: Oxford, 1977.
14. Michelsen, D. L.; Fulk, L. L.; Woodby, R. M.; Boardman, G. D. 1993, 518, 119.
15. Stefancich, S.; Delben, F.; Muzzarelli, R. A. A. *Carbohydr Polym* 1994, 24, 17.
16. Smith, B.; Koonce, T.; Hudson, S. *Am Dyestuff Reporter* 1993, 8, 66.
17. Shimizu, Y.; Kono, K.; Kim, I. S.; Takagishi, T. *J Appl Polym Sci* 1995, 55, 255.
18. Knorr, D. *J Food Sci* 1983, 48, 36.
19. Kumar, M. N. V. R.; Sridhari, T. R.; Bhavani, K. D.; Dutta, P. K. *Colourage* 1998, 45, 25.
20. McKay, G.; Blair, H. S.; Gardner, J. R. *J Appl Polym Sci* 1982, 27, 3043.
21. Yoshida, H.; Fukuda, S.; Okamoto, A.; Kataoka, T. *Water Sci Technol* 1991, 23, 1667.
22. Yoshida, H.; Okamoto, A.; Kataoka, T. *Chem Eng Sci* 1993, 48, 2267.
23. Yoshida, H.; Takemori, T. *Water Sci Technol* 1997, 35, 29.
24. Safarik, I. *Water Res* 1995, 29, 101.
25. Wong, Y. C.; Szeto, Y. S.; Cheung, W. H.; McKay, G. *Langmuir* 2003, 19, 7888.
26. Low, M. J. D. *Chem Rev* 1960, 60, 267.
27. Ritchie, A. G. *J Chem Soc-Farad Trans I* 1977, 73, 1650.
28. Ho, Y. S.; McKay, G. *Water Res* 2000, 34, 735.
29. Ungarish, M.; Aharoni, C. *J Chem Soc-Farad Trans I* 1981, 77, 975.
30. Teng, H.; Hsieh, C. T. *Ind Eng Chem Res* 1999, 38, 292.