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Sorption of dye from aqueous solution by peat

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Abstract

The sorption of two dyes, namely, Basic Blue 69 and Acid Blue 25 onto peat has been studied in terms of pseudo-second order and first order mechanisms for chemical sorption as well as an intraparticle diffusion mechanism process. The batch sorption process, 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 agitation, initial dye concentration and temperature. An activation energy of sorption has also been evaluated with the pseudo-second order rate constants. A comparison of the equilibrium sorption capacity evaluated has been made from pseudo-second order model and Langmuir isotherm.

Keywords: Peat; Dye; Kinetics; Sorption

1. Introduction

For over 20 years, peat has been recognized as a potential agent for the treatment of wastewaters. Several studies have been reported in the literature including its use in cleaning oil spills [1], the removal of heavy metals from wastewaters [2–5], the removal of the herbicide [6], the treatment of slaughterhouse wastewaters, septic tank effluents and dairy wastes [7,8]. Pilot plant studies have also been carried out. A peat moss pilot plant filter was used to remove nickel [9]. A moving mat filter was developed on a pilot plant scale to treat textile wastewater [10]. In addition, the search for new commercial uses of peat has been rewarding in the area of pollution control. For the reason of cheaper pollution control methods, Harrison Western Environmental Services of Lakewood, CO, has developed such a process, called membrane-media extraction, which uses peat moss 'capsules' to be effective at reducing concentrations of arsenic, cadmium, lead, nickel, selenium, and other metals from electroplating rinsewater, pulp and paper mill discharge, municipal wastewater, and acid mine drainage [11].

Peat is a complex material containing lignin, cellulose, fulvic and humic acids as its major constituents. These compounds carry polar functional groups such as alcohols, aldehydes, carboxylic acids, ketones and phenolic hydroxides, which will become involved in bonding with sorbed pollutant species. The composition of peat from various sources may vary considerably depending on age, the nature of its original vegetation, the regional climate, the acidity of the water and the degree of metamorphosis. The variation of metal ion uptake using 12 types of peat has been demonstrated [12].

The ability of peat to remove several dyes from aqueous effluent was reported some time ago [13]. Further studies on single component adsorption of basic and acid dye were carried out to study equilibrium isotherms [14] and diffusion based mass transport processes [15]. Single and multicomponent adsorption isotherms were carried out for three basic dyes [16,17]. Detailed analysis of the mass transport/kinetic mechanisms involved in the sorption process take extensive mathematical and computational development [18]. The aim of the present paper is to test three simple models for analysing the sorption of a basic dye, Basic Blue 69, and an acid dye, Acid Blue 25, onto peat and assess their usefulness and accuracy.

The three models tested are based on:

- a pseudo-first order process;
- a pseudo-second order process;
- an intraparticle diffusion process.

This work applies the batch sorption results of two dyes, namely, Basic Blue 69 and Acid Blue 25 onto peat, to investigate the influence of intraparticle diffusion and two chemical sorption mechanisms. It compares three rate parameters, k_i, for intraparticle diffusion, k_2 for the pseudo-second order mechanism and k_1 for the pseudo-first order mechanism.

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2. Materials and methods

The experiments were conducted with sphagnum moss peat obtained from Northern Ireland. The peat as supplied, was dried at a temperature of 85 ± 5°C for 3 h. The dyes used in the experiments, namely Telon Blue (Acid Blue 25) and Astrazone Blue (Basic Blue 69) were supplied by Bayer.

Equilibrium isotherms were determined by shaking a fixed mass of peat (0.1 g) with 50 ml dye solution in screw cap flasks. A range of dye concentrations were used. Shaking was carried out until equilibrium had been achieved.

2.1. Sorption dynamics

2.1.1. Effect of agitation

The effect of agitation on contact time was carried out using a baffled agitated 2 dm^3 adsorber vessel. The vessel contained 1.7 dm^3 dye solution and was designed to conform to specified standards [19,20].

2.1.2. Effect of initial concentration

A 0.1-g sample of peat (500–710 μm) was added to each 50 ml volume of Basic Blue 69 dye solution. The initial concentration of dye solution tested were 50, 100, 200 and 500 mg dye/dm^3. A 0.5-g peat (500–710 μm) was added to each 50 ml volume of Acid Blue 25 dye solution. The initial concentrations of dye solutions tested were 20, 50, 100 and 200 mg dye/dm^3 and the experiments were carried out at 18°C in a constant temperature shaker bath.

2.1.3. Effect of temperature

A 0.1-g peat (355–500 μm) was added to each 50 ml of Basic Blue 69 dye solution having an initial concentration 500 mg dye/dm^3. The experiments were carried out at 18, 40, 60 and 80°C in a constant temperature shaker bath. A 0.5-g peat (355–500 μm) was added to each 50 ml of Acid Blue 25 dye solution using an initial dye concentration 100 mg dye/dm^3. All experiments were carried out at 18, 40, 60 and 80°C in a constant temperature shaker bath which controlled the temperature to within ± 1°C.

2.1.4. Sampling

In the sorption dynamic experiments for the effect of initial dye concentration and temperature each data point was obtained from an individual flask and therefore no corrections were necessary due to withdrawal of sampling volumes. In the case of the agitation studies, 12 2-ml samples were taken over the duration of the experiment. This represents a change in the original volume 1.7 dm^3 of less than 1.5%. Therefore, no correction was applied to the optical density readings for each dilution as it was considered too small to be significant. The concentrations of all dye solutions were determined using an Optica Double Beam Spectrophotometer.

2.2. Equilibrium isotherms

2.2.1. Effect of temperature

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

3. Results and discussion

Peat has been studied for its potential to be a sorbent for dyes. Peat contains polar functional groups such as aldehydes, ketones, acids, and phenolics which indicate that peat could be involved in chemical bonding and these groups may be responsible for cation exchange capacity. It is thus expected that dyes will be adsorbed by peat.

3.1. Sorption dynamics

Sorption of dyes on peat may involve a chemical sorption which could control the reaction rate. Over 50 papers are reported in the literature covering the sorption of various metal ions onto biosorbents. Many of the papers involve kinetic analyses [21–28]; in all cases these are based on reaction kinetics mostly pseudo-first order or multiple pseudo-first order mechanisms. Although dyes are considered to be organic compounds both acid and basic dyes, the types used in this study, ionize in solution to form positive and negative ions, respectively. Therefore, the basis of this paper is to test the dye sorption characteristics using chemisorption pseudo-kinetic models. In order to investigate the mechanism of sorption, the rate constants of chemical sorption and intraparticle diffusion for the dyes were determined using the equations of a pseudo-first order system by Lagergren [29], an intraparticle diffusion process by Weber and Morris [30] and a pseudo-second order mechanism, respectively. These are described as follows.

For the rate constant for first order chemical sorption,

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

Integrating this for the boundary conditions $t=0$ to $t=t$ and $q_t=0$ to $q_t=q_t$, gives:

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

where q_1 is the amount of dye sorbed at equilibrium (mg/g); q_t is the amount of dye sorbed at time t (mg/g), and k_1 is the equilibrium rate constant of first order sorption (1/min).

The intercept of the straight line plots of $\log(q_1 - q_t)$ against t should equal $\log(q_1)$. However, if the intercept does not equal q_1 then the reaction is not likely to be a first order reaction even this plot has high correlation coefficient with the experimental data.

In order to obtain the rate constants the straight line plots of $\log(q_t)$ against t for different dyes and different conditions have been tested. The k_1 values and correlation coefficients r_1^2 of dyes under different conditions were calculated from these plots and are given in Tables 1–5 .

Table 1
Parameters for the effect of agitation for BB69

S	r_2^2	SE	q_2	k_2	h	r_1^2	SE	q_1	k_1	r_i^2	SE	k_i
200	0.989	0.111	10.4	5.79×10^{-3}	0.623	0.983	2.12×10^{-2}	9.61	3.39×10^{-2}	0.992	0.211	1.41
400	0.953	0.203	12.2	6.27×10^{-3}	0.927	0.997	1.09×10^{-2}	11.2	4.10×10^{-2}	0.995	0.202	1.76
800	0.942	0.226	12.1	7.70×10^{-3}	1.13	0.996	1.35×10^{-2}	11.0	4.62×10^{-2}	0.992	0.277	1.79

S (rpm); q_1,q_2 (mg/g); k_2 (g/mg min); h (mg/g min); k_1 (1/min); k_i (mg/g min$^{0.5}$).

Table 2
Parameters for the effect of initial concentrations for BB69

C_0	r_2^2	SE	q_2	k_2	h	r_1^2	SE	q_1	k_1	r_i^2	SE	k_i
50	1.00	2.05×10^{-2}	23.8	2.95×10^{-2}	16.7	0.661	0.362	2.22	1.33×10^{-2}	0.436	2.00	0.359
100	1.00	2.59×10^{-2}	47.2	6.62×10^{-3}	14.8	0.653	0.346	8.45	1.25×10^{-2}	0.534	5.60	1.23
200	1.00	7.64×10^{-3}	86.4	1.84×10^{-3}	13.8	0.855	0.190	28.3	1.21×10^{-2}	0.716	8.97	2.92
500	0.997	2.25×10^{-2}	195	2.62×10^{-4}	9.94	0.920	0.110	119	9.82×10^{-3}	0.834	21.6	9.94

C_0 (mg/dm^3); q_1, q_2 (mg/g); k_2 (g/mg min); h (mg/g min); k_1 (1/min); k_i (mg/g min$^{0.5}$).

Table 3
Parameters for the effect of initial concentrations for AB25

C_0	r_2^2	SE	q_2	k_2	h	r_1^2	SE	q_1	k_1	r_i^2	SE	k_i
20	0.999	1.50	1.85	4.42×10^{-2}	0.152	0.907	3.13×10^{-2}	0.915	1.10×10^{-2}	0.859	0.0490	0.0805
50	0.999	0.550	4.40	1.10×10^{-2}	0.213	0.932	4.92×10^{-2}	2.77	9.65×10^{-3}	0.878	0.240	0.228
100	0.994	0.849	7.76	1.56×10^{-3}	0.0941	0.968	7.90×10^{-3}	6.92	5.56×10^{-3}	0.978	0.138	0.418
200	0.924	1.97	12.7	4.74×10^{-4}	0.121	0.972	1.55×10^{-2}	11.6	4.84×10^{-3}	0.978	0.380	0.645

C_0 (mg/dm^3); q_1,q_2 (mg/g); k_2 (g/mg min); h (mg/g min); k_1 (1/min); k_i (mg/g min$^{0.5}$).

Table 4
Parameters for the effect of temperature for BB69

T	r_2^2	SE	q_2	k_2	h	r_1^2	SE	q_1	k_1	r_i^2	SE	k_i
18	0.998	9.02×10^{-3}	201	3.25×10^{-4}	13.1	0.958	6.23×10^{-2}	117	1.16×10^{-2}	0.930	12.0	13.9
40	0.999	4.57×10^{-3}	215	5.56×10^{-4}	25.6	0.947	8.23×10^{-2}	120	1.13×10^{-2}	0.855	15.7	12.1
60	0.999	4.62×10^{-3}	217	9.92×10^{-4}	46.9	0.960	8.00×10^{-2}	126	1.02×10^{-2}	0.832	12.0	8.49
80	0.999	5.35×10^{-3}	226	1.68×10^{-3}	85.9	0.955	9.64×10^{-2}	140	7.24×10^{-3}	0.941	3.62	4.58

T (°C); q_1,q_2 (mg/g); k_2 (g/mg min); h (mg/g min); k_1 (1/min); k_i (mg/g min$^{0.5}$).

Table 5
Parameters for the effect of temperature for AB25

T	r_2^2	SE	q_2	k_2	h	r_1^2	SE	q_1	k_1	r_i^2	SE	k_i
18	0.994	0.393	8.57	3.03×10^{-3}	0.223	0.973	0.0345	4.49	1.08×10^{-2}	0.981	0.286	0.644
40	0.997	0.353	6.24	1.18×10^{-2}	0.461	0.980	0.0446	6.60	7.88×10^{-3}	0.932	0.345	0.406
60	1.00	0.0777	5.64	2.63×10^{-2}	0.839	0.910	0.112	6.92	5.56×10^{-3}	0.812	0.451	0.298
80	0.999	0.228	4.53	5.13×10^{-2}	1.05	0.934	0.105	7.82	3.78×10^{-3}	0.888	0.186	0.166

T (°C); q_1,q_2 (mg/g); k_2 (g/mg min); h (mg/g min); k_1 (1/min); k_i (mg/g min$^{0.5}$).

For the rate constant of the pseudo-second order chemical sorption process,

$$\frac{dq_t}{dt}=k_2(q_2-q_t)^2 \tag{3}$$

integrating this for the boundary conditions $t=0$ to $t=t$ and $q_t=0$ to $q_t=q_t$, gives:

$$\frac{1}{(q_2-q_t)}=\frac{1}{q_2}+k_2t \tag{4}$$

where q_2 is the amount of dyes sorbed at equilibrium (mg/g) and k_2 is the equilibrium rate constant of pseudo-second order chemical sorption (g/mg min). Again q_2 should equal the experimentally obtained equilibrium capacity for this model to be valid.

Eq. (4) can be rearranged to obtain a linear form of

$$\frac{t}{q_t}=\frac{1}{k_2q_2^2}+\frac{1}{q_2}t \tag{5}$$

The straight line plots of t/q_t against t have also been tested to obtain rate parameters. The k_2, q_2, correlation coefficients, r_2^2, values and standard error (SE), of dyes under different conditions were calculated from these plots and are given in Tables 1–5.

The initial sorption rate is

$$h=kq_e^2 \tag{6}$$

For the rate constant of intraparticle diffusion,

$$q_t=k_it^{0.5} \tag{7}$$

where k_i is intraparticle diffusion rate constant (mg/g min$^{0.5}$). The k_i values under different conditions were calculated from the slopes of the straight line portions of the respective plots and are given in Tables 1–5.

3.1.1. Effect of agitation

A series of contact time experiments were undertaken at various degrees of agitation and the results shown in Fig. 1 which shows plots of the amount of dye adsorbed per gram of peat, q_t, against time, t, for the sorption of Basic Blue 69, BB69, onto peat in which the degree of agitation was varied from 200 to 800 rpm. In all the experiments for the effect of agitation, the initial BB69 concentration was 200 mg/dm^3, the peat dose was 10 g/dm^3 and the peat particle size range was 710–1000 μm. The values of the rate constant, k_2, are increasing slightly from 5.79×10^{-3} to 7.70×10^{-3} g/mg min with an increase in the agitation rate. The values of initial sorption rate, h, were found to increase from 0.623 to 1.13 mg/g min; and the values of the equilibrium sorption capacity, q_2, were found to increase from 10.4 to 12.1 mg/g, for an increase in the agitation speed from 200 to 800 rpm, respectively. It is clear that the degree of agitation influences the sorption rate as the agitation rate increases from 200 to 400 rpm.

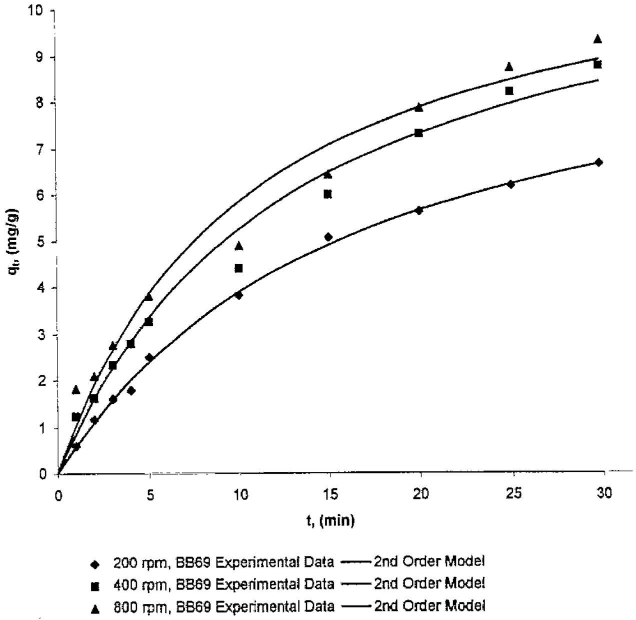

Fig. 1. Effect of agitation on the sorption of BB69 onto peat.

However, at 200 rpm the peat particles are not fully suspended in the solution. Fig. 1 shows the difference between 400 rpm and 800 rpm is much less significant. At the two higher agitation rates the sorption capacities only differ to a small extent and these data were only analysed for the initial 30 min of the sorption process. The effect of increasing agitation is to decrease the boundary layer resistance to mass transfer [31]. Since the change in the magnitude of all the k values is less than 1.3 mg/g min$^{0.5}$ for the diffusion parameter k_i then this is probably the best representation for the effect of the small change due to boundary layer resistance. From Fig. 1, the effect of a 2-fold change in agitation speed from 400 to 800 rpm has only a small influence on the two sets of experimental data, indicating that external mass transfer has only a small influence on the dye sorption kinetics.

3.1.2. Effect of initial concentration

The experimental results of sorption of BB69 on peat at various concentrations are shown in Fig. 2. The sorption capacity at equilibrium increases from 23.8 to 195 mg/g with an increase in the initial dye concentration from 50 to 500 mg/dm^3 and an increase from 1.85 to 12.7 mg/g in the equilibrium sorption capacity with an increase in the initial concentration from 20 to 200 mg/dm^3 for AB25. It is clear that the sorption capacity of basic dye is always much higher than acid dye in the peat sorption system. Similar results were observed by Ho and McKay [32] for the sorption capacity of basic dye, BB69, and acid dye, AB25 onto pith. The rate constants, k_1, k_2 and k_i obtained from the plots of Eq. (1)Eqs. (3) and (4), are shown in Tables 2 and 3. Fig. 3 shows a plot of the linearised form of the pseudo-first order model in Eq. (2) for the sorption of AB25 onto peat at different initial dye concentrations. The best fit straight lines for the initial 60 min have been analysed. Fig. 4 shows the best fit straight line plots of the amount AB25 sorbed per unit weight of peat against square root of time for the initial 60 min. The results are also shown in Fig. 5 as a plot of t/q_t against time for

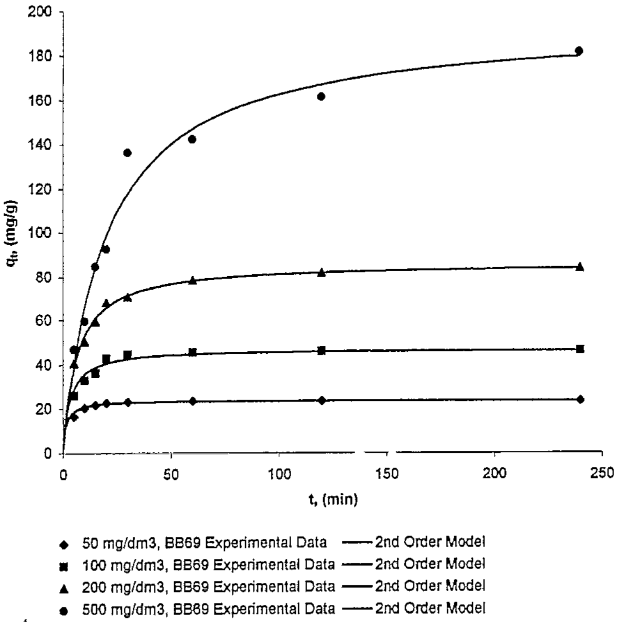

Fig. 2. Effect of initial concentration on the sorption of BB69 onto peat.

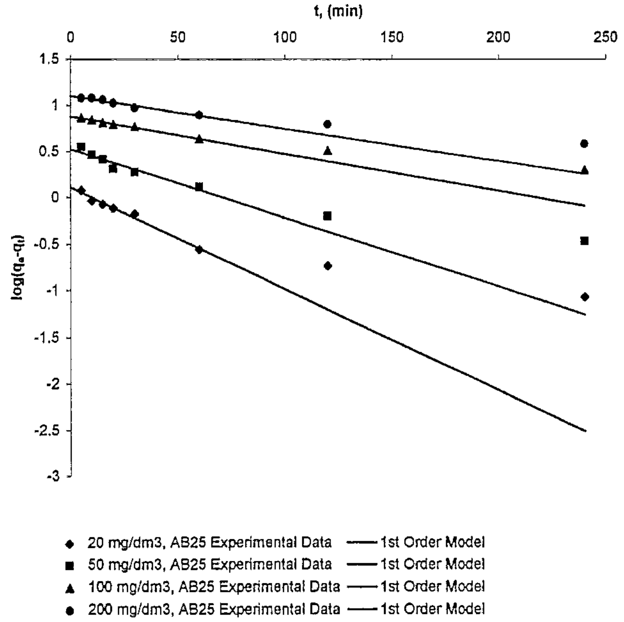

Fig. 3. Pseudo-first order sorption kinetics of AB25 onto peat at various initial concentrations.

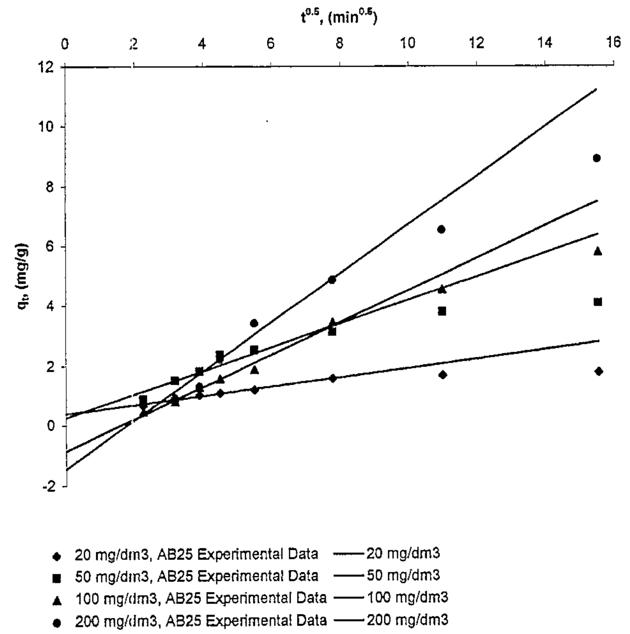

Fig. 4. Intraparticle diffusion kinetics of AB25 onto peat at various initial concentrations.

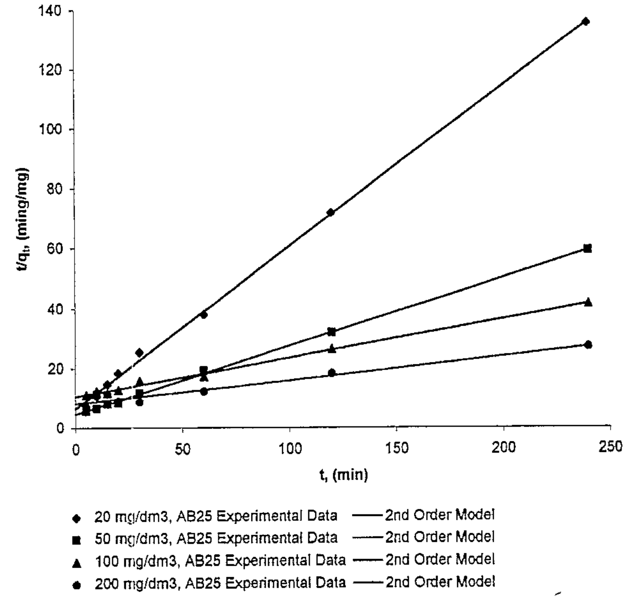

Fig. 5.

sorption of AB25 for the pseudo-second order model and there are good fit straight lines for all of the experimental data. Tables 2 and 3 also indicates that the regression coefficients for the linear plots from the pseudo-second order equation are much better than those obtained for the first order equation in the case of Basic Blue 69.

Although, in the case of Acid Blue 25, there is a good correlation coefficient, r_1^2, for the application of the first order model, all the intercepts of the straight line plots of $\log(q_1-q_t)$ against t do not give values equal to $\log(q_1)$ or even reasonably close values. The reaction is therefore not likely to be a first order reaction. It is clear that the correlation coefficients for the first order analyses are lower than those for the second order model analyses in most of cases in this studies. The correlation coefficients, r_2^2, for the pseudo-second order kinetic model are greater than the intraparticle diffusion coefficients for the sorption of BB69 and AB25 onto peat, strongly suggesting an activated sorption mechanism which could occur because of the chemical character of peat.

3.1.3. Effect of temperature

The temperature dependence of sorption was studied with a constant initial dye concentration of 500 mg/dm^3 for BB69 and 100 mg/dm^3 for AB25, peat dose 2 g/dm^3 for BB69 and

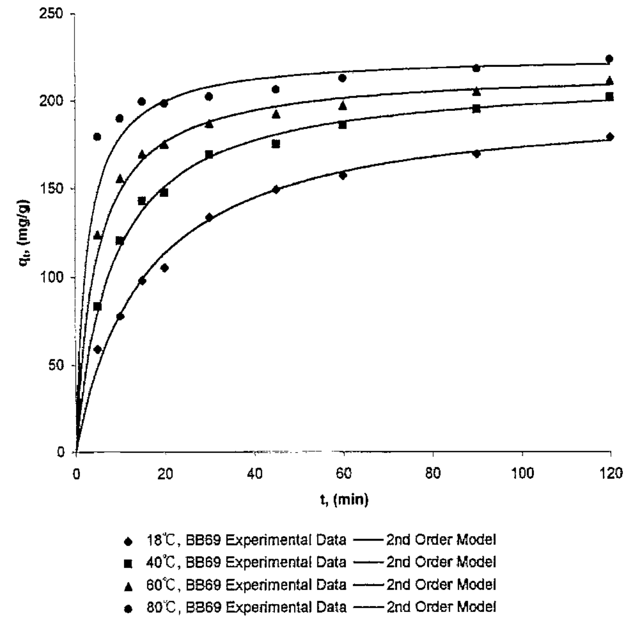

Fig. 6. Effect of temperature on the sorption of BB69 onto peat.

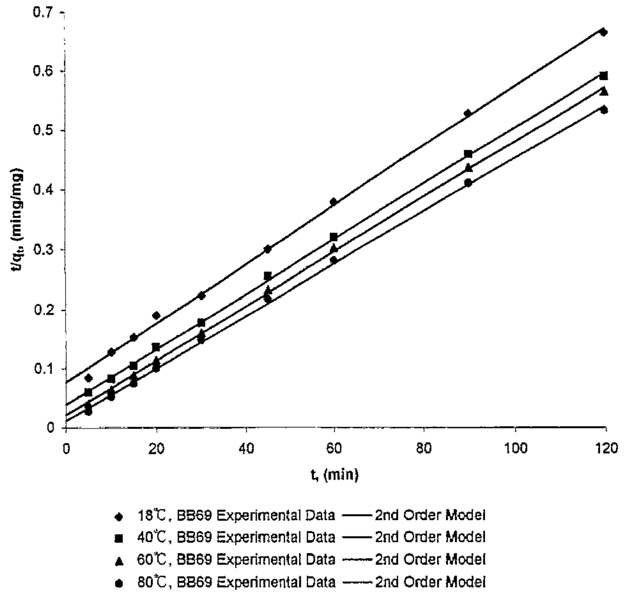

Fig. 8. Pseudo-second order sorption kinetics of BB69 onto peat at various temperatures.

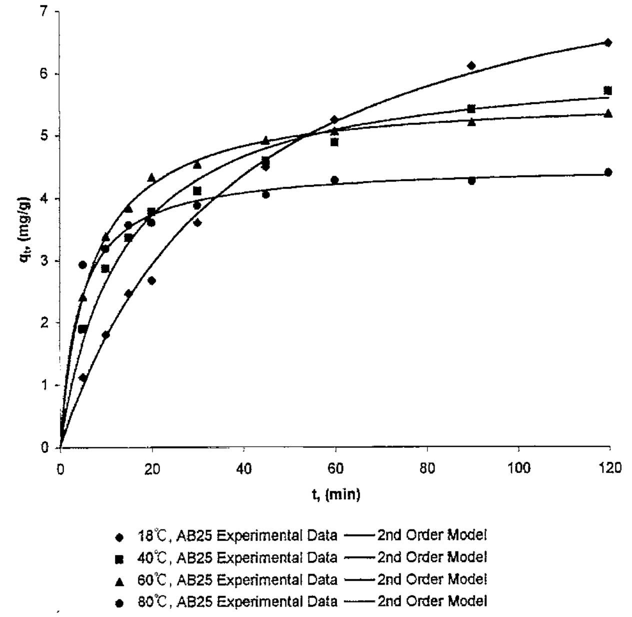

Fig. 7.

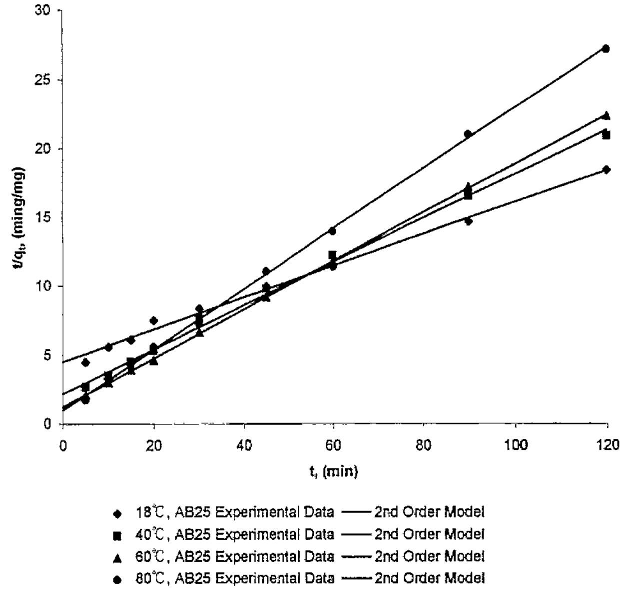

Fig. 9. Pseudo-second order sorption kinetics of AB25 onto peat at various temperatures.

10 g/dm^3 for AB25 at various sorption temperatures and shown in Figs. 6 and 7. Figs. 8 and 9 show good compliance with the pseudo-second order equation. The experimental points are shown together with the theoretically generated lines. The agreement between the sets of data are reflected by the extremely high correlation coefficients obtained and these values are shown in Tables 4 and 5.

The initial sorption rate, h, increases with an increase in the temperature. Tables 4 and 5 show that h varies from 13.1 to 86.0 mg/g min for BB69; and h varies from 0.223 to 1.05 mg/g min for AB25, respectively for a temperature variation from 18°C to 80°C. On increasing the temperature from 18 to 80°C, the specific sorption at equilibrium, q_2, increased from 201 to 226 mg/g for BB69. However there is a decrease in capacity from 8.57 to 4.53 mg/g for the sorption of AB25 over the same temperature range. The increase in the equilibrium sorption of BB69 with temperature indicates that a high temperature favors BB69 removal by adsorption on peat. A similar increasing was observed by Ho and McKay [32] with increasing temperature from 20 to 80°C in the case of sorption of BB69 and AB25 onto pith. The sorption of BB69 by peat may involve not only physical but also chemical sorption. This effect may be due to the fact that at higher temperatures, an increase in free volume occurs due to increased mobility of the solute [33]. However in the case of AB25 the increase in the equilibrium sorption of AB25 with temperature indicates that a low temperature favors AB25 removal by sorption on peat, since an elevation in temperature increases the escaping tendency of AB25 from an interface. This effect suggests that an explanation of the sorption mechanism associated with the removal of AB25 onto peat involves a physical process. Both dye/peat systems show extremely high reaction correlation coefficients, r_2^2, which are all greater than 0.994. The intraparticle coefficients, r_i^2, are much lower than r_2^2 and the pseudo-second order analysis also produces lower r_1^2. The pseudo-second order rate constants for both of dye BB69 and AB25 on peat system show a steady increase with temperature. The high r_2^2 values suggest the BB69/peat system may be an activated or chemisorption process.

The values of rate constant, k_2, were found to increase from 3.25×10^{-4} to 1.68×10^{-3} g/mg min, for an increase in the solution temperature from 293 to 353 K for the sorption of BB69 and from 3.03×10^{-3} to 5.13×10^{-2} g/mg min, for an increase in the solution temperature from 293 to 353 K for the sorption of AB25. There is a linear relationship between the pseudo rate constant and temperature with correlation coefficients of 0.993 for BB69 and 0.992 for AB25. The k values were plotted as a function of the reciprocal of the Kelvin temperature. Linear variations were observed as shown in Fig. 10. Therefore, the sorption rate constant may be expressed as a solution function of temperature by the following relationship:

$$k_2=k_0\exp\left(\frac{-E}{RT}\right) \tag{8}$$

where k_2 is the rate constant of sorption (g/mg min); k_0 is the temperature independent factor (g/mg min); E is activation energy of sorption (kJ/mol); R is the gas constant (8.314 J/mol K); T is solution temperature (K).

Therefore, the relationship between k_2 and T can be represented in an Arrhenius form as: for BB69,

$$k_2=3.73\exp\left(\frac{-227\times10^3}{8.314T}\right) \tag{9}$$

and for AB25,

$$k_2=3.12\times10^4\exp\left(\frac{-38.8\times10^3}{8.314T}\right) \tag{10}$$

From this equation, the rate constants of sorption, k_0, is 3.73 g/mg min for BB69 and 3.12×10^4 g/mg min for AB25 as well as the activation energy of sorption while E is 22.7 kJ/mol for the sorption of BB69/peat and 38.8 kJ/mol for the sorption of AB25/peat. 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 dye on peat and AB25 dye on peat involve some chemical sorption.

3.2. Equilibrium isotherms

The analysis of the isotherm data is important to develop an equation which accurately represents the results and which could be used for design purposes. A series of Langmuir isotherms with operating lines were determined at temperatures of 18, 40, 60 and 80°C, respectively and results are shown in Fig. 11 for AB25.

The operating line is the line which predicts the time dependence of a sorption process and integrates this dependence into the equilibrium isotherm. The dye material balance equation for the batch dynamic studies is:

$$(C_0-C_t)V=(q_t-q_0)m \tag{11}$$

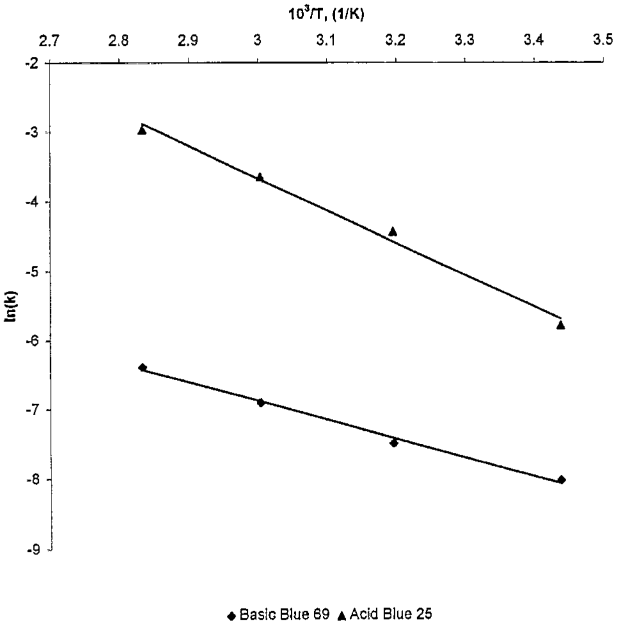

Fig. 10. Plot of ln(k) against reciprocal temperature for BB69 and AB25 sorption on peat.

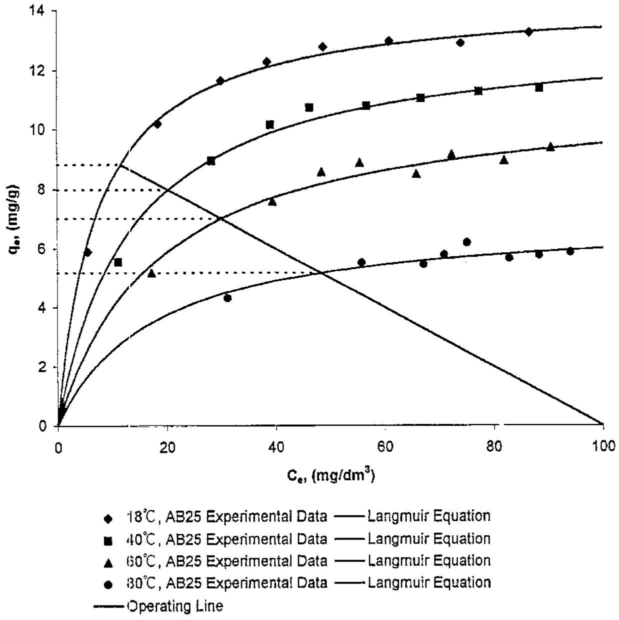

Fig. 11. Langmuir isotherms of Acid Blue 25 onto peat at various temperatures.

At equilibrium, this becomes:

$$(C_0-C_e)V=(q_e-q_0)m \tag{12}$$

For fresh peat, $q_0=0$ mg dye/g peat. Rearranging Eq. (12) gives:

$$\frac{(q_e-q_0)}{(C_0-C_e)}=\frac{V}{m} \tag{13}$$

or

$$q_e=-\frac{V}{m}C_e+\frac{V}{m}C_0 \tag{14}$$

This material balance provides the operating line equation in Fig. 11, using an Acid Blue 25 initial concentration of 100 mg dye/dm^3 a peat mass of 0.5 g and dye solution volume of 0.05 dm^3.

The initial and final coordinates of the operating line are (C_0, $q_0=0$) and (C_e, q_e) with a slope of $-V/m$. The significance of this approach for the two pseudo-kinetic model presented in this paper is that q_e (experimental) can be obtained accurately and compared with q_e (model prediction).

The graphs are plotted in the form of dye adsorbed per unit mass of peat, q_2, against the concentration of dye remaining in solution, C_e, with the Langmuir equation. Fig. 11 also shows the operating lines which are generated with a slope of solution volume per peat mass. The final solution concentration is predicted from the point of intersection of operating line on the sorption isotherm, for the sorption of BB69 and AB25. Therefore an expression for the operating line can be obtained as follows: for BB69,

$$q_e=-0.5C_e+250 \tag{15}$$

for AB25,

$$q_e=-0.1C_e+10 \tag{16}$$

The equilibrium sorption capacity, q_2, can be obtained from the operating line or the Langmuir equation. The equilibrium data were analysed according to three isotherm equilibrium models, namely, Langmuir, Freundlich and Redlich–Peterson.

The Langmuir isotherm is represented by Eq. (17):

$$q_e=\frac{X_m a_L C_e}{1+a_L C_e} \tag{17}$$

The linearised form of this equation for plotting and analysis purposes is:

$$\frac{C_e}{q_e}=\frac{1}{X_m a_L}+\frac{C_e}{X_m} \tag{18}$$

or

$$\frac{1}{q_e}=\frac{1}{X_m a_L C_e}+\frac{1}{X_m} \tag{19}$$

The Freundlich expression is based on an exponential relationship and is generally applicable to a heterogeneous surface energy distribution. The equation is shown:

$$q_e=K_F C_e^{b_F} \tag{20}$$

The linear form is:

$$\ln q_e=\ln K_F+b_F\ln C_e \tag{21}$$

The Redlich–Peterson equation incorporates features of the Langmuir and the Freundlich equations and is represented by Eq. (22):

$$q_e=\frac{K_R C_e}{1+a_R C_e^{b_R}} \tag{22}$$

Eq. (22) is linearized as shown by Eq. (23):

$$\ln\left(\frac{K_R C_e}{q_e}-1\right)=\ln a_R+b_R\ln C_e \tag{23}$$

Since this is a three-parameter equation, a minimisation routine is set up to determine the 'best fit' values of K_R, b_R and a_R.

The isotherm constants and their correlation coefficients, r^2, are shown in Tables 6 and 7. Although the Langmuir and Redlich–Peterson equations have similar correlation coefficients, the Langmuir is a simpler equation and therefore easier to use. Consequently, it was selected to predict q_e values in the present work.

The Langmuir results are reasonable when compared with the equilibrium sorption capacity, q_2, which were obtained from the pseudo-second order model. A comparison is made between the equilibrium sorption capacity evaluated from Langmuir equation and the pseudo-second order model in Table 8, which shows both equilibrium sorption capacity evaluated are reasonable in all cases.

In the application of the first order model to the sorption results, the q_e (experimental) and q_e (model), the values

Table 6
Parameters for Langmuir, Freundlich and Redlich–Peterson equations for BB69

T	r^2	X_m	$a_{L,i}$	r^2	K_F	$1/n$	r^2	a_R	b_R	K_R
18	0.998	200	0.0888	0.916	31.5	0.406	0.967	0.446	0.766	31.5
40	0.996	253	0.126	0.789	42.2	0.432	0.866	4.13×10^6	0.568	1.66×10^8
60	0.999	251	0.239	0.868	57.7	0.372	0.979	0.544	0.876	82.6
80	1.000	249	0.444	0.870	71.4	0.343	0.982	1.53	0.817	1.94×10^2

T (°C); X_m (mg/g); $a_{L,i}$ (dm^3/mg); K_F (mg/g)(dm^3/mg)$^{1/n}$; a_R: (dm^3/mg)^{b_R}; K_R (dm^3/g).

Table 7
Parameters for Langmuir, Freundlich and Redlich–Peterson equations for AB25

T	r^2	X_m	$a_{L,i}$	r^2	K_F	$1/n$	r^2	a_R	b_R	K_R
18	0.999	14.4	0.136	0.909	3.99	0.290	1.000	9.61×10^{-2}	1.04	1.66
40	0.997	13.3	0.0737	0.912	2.65	0.344	0.999	2.25×10^{-2}	1.17	0.685
60	0.988	11.3	0.0540	0.913	2.01	0.352	0.995	1.37×10^{-2}	1.21	0.427
80	0.972	7.09	0.0560	0.826	1.68	0.284	0.989	1.14×10^{-2}	1.64	0.181

T (°C); X_m (mg/g); $a_{L,i}$ (dm^3/mg); K_F (mg/g)(dm^3/mg)$^{1/n}$; a_R dm^3/mg^{b_R}; K_R (dm^3/g).

Table 8
Comparison of the equilibrium sorption capacity evaluated from Langmuir equation and the pseudo-second order model

T (°C)	BB69		AB25	
	q_e (mg/g)	q_2 (mg/g)	q_e (mg/g)	q_2 (mg/g)
18	184	201	8.84	8.57
40	222	215	7.97	6.24
60	228	217	6.99	5.64
80	233	226	5.18	4.53

differ by a factor of 2 to 3 which is unreasonable. Furthermore, in the application of the Lagergren pseudo-first order model or multiple first order reaction models, none of the literature sources report this discrepancy [34–38,25,39,40] and, in addition, many of the pseudo order kinetic models fail to report any equilibrium data [41,42]. Consequently, this comparison of equilibrium saturation capacities adds support to the validation of the proposed pseudo-second order model.

4. Conclusion

The sorption of dyes, namely, Basic Blue 69 and Acid Blue 25 onto peat is favoured at higher concentrations of dye solution, and high temperatures for BB69. However in the case of AB25, sorption is favoured at lower temperatures. The kinetics of the sorption process were found to follow a pseudo-second order rate law and equilibrium data agrees well with the Langmuir isotherm. The sorption 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 peat. The activation energy of sorption can be evaluated using the pseudo-second order rate constants. The sorption of BB69 and AB25 by peat are exothermic activated processes. For both dye/peat systems chemical reaction is important and significant in the rate controlling step and for the sorption of dye onto peat the pseudo-second order chemical reaction kinetics provides the best correlation of the experimental data.

5. Nomenclature

AB25	Acid Blue 25 dye
a_L	Langmuir constant in Eq. (17) (dm^3/mg dye)
a_R	Redlich–Peterson constant in Eq. (22), (dm^3/mg)^{b_R}
BB69	Basic Blue 69 dye
b_R	Redlich–Peterson exponent in Eq. (22), dimensionless
C_e	Equilibrium solution phase dye concentration (mg/dm^3)
C_0	Initial solution phase dye concentration (mg/dm^3)
C_t	Solution phase dye concentration at time t (mg/dm^3)
E	Activation energy of sorption (kJ/mol)
h	Initial dye sorption rate (mg dye/g peat min)
K_F	Freundlich equilibrium constant in Eq. (20), (mg/g)(dm^3/mg)$^{1/n}$
K_R	Redlich–Peterson equilibrium constant in Eq. (22) (dm^3/g)
k	Temperature independent factor in Eq. (8) (g peat/mg dye min)
k	Pseudo-first order rate constant (min^{-1})
k	Pseudo-second order rate constant (g peat/mg dye min)
k	Intraparticle diffusion rate parameter [mg dye/peat (min)$^{0.5}$]
m	Mass of sorbent peat (g)
n	Exponent in the Freundlich Eq. (20), dimensionless
q_0	Mass of dye adsorbed onto peat at time zero (mg dye/g peat)
q_1	Equilibrium mass of dye sorbed on peat based on pseudo-first order model prediction (mg dye/g peat)
q_2	Equilibrium mass of dye sorbed on peat based on pseudo-second order model prediction (mg dye/g peat)
q_t	Mass of dye sorbed at time t (mg dye/g peat)
r^2	Statistical correlation coefficient based on least squares best fit analysis of a straight line correlation
R	Gas constant (8.314 J/mol K)
SE	Standard error
t	Contact time (min)
T	Temperature (K, °C)

V Solution volume (dm^3)
X_m Langmuir monalayer sorption saturation capacity (mg/g)

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