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KINETIC MODELS FOR THE SORPTION OF DYE FROM AQUEOUS SOLUTION BY WOOD

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The sorption of Basic Blue 69 and Acid Blue 25 onto wood has been studied in terms of pseudo-second order, intraparticle diffusion and pseudo-first order chemical sorption processes. The batch sorption model, based on the assumption of a pseudo-second order mechanism, has been developed to predict the rate constant of sorption, the equilibrium capacity and initial sorption rate with the effect of initial dye concentration, wood particle size and temperature. An equilibrium capacity of sorption has been evaluated with the pseudo-second order rate equation as well as by the Langmuir isotherm and operating line method. In addition, an activation energy of sorption has also been determined based on the pseudo-second order rate constants.

Key words: wood; dye; kinetics; sorption.

INTRODUCTION

Adsorption of dyes from waste water has been studied. The rate at which sorption takes place is of the utmost importance when designing batch sorption systems; consequently it is important to establish the time dependence of such systems under various process conditions. A number of sorption processes for dyes has been studied in an attempt to find a suitable explanation of the mechanism and the kinetics. Alexander *et al.*[1] evaluated an overall diffusion coefficient for the kinetics of the adsorption of Astrazone Blue on silica. Khare *et al.*[2] reported that removal of Victoria Blue from aqueous solution by fly ash follows a first order adsorption rate expression. In 1984, McKay[3,4] developed a model to predict the rate of adsorption of Astrazone Blue dye onto Sorbsil silica which is controlled by the internal mass transport processes based on a pore diffusion mechanism. The author presented a two resistance mass transfer model which is based on film resistance and homogeneous solid phase diffusion for the adsorption of Basic Blue 69 by silica. In addition, McKay *et al.*[5] presented a three-step model for the adsorption of Astrazone Blue dye on peat. In the case of the adsorption of dyes on chitin, McKay *et al.*[6] found that there is a branched pore mechanism and that the rate of adsorption of dyes onto chitin in the initial stages of the adsorption process depends on the film mass transfer coefficient[7].

In the present research the mechanism of basic and acid dye sorption on wood has been studied. The factors studied include the influence of wood particle size, temperature and initial dye concentration on the diffusion processes and the sorption kinetics of the system. A method is discussed for the determination of the activation energy of sorption of basic dye and acid dye onto wood based on a pseudo-second order sorption process. A rate parameter, k, has been defined and used to describe the sorption of acidic and basic dyes onto wood and a method for determining the diffusion rate coefficients, using data plotting techniques, has been developed. A comparison of the intraparticle diffusion parameter, k_i, a pseudo-second order sorption parameter, k, and a pseudo-first order rate parameter, k_1, is also discussed.

MATERIALS AND METHODS

Sorbent

The wood sawdust particles were of the spruce wood type, and no form of pretreatment was applied except for sieving into various particle size ranges.

Sorbates

The sorbates and their structures used in the experiments are listed below. The dyestuffs were used as the commercial salts.

Acid Blue 25 (Telon Blue ANL) CI 62055 was supplied by Bayer.
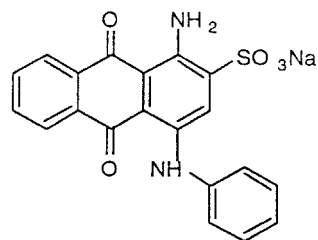
Basic Blue 69 (Astrazone Blue FRR) was supplied by Bayer. No structure is available for this dye. It belongs to the methine class, of which the chromophore is a conjugate chain of carbon atoms terminated by an equivalent

unsaturated group. A general structure for the methine class is:
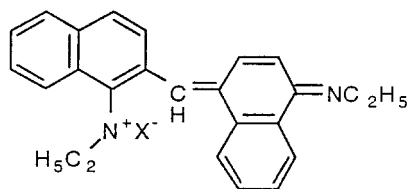
The experimental methods were described in a previous paper[8].

Sorption Dynamics

Effect of particle size

A 0.1 g sample of wood was added to each 50 ml volume of Basic Blue 69 solution (200 mg dm^{-3}). The wood particle size ranges were 150–250, 250–355, 355–500 and 710–1000 μm. A 0.5 g sample of wood was added to each 50 ml volume of Acid Blue 25 solution (100 mg dm^{-3}). The wood particle size ranges were 150–250, 250–355, 355–500 and 710–1000 μm.

Effect of temperature

A 0.1 g sample of wood (355–500 μm) was added to each 50 ml of Basic Blue 69 dye solution (200 mg dm^{-3}). The experiments were carried out at 18, 40, 60 and 80°C in a constant temperature shaker bath. A 0.5 g sample of wood (355–500 μm) was added to each 50 ml of Acid Blue 25 dye solution (100 mg dm^{-3}). The experiments were carried out at 18, 40, 60 and 80°C in a constant temperature shaker bath.

Effect of initial concentration

A 0.1 g sample of wood (500–710 μm) was added to each 50 ml volume of Basic Blue 69 solution. The initial concentrations of dye solution tested were 50, 100, 200 and 500 mg dm^{-3}. A 0.5 g sample of wood (500–710 μm) was added to each 50 ml volume of Acid Blue 25 solution. The initial concentrations of dye solution tested were 20, 50, 100 and 200 mg dm^{-3}.

Equilibrium Isotherms

Effect of particle size

To determine the effect of particle size on the dye removal capacities of the various dye/wood systems, isotherm experiments were carried out and the data were analysed using the Langmuir equation. Isotherms were determined for four various wood particle size ranges— 150–250, 250–355, 355–500 and 710–1000 μm—and the contact time given for each experiment was 8 hours. In each case a fixed weight of wood (0.02 to 0.3 g) was added to a 50 ml volume of Basic Blue 69 dye solution of initial concentration 200 mg dm^{-3} and wood mass was from 0.05 to 0.8 g with Acid Blue 25 dye solution of initial concentration 100 mg dm^{-3}.

Effect of temperature

The effect of temperature on the capacity of the wood to remove dye from solution was determined by establishing sorption isotherms at temperatures of 18, 40, 60 and 80°C by the Langmuir equation. The wood particle size range used in these studies was 355–500 μm. In each case a fixed mass of wood (0.02 to 0.3 g) was added to a 50 ml volume of Basic Blue 69 dye solution of initial concentration 200 mg dm^{-3} and the wood mass was from 0.05 to 0.8 g with an Acid Blue 25 dye solution of initial concentration 100 mg dm^{-3}.

RESULTS AND DISCUSSION

Sorption Dynamics

Several steps can be used to express the mechanism of solute sorption onto a sorbent. In order to investigate the mechanism of sorption, the constants of sorption and intraparticle diffusion of dyes were determined using equations of Lagergren[9], a pseudo-second order mechanism and Weber and Morris[10] respectively which are as follows:

Pseudo-first order model

The sorption kinetics may be described by a pseudo-first order[9]. The differential equation is the following:

$$\frac{dq_t}{dt} = k_1(q_1 - q_t) \tag{1}$$

Integrating equation (1) for the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, gives:

$$\log\left(\frac{q_1}{q_1 - q_t}\right) = \frac{k_1}{2.303}t \tag{2}$$

which is the integrated rate law for a pseudo-first order reaction, where:

q_1 is the amount of dye sorbed at equilibrium, mg g^{-1};
q_t is the amount of dye sorbed at time t, mg g^{-1};
k_1 is the equilibrium rate constant of pseudo-first sorption, min^{-1}.

Equation (2) can be rearranged to obtain a linear form:

$$\log(q_1 - q_t) = \log(q_1) - \frac{k_1}{2.303}t \tag{3}$$

In order to obtain the rate constants, the straight line plots of $\log(q_1 - q_t)$ against t for different dyes and different experimental conditions have been analysed. The rate constant, k_1, and correlation coefficients, r_1^2, values of the dyes under different conditions were calculated from these plots.

Pseudo-second order model

The sorption kinetics may be described by a pseudo-second order. The differential equation is the following:

$$\frac{dq_1}{dt} = k(q_e - q_t)^2 \tag{4}$$

Integrating equation (4) for the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, gives:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + kt \tag{5}$$

which is the integrated rate law for a pseudo-second order reaction, where:

q_e is the amount of dyes sorbed at equilibrium, mg g^{-1};
k is the equilibrium rate constant of pseudo-second order sorption, g mg^{-1}min^{-1}.

Equation (5) can be rearranged to obtain a linear form:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t \qquad (6)$$

and

$$h = kq_e^2 \qquad (7)$$

where:

h is the initial sorption rate, $mg\,g^{-1}min^{-1}$.

The straight line plots of t/q_t against t have also been tested to obtain rate parameters. The k, q_2 and correlation coefficients, r^2, values of dyes under different conditions were calculated from these plots.

Intraparticle diffusion model

Theoretical treatments of intraparticle diffusion yield rather complex mathematical relationships which differ in form as functions of the geometry of the sorbent particle[11]. Although a mathematical treatment of the diffusion process will not be presented here, it is useful to describe one characteristic of the theoretical expressions in order to facilitate the presentation of the data. A functional relationship common to most treatments of intraparticle diffusion is that uptake varies almost proportionately with the half-power of time, $t^{0.5}$, rather than t; nearly linear variation of the quantity sorbed with $t^{0.5}$ is predicted for a large initial fraction of reactions controlled by rates of intraparticle diffusion. Good linearization of the data is observed for the initial phase of the reaction in accordance with expected behaviour if intraparticle diffusion is the rate-limiting step[10].

The intraparticle diffusion equation is the following:

$$q_t = k_i t^{0.5} \qquad (8)$$

where:

k_i is the intraparticle diffusion rate constant, $mg\,g^{-1}min^{-0.5}$.

The k_i values under different conditions were calculated from the slopes of the straight line portions of the respective plots.

Effect of particle size

Two series of experiments were undertaken to study the influence of wood particle size. Experimental results for the sorption of Basic Blue 69 dye, BB69, and Acid Blue 25, AB25, onto wood are shown in Figures 1 and 2 respectively. The results show that the sorption capacity of BB69 increases from 63.7 to 73.0 $mg\,g^{-1}$ with the decrease of the wood particle size ranging from 710–1000 to 250–355 μm and in the case of AB25 the sorption capacity increases from 3.69 to 5.99 $mg\,g^{-1}$ with the decrease of the wood particle size ranging from 710–1000 to 250–355 μm. This indicates that the smaller the wood particle size, then for a given mass wood, more surface area is made available and therefore the number of sites increases. The kinetics of AB25 and BB69 sorption on wood follow the pseudo-second order rate expression. Linear plots of t/q_t against t in Figure 3 show the applicability of the pseudo-second order equation for the system of BB69 with wood for particle sizes
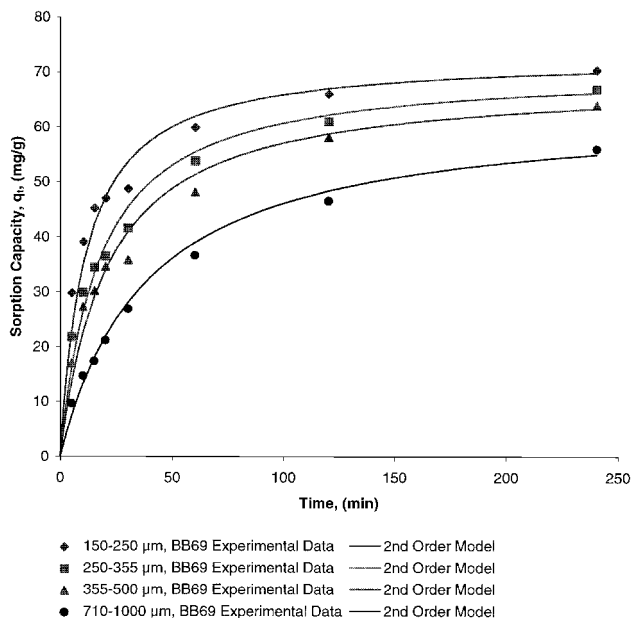

Figure 1. Effect of particle size on the sorption of BB69 onto wood.

ranging from 250–355 to 710–1000 μm. Figure 4 shows plots of q_t against t for the first-order equation for the sorption of BB69 dye. k, h and q_2 were calculated and are presented in Table 1. The correlation coefficients, r^2, and the pseudo-second order rate parameters, k, are shown and compared with r_1^2 and k_1 values for the first-order reaction mechanism as well as with r_i^2 and k_i values for the intraparticle diffusion based model. The data show a good compliance with the pseudo-second order equation and the regression coefficients for the linear plots were higher than 0.980 for all the systems in these studies. The correlation coefficients of the intraparticle diffusion model for the initial 30 minute period are given in Table 1 for the effect of particle size of BB69 and AB25. Although the values are all
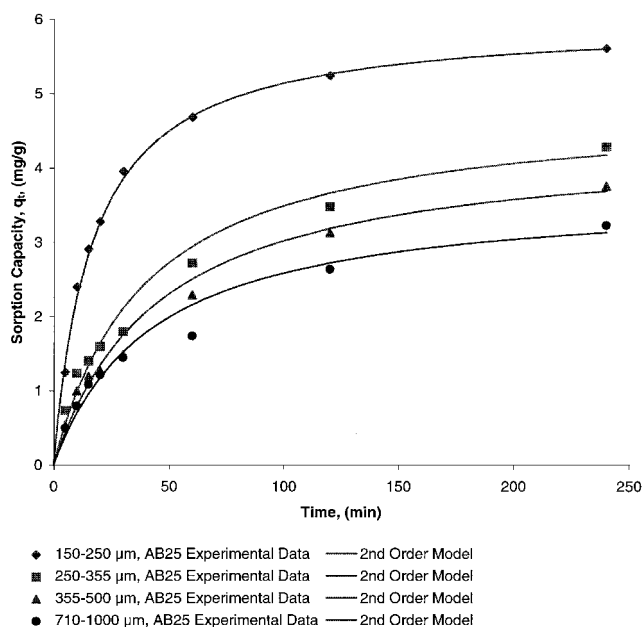

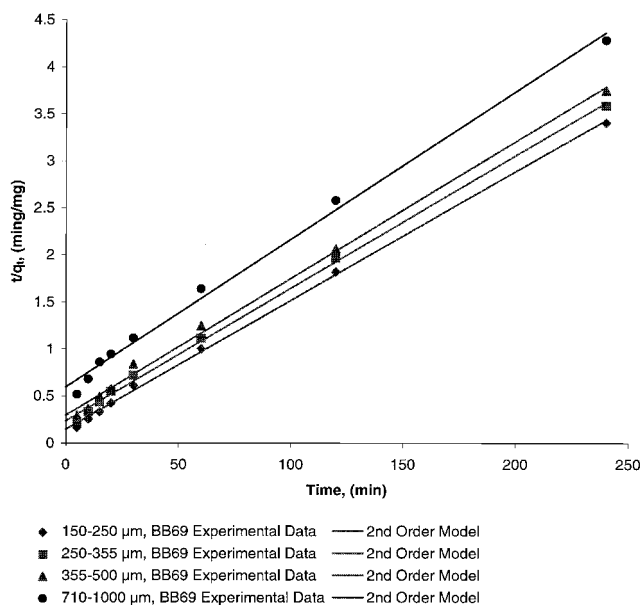*Figure 2.* Effect of particle size on the sorption of AB25 onto wood.

Figure 3. Pseudo-second-order sorption kinetics of BB69 onto wood at various particle sizes.
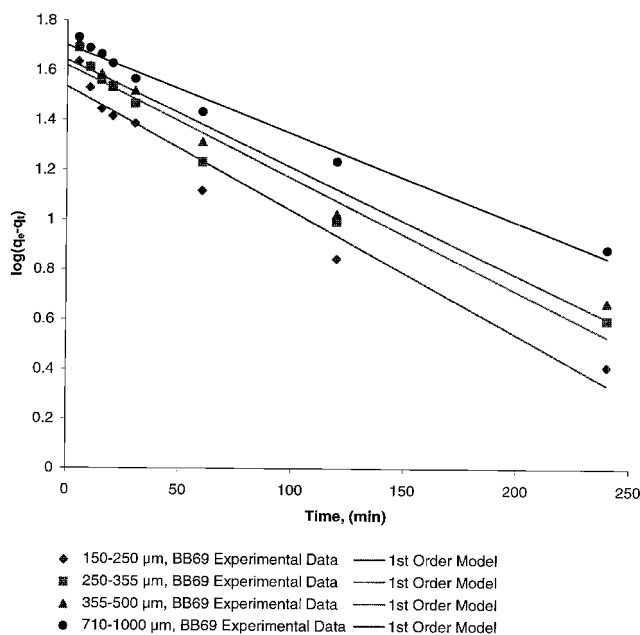

Figure 4. First-order sorption kinetics of BB69 onto wood at various particle sizes.

greater than 0.882 they are significantly lower than the coefficients obtained using the second-order kinetic model.

Figure 5 shows that plotting the amount of AB25 per unit weight of wood against square root of time generates best fit straight lines for the initial 30 minutes of sorption which pass close to the origin, indicating that intraparticle diffusion might be the rate limiting step in the period of the first 30 minutes of sorption. This initial period of 30 minutes is typical of the times used in the literature for intraparticle diffusion based on the macropore diffusion process. The $t^{0.5}$ versus time plots are then usually divided into two other linear sections attributed to mesopore and micropore diffusion. In Table 1, all correlation coefficients, r^2, are extremely high and furthermore, they are based on an analysis of sorption data taken for four hours as opposed to 30 minutes. The correlation coefficients of equation (8), for intraparticle diffusion, are high for the effect of particle size for the sorption of the two dyes on wood. The sorption process may involve a chemical reaction process and demonstrates that the pseudo-second order rate constant, k, is a function of the available surface area of the wood.

Effect of temperature

The effect of temperature was studied in contact time experiments carried out with a constant initial dye concentration of $200 \, mg \, dm^{-3}$, wood dose $2 \, g \, dm^{-3}$ for BB69 and $100 \, mg \, dm^{-3}$, wood dose $10 \, g \, dm^{-3}$ at various temperatures of reaction sorption. Figures 6 and 7 show that the equilibrium sorption capacity of BB69 increases with temperature, indicating that a high temperature favours BB69 removal by adsorption on wood. This effect is characteristic of a chemical reaction or bond being involved in the sorption process with the increase in temperature increasing the equilibrium conversion. Thus, increasing the temperature of the reaction from 18 to 80°C, the removal of the dye increased from 63.3 to 74.7% for BB69 but decreased from 42.2 to 18.7% for AB25. This effect can be explained by assuming that at higher temperatures the total energy of the sorbate molecules is increased and consequently their escaping tendency is also increased, therefore the sorption of the sorbate species is lowered[12]. This suggests that the sorption of AB25 is likely to be a physical process rather than a chemical reaction and therefore if the sorption temperature increases the dye would escape from the interface of the wood more easily. Thus the sorption capacity of AB25 decreases with increasing temperature. Consequently, it is clear that adsorption equilibrium capacity is dependent on temperature.

Table 1. Parameters for effect of particle size.

	d_p, μm	r^2	q_2, mg g^{-1}	k, g mg^{-1} min^{-1}	h, mg g^{-1} min^{-1}	q_1, mg g^{-1}	r_1^2	k_1, l min^{-1}	r_i^2	k_i, mg g^{-1} min$^{-0.5}$
BB69	150−250	0.999	73.0	1.28×10^{-3}	6.80	34.2	0.961	1.15×10^{-2}	0.882	5.85
	250−355	0.998	70.9	8.45×10^{-4}	4.25	41.7	0.964	1.04×10^{-2}	0.971	5.96
	355−500	0.997	68.7	7.20×10^{-4}	3.40	43.8	0.968	9.94×10^{-3}	0.893	5.74
	710−1000	0.995	63.7	4.14×10^{-4}	1.68	50.2	0.983	8.16×10^{-3}	0.995	5.26
AB25	150−250	1.00	5.99	1.01×10^{-2}	0.363	3.37	0.906	1.01×10^{-2}	0.973	0.812
	250−355	0.988	4.86	5.28×10^{-3}	0.125	3.89	0.992	8.22×10^{-3}	0.953	0.319
	355−500	0.988	4.38	5.08×10^{-3}	0.0976	3.60	0.984	7.65×10^{-3}	0.935	0.281
	710−1000	0.980	3.69	6.37×10^{-3}	0.0868	3.02	0.990	8.02×10^{-3}	0.984	0.297
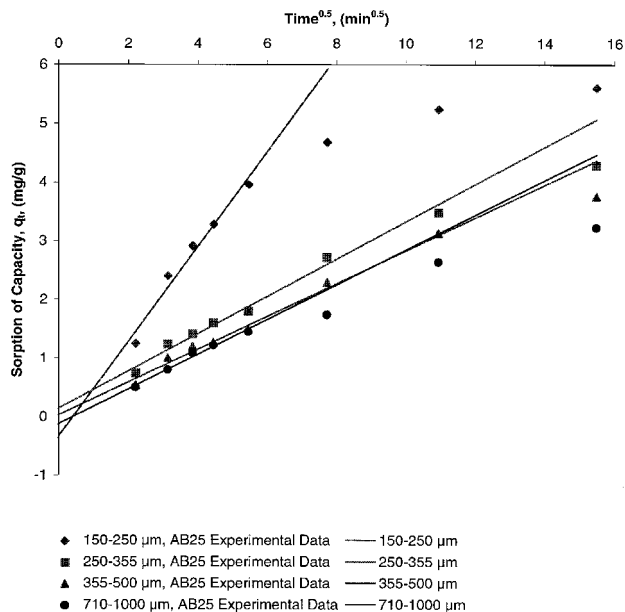
Figure 5. Intraparticle diffusion kinetics of AB25 onto wood at various particle sizes.

Figure 7. Effect of temperature on the sorption of AB25 onto wood.

Figures 6 and 7 show a good compliance with the pseudo-second order equation. The experimental points are shown together with the theoretically generated curves. The agreement between the sets of data reflects the extremely high correlation coefficients obtained and shown in Table 2.

The results in Table 2 also show the sorption rate constant, k, initial sorption rate, h, and equilibrium sorption capacity, q_2, as a function of solution temperature. Thus, on increasing the temperature from 18 to 80°C, the specific sorption at equilibrium, q_2, increased from 63.3 to 74.4 mg g^{-1} for BB69 and decreased from 4.22 to 1.87 mg g^{-1} for AB25.

The initial sorption rate increases with an increase in temperature. Table 2 shows that h varies from 3.72 to
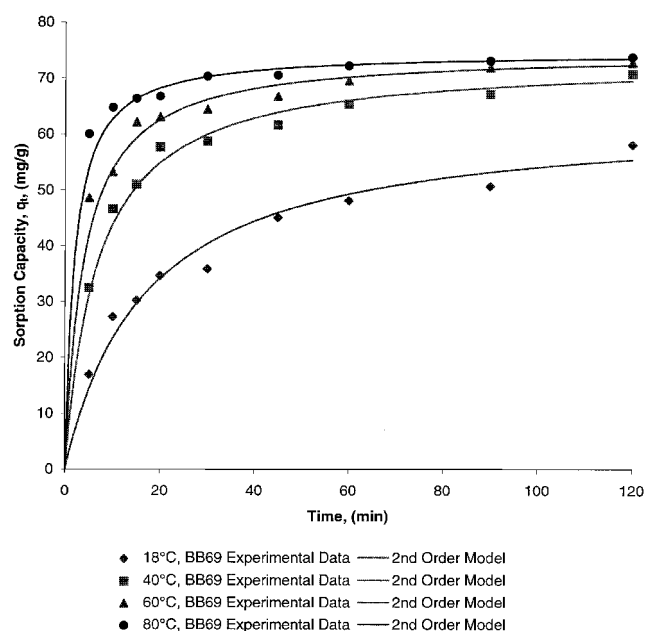
39.3 mg g^{-1} min^{-1} for BB69, and h varies from 0.138 to 0.845 mg g^{-1} min^{-1} for AB25 respectively for a temperature variation from 18 to 80°C. Both dye/wood systems show extremely high reaction correlation coefficients, r^2, which are all greater than 0.981. This trend suggests that a chemisorption reaction or an activated process was becoming more predominant in the rate controlling step. The pseudo-second order rate constants for the BB69 on wood system show a steady increase with temperature whereas the k values for AB25 on wood show a decrease with temperature.

The values of rate constant, k, were found to increase from 9.30×10^{-4} to 7.03×10^{-3} g mg^{-1} min^{-1} for BB69 and 7.75×10^{-3} to 0.241 g mg^{-1} min^{-1} for AB25, for an increase in the solution temperature from 293 to 353°K. There is a linear relationship between the pseudo rate constant and temperature with correlation coefficients of 0.994 for BB69 and 0.951 for AB25. The k values were plotted as a function of the reciprocal of the Kelvin temperature. Linear variations were observed as shown in Figure 8. Therefore the sorption rate constant may be expressed as a function solution of temperature by the following relationship:

$$k = k_0 \exp\left(\frac{-E}{RT}\right) \tag{9}$$

where:

k is the rate constant of sorption, g mg^{-1} min^{-1};
k_0 is the temperature independent factor, g mg^{-1} min^{-1};
E is activation energy of sorption, kJ mol^{-1};
R is the gas constant, 8.314 J mol^{-1} K^{-1};
T is solution temperature, K.

Therefore, the relationship between k and T can be represented in an Arrhenius form as:

for BB69:

$$k_2 = 72.5 \exp\left(\frac{-27.3 \times 10^3}{8.314T}\right)$$

Figure 6. Effect of temperature on the sorption of BB69 onto wood.

Table 2. Parameters for the effect of temperature.

	T, °C	r^2	q_2, mg g^{-1}	k, g mg^{-1}min^{-1}	h, mg g^{-1}min^{-1}	r_1^2	k_1, 1 min^{-1}	r_i^2	k_i, mg g^{-1}min$^{-0.5}$
BB69	18	0.989	63.3	9.30×10^{-4}	3.72	0.964	1.68×10^{-2}	0.952	4.29
	40	0.999	73.5	2.01×10^{-3}	10.9	0.942	2.03×10^{-2}	0.820	3.65
	60	0.999	74.7	3.44×10^{-3}	19.2	0.955	2.16×10^{-2}	0.839	2.54
	80	1.00	74.7	7.03×10^{-3}	39.3	0.960	2.29×10^{-2}	0.862	1.43
AB25	18	0.981	4.22	7.75×10^{-3}	0.138	0.994	1.31×10^{-2}	0.989	0.312
	40	0.998	3.89	1.47×10^{-2}	0.222	0.963	1.56×10^{-2}	0.943	0.278
	60	0.999	2.66	7.60×10^{-2}	0.538	0.846	2.15×10^{-2}	0.756	0.121
	80	0.999	1.87	0.241	0.845	0.890	2.59×10^{-2}	0.883	0.0386

for AB25:

$$k_2 = 3.41 \times 10^6 \exp\left(\frac{-48.9 \times 10^3}{8.314T}\right)$$

From these equations the rate constant of sorption, k_0, is 72.5 g mg^{-1}min^{-1} for BB69 and 3.41×10^6 g mg^{-1}min^{-1} for AB25. Furthermore the activation energy of sorption, E, is 27.3 kJ mol^{-1} for the sorption system BB69 on wood and 48.9 kJ mol^{-1} for the sorption system AB25 on wood. Since sorption is an exothermic process, it would be expected that an increased solution temperature would result in a decreased sorption capacity. The results of this study on the effect of temperature indicate that the sorption of BB69 and AB25 dye on wood involves some chemical sorption.

Effect of initial concentration

The influence of initial dye concentration was studied with BB69 and AB25. The kinetic data obtained from batch studies have been analysed using the first order model proposed by Lagergren[9] and shown in Figure 9 for the sorption of BB69. The kinetics of BB69 and AB25 sorption on wood follow the pseudo-second order rate expression. Linear plots of t/q_t against t indicate the applicability of equation (6). Figures 10 and 11 show a series of contact time curves with wood for initial dye concentrations of 50 to 500 mg dm^{-3} for BB69 and of 20 to 200 mg dm^{-3} for AB25. The equilibrium capacity of wood for BB69 decreases from 96.4 to 27.6% and for AB25 the decrease in capacity is from 50.3 to 37.7% with the increase of the initial concentration from 50 to 500 mg dm^{-3} for BB69 and 20 to 200 mg dm^{-3} for AB25. However, the sorption capacity increases from 24.1 to 69.1 mg g^{-1}, as C_0 varies from 50 to 500 mg dm^{-3} for BB69 and from 1.01 to 7.53 mg g^{-1}, as C_0 varies from 20 to 200 mg dm^{-3} for AB25 respectively. Figures 12 and 13 show that plotting the amount of dye sorbed per unit mass of wood against square root of time generates best fit straight lines for the initial 30 minutes for BB69 and for 240 minutes for AB25. The pseudo-second order rate parameters, k, are shown and compared with r_i^2 and k_i values for the intraparticle diffusion based model in Table 3. The data show a good compliance with the pseudo-second order equation and the regression coefficients for the linear plots were higher than 0.990 for all the systems in these studies.

Sorption isotherms

A series of isotherms are shown in Figures 14 and 15 for the sorption of BB69 and AB25 onto various particle size ranges of wood. The graphs are plotted in the form of dye adsorbed per unit mass of wood, q_e, against the concentration
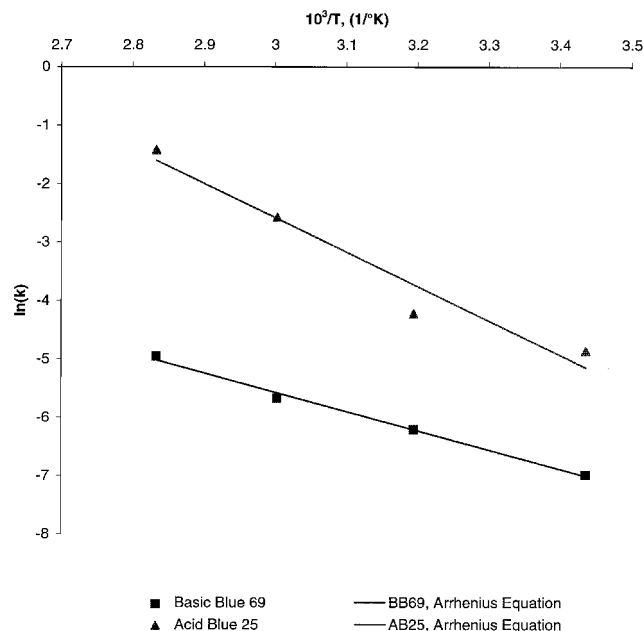

Figure 8. Plot of ln(k) against reciprocal temperature for BB69 and AB25 sorption onto wood.
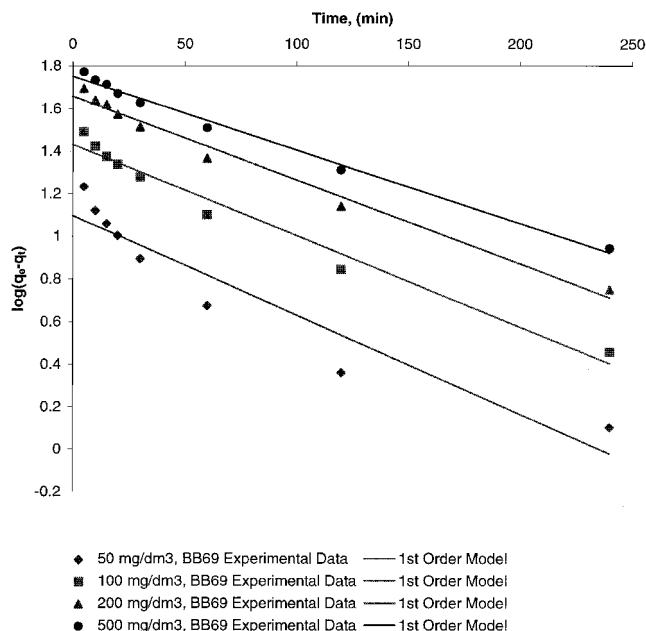

Figure 9. First order sorption kinetics of BB69 onto wood at various initial concentrations.
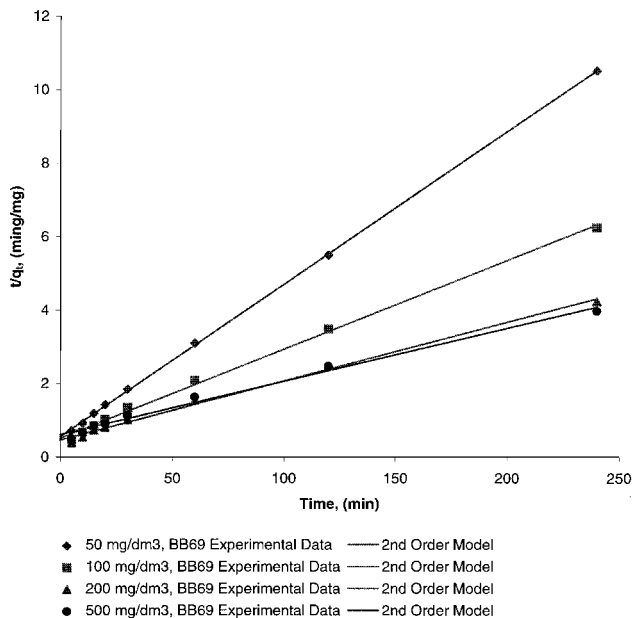
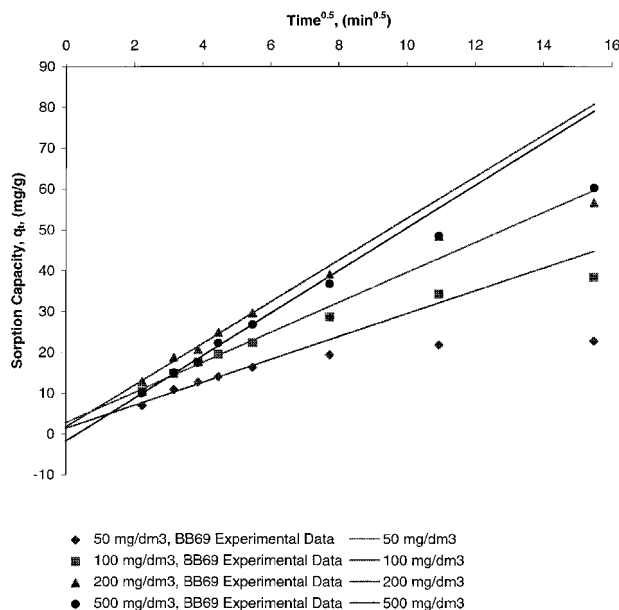*Figure 10.* Pseudo-second order sorption kinetics of BB69 onto wood at various initial concentrations.

Figure 12. Intraparticle diffusion kinetics of BB69 onto wood for various initial concentrations.
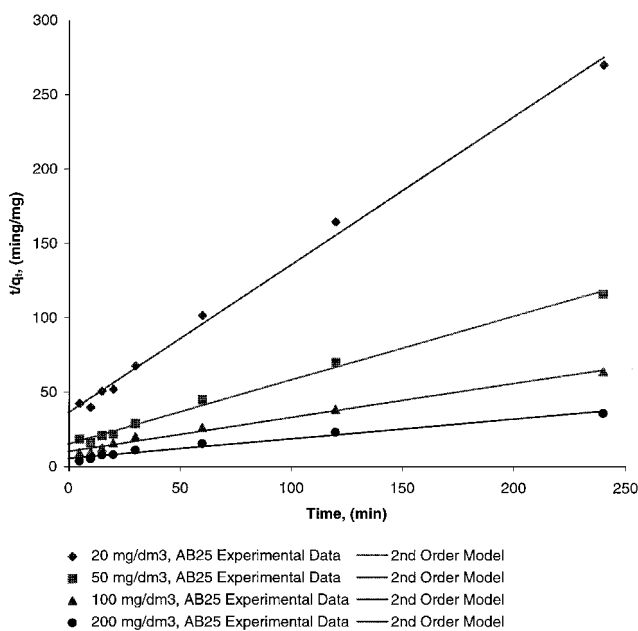

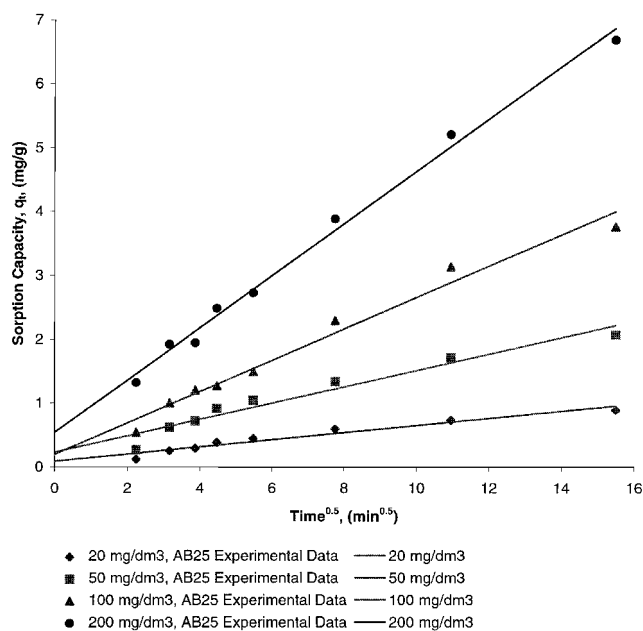*Figure 11.* Pseudo-second order sorption kinetics of AB25 onto wood at various initial concentrations.

Figure 13. Intraparticle diffusion kinetics of AB25 onto wood for various initial concentrations.

Table 3. Parameters for effect of initial concentrations.

	C_0, mg dm^{-3}	r^2	q_2, mg g^{-1}	k, g mg^{-1}min^{-1}	h, mg g^{-1}min^{-1}	r_1^2	k_1, 1 min^{-1}	r_i^2	k_i, mg g^{-1}min$^{-0.5}$
BB69	50	1.00	24.1	3.09×10^{-3}	1.80	0.906	1.07×10^{-2}	0.974	2.80
	100	0.997	41.3	1.14×10^{-3}	1.94	0.974	9.85×10^{-3}	0.984	3.67
	200	0.995	62.2	5.58×10^{-4}	2.16	0.985	9.05×10^{-3}	0.990	5.10
	500	0.990	69.1	3.43×10^{-4}	1.63	0.992	7.94×10^{-3}	0.991	5.21
AB25	20	0.996	1.01	2.72×10^{-2}	2.76×10^{-2}	0.978	8.21×10^{-3}	0.949	0.0556
	50	0.994	2.33	1.20×10^{-2}	6.53×10^{-2}	0.981	8.29×10^{-3}	0.949	0.128
	100	0.988	4.38	5.08×10^{-3}	9.76×10^{-2}	0.984	7.65×10^{-3}	0.977	0.245
	200	0.977	7.53	3.21×10^{-3}	1.82×10^{-1}	0.998	8.26×10^{-3}	0.993	0.408

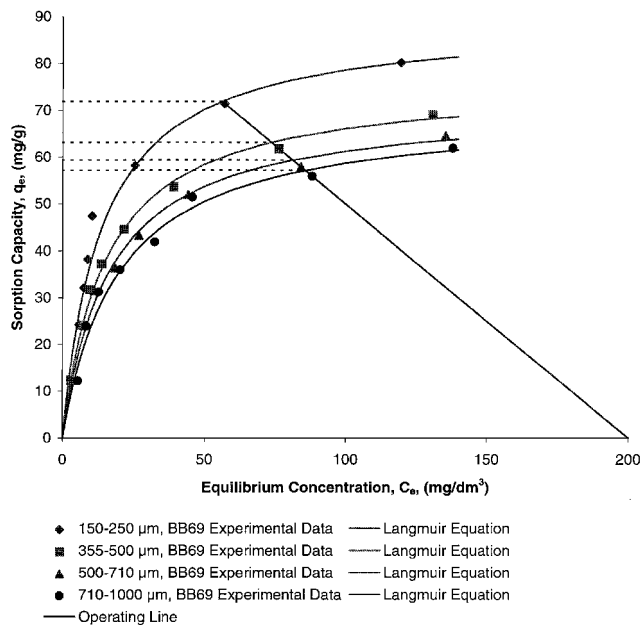*Figure 14.* Langmuir isotherms of Basic Blue 69 onto wood at various particle sizes.

Figure 16. Langmuir isotherms of Basic Blue 69 onto wood at various temperatures.

of dye remaining in solution, C_e, with the Langmuir equation. Figures 14 and 15 also show the operating line which is generated with a slope of solution volume/wood mass. The final equilibrium solution concentration is predicted from the point of intersection of the operating line on the sorption isotherm, for the sorption of BB69 and AB25. It is therefore an operating line and can be expressed as follows:

for BB69:

$$q_e = -0.5C_e + 100$$
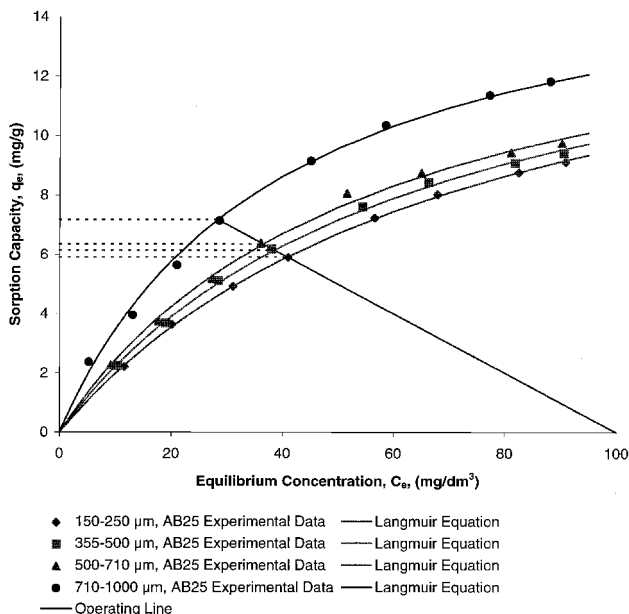
for AB25:

$$q_e = -0.1C_e + 10$$

The equilibrium sorption capacity, q_e, can be obtained from the operating line and the Langmuir equation (Figures 14 and 15). The results are in reasonable agreement with the equilibrium sorption capacity, q_2, obtained from the pseudo-second order model. A comparison is made between the equilibrium sorption capacity evaluated from the Langmuir equation and the pseudo-second order model in Table 4, which shows that the equilibrium sorption capacities evaluated are reasonable in all cases.

A series of sorption isotherms were also measured at varied temperatures, namely 18, 40, 60 and 80°C. The Langmuir isotherms are shown in Figures 16 and 17 with the

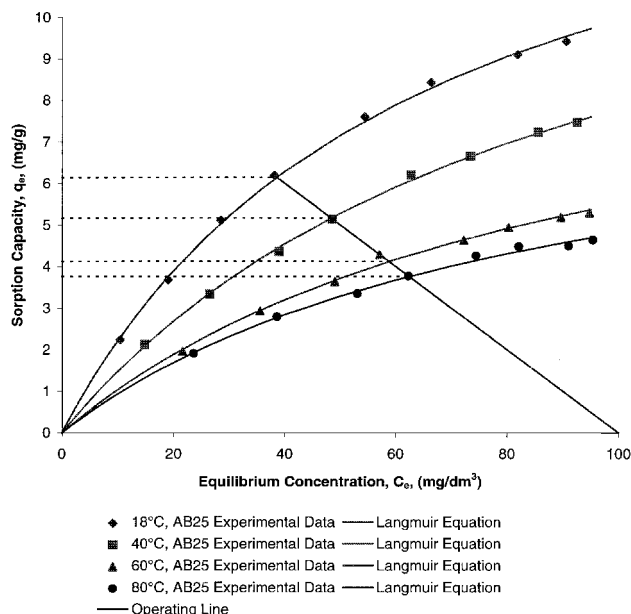*Figure 15.* Langmuir isotherms of Acid Blue 25 onto wood at various particle sizes.

Figure 17. Langmuir isotherms of Acid Blue 25 onto wood at various temperatures.

Table 4. Comparison of the equilibrium sorption capacity evaluated from the Langmuir equation and the pseudo-second order model.

	d_p, μm	q_e, mg g^{-1}	q_2, mg g^{-1}
BB69	150–250	71.9	73.0
	250–355	63.1	70.9
	355–500	59.3	68.7
	710–1000	57.1	63.7
AB25	150–250	5.92	5.99
	250–355	6.14	4.86
	355–500	6.35	4.38
	710–1000	7.17	3.69

Table 5. Comparison of the equilibrium sorption capacity evaluated from the Langmuir equation and the pseudo-second order model.

	T, °C	q_e, mg g^{-1}	q_2, mg g^{-1}
BB69	18	63.1	63.3
	40	71.1	73.5
	60	74.6	74.7
	80	77.0	74.7
AB25	18	6.14	4.22
	40	5.17	3.89
	60	4.12	2.66
	80	3.76	1.87

operating line. The equilibrium sorption capacity, q_e, can be obtained from the operating line and the Langmuir equation. A comparison is made between the equilibrium sorption capacity evaluated from the Langmuir equation and the pseudo-second order model in Table 5, which shows that both equilibrium sorption capacities evaluated are reasonable in all cases.

CONCLUSIONS

The kinetics of sorption of BB69 and AB25 on wood were studied on the basis of the pseudo-second order rate mechanism. The sorption of capacity of basic dye (BB69) is much higher than acid dye (AB25) because of the ionic charges on the dyes and the character of the biomaterials. The activation energy of sorption can be evaluated with the pseudo-second order rate constants. The sorption of BB69 and AB25 by wood is an exothermic activated process. For both dye/wood systems chemical reaction seems significant in the rate controlling step and also the pseudo-second order chemical reaction kinetics provide the best correlation of the data. An equilibrium capacity of sorption has also been evaluated with the pseudo-second order rate equation as well as the Langmuir isotherm and operating line.

NOMENCLATURE

C_e equilibrium liquid phase dye concentration, mg dm^{-3}

C_o initial liquid phase dye concentration, mg dm^{-3}
d_p mean wood particle diameter, micron
E activation energy of sorption, kJ mol^{-1}
h initial sorption rate, mg dye g^{-1} wood min^{-3}
k rate constant for pseudo-second order sorption, g wood mg^{-1} dye min^{-1}
k_i intraparticle diffusion rate parameter, mg dye g^{-1} wood min^{-1}
k_1 rate constant for pseudo-first order sorption, min^{-1}
k_o temperature independent factor, g wood mg^{-1} dye min^{-1}
q_e amount of dye adsorbed at equilibrium in the pseudo-first order model, mg dye g^{-1} wood
q_t amount of dye adsorbed at time, t, mg dye g^{-1} wood
q_1 amount of dye adsorbed at equilibrium in the pseudo-first order model, mg dye g^{-1} wood
q_2 amount of dye adsorbed at equilibrium in the pseudo-second order model, mg dye g^{-1} wood
r^2 linear correlation coefficient
t sorption contact time, min
T solution temperature, K
R universal gas constant, 8.314 J mol^{-1} k^{-1}

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