

Sorption of dyes and copper ions onto biosorbents

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Abstract

The batch kinetic sorption of copper ions and dyes onto two low-cost biosorbents, peat and pith, has been studied. A 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 concentration, particle size, temperature and sorbent concentration dose. An activation energy of sorption has also been evaluated as 7.13 kJ/mol for the sorption of BB69 onto pith. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Biosorbent; Copper; Dye; Kinetics and sorption

1. Introduction

Increasing limits imposed by Environmental Legislation on the concentrations of pollutants in aqueous effluents make treatment imperative. Adsorption is an attractive method for the removal of solutes from effluents since if the adsorption system is designed correctly it will produce a high-quality treated effluent [1,2]. The sorption process, in comparison with the other listed processes for the treatment of polluted aqueous effluents, allows flexibility in design and operation, and produces aesthetically superior effluent suitable for re-use, free of pollutant. In addition, because adsorption is sometimes reversible, the regeneration of the sorbent with resultant economy of operation may be possible. Adsorption is a physicochemical wastewater treatment process, which has gained prominence as a means of producing quality treated effluents from effluents, which contained low concentrations of dissolved organic compounds and metal ions. Dissolved molecules are attracted to the surface of the adsorbent and this interaction may be expressed both in terms of adsorptive characteristics and physical properties. The most widely used adsorbent is activated carbon but it is expensive and if lower cost adsorbents could be found it would

reduce adsorption process costs. Several of the alternatives which have been investigated are activated silica, activated alumina, peat, wood, lignite, bagasse pith, waste red mud and fly ash. Consequently in the present paper, two low-cost adsorbents, namely peat and pith have been used to treat two common effluents—a copper ion containing effluent and two dye containing effluents.

Peanut hull has been used to sorb copper ions [3] and agricultural waste has been used for the same purpose [4]. Over 100 sorption systems for copper uptake onto plants, fungi, algae and several other sorbents have been reported [5–7]. Activated silica has been shown to be useful in treating textile mill effluent [8] and to remove basic dyes using a fluidised bed system [9] and its economic viability is enhanced by the possibility of its regeneration and re-use. Activated alumina has also been investigated for removing phosphates from wastewaters [10]. Peat has been used to sorb heavy metal ions [11,12]. A considerable amount of research work has been done recently on the adsorption of dyes on both peat and wood [13–19]. In search for cheaper adsorbents, it was decided to undertake a study to assess the potential of bagasse pith as an adsorbent for dyestuffs and sphagnum moss peat for metal ion removal. Bagasse pith is a waste product from the sugarcane industry. Waste banana pith [20] has been used for colour removal from wastewaters, and waste red mud [21] has been used to adsorb Congo Red dye.

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Table 1
Chemical analysis of the bagasse pith

Determination	%
α -Cellulose	53.7
Pentosan	27.9
Lignin	20.2
Alcohol/benzene solubility	7.5
Ash	6.6

In order to design sorption treatment systems, a knowledge of kinetic/diffusion processes is essential. The simpler the model, the easier and more economic becomes the design procedure but accuracy should not be sacrificed. This paper uses two models—one reaction kinetic-based and another intraparticle diffusion-based models to analyse sorption data for three systems. The three systems studied are copper onto peat, Acid Blue 25 (AB25) dye and Basic Blue 69 (BB69) dye onto pith.

2. Materials and methods

2.1. Materials

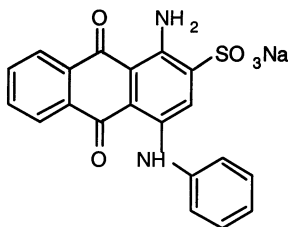
The sphagnum moss peat used in this study, which was from northern Ireland, was obtained from a local Garden Centre. It was dried at 105 °C for 24 h and then screened through a 14-mesh sieve (B.S. 410/43) before being used. The Egyptian bagasse pith was provided by Abou-Korkas sugar mill (El-Minia, Egypt). The pith particles were sieved in the laboratory into various particle size ranges.

The bagasse pith had the compositions based on a chemical analysis, as shown in Table 1.

2.1.1. Sorbates

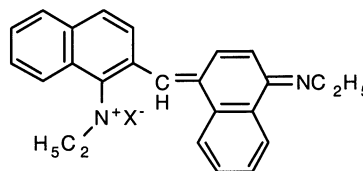
The sorbates used in the experiments and their structures are listed below. The dyestuffs were used as the commercial salts.

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:



2.2. Methods

The sorption of copper ions onto peat and BB69 and AB25 dyes onto pith were carried out by batch sorption and the variables studied were initial sorbate concentration, particle size and temperature. Samples were withdrawn at suitable time intervals and were filtered and their concentrations determined by spectrophotometry for the dyes and an atomic absorption spectrophotometer for copper. The effect of concentration of dye solution on the sorption was studied by contacting a fixed mass of pith (1.7 g for BB69 and 3.4 g for AB25) at a fixed particle size (500–710 μm) with 1.7 dm^3 of solution in a range of concentration (200–300 mg/dm^3 for BB69 and 100–166 mg/dm^3 for AB25) using a fixed impeller speed (400 rpm) at a fixed temperature (20 °C).

The effect of concentration of copper solution on the sorption was studied in capped conical flasks (500 ml), by suspending the peat in the copper ion solution, adjusting the pH to a value of 5 with either sulphuric acid or sodium hydroxide solution and mixing on a shaker with a constant speed of 100 rpm.

The effect of particle size on sorption was studied by contacting a fixed mass of pith (1.7 g for BB69 and 3.4 g for AB25) at a range of particle sizes (500–710, 355–500, 500–710 and 710–1000 μm) with 1.7 dm^3 of a dye solution of a fixed initial concentration (200 mg/dm^3 for BB69 and 100 mg/dm^3 for AB25) using a fixed impeller speed (400 rpm) at a fixed temperature (20 °C).

The effect of temperature on dye sorption was studied by contacting a fixed mass of pith (1.7 g for BB69 and 3.4 g for AB25) at a fixed particle size (500–710 μm) with 1.71 dm^3 of a dye solution of a fixed concentration (200 mg/dm^3 for BB69 and 170 mg/dm^3 for AB25) using a fixed impeller speed (400 rpm) at a range of temperatures (20, 40, 60 and 80 °C).

The effect of pith dose on sorption was studied by contacting a fixed particle size (500–700 μm) at a range of pith dosages (0.25–0.75 g/dm^3 for BB69 and 0.5–1 g/dm^3 for AB25) with 1.7 dm^3 of a dye solution of a fixed initial concentration (200 mg/dm^3 for BB69 and 100 mg/dm^3 for AB25) using a fixed impeller speed (400 rpm) at a fixed temperature (20 °C).

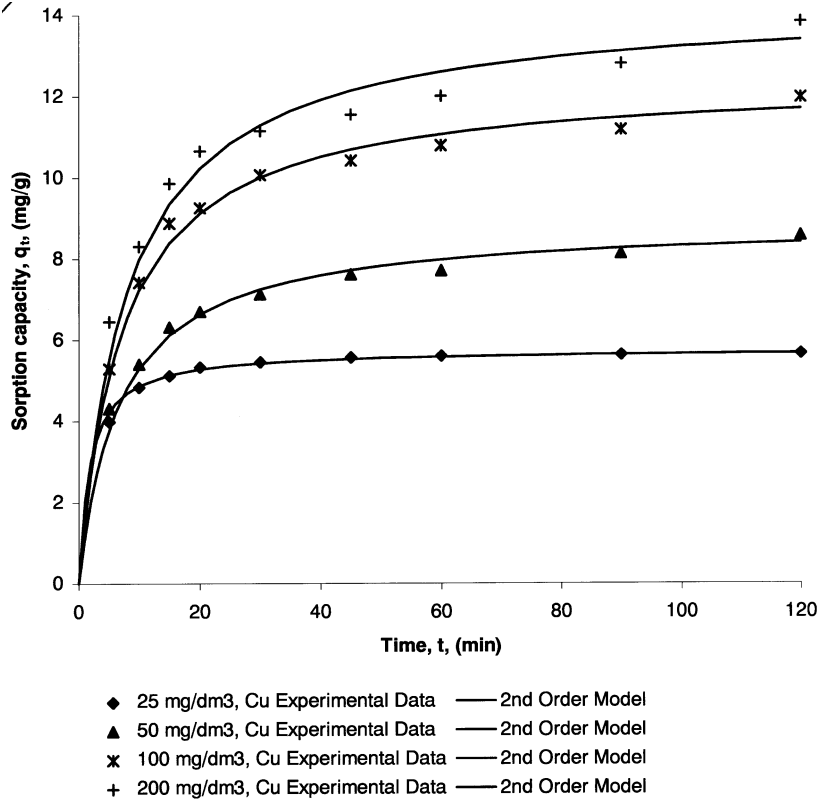


Fig. 1. Effect of initial concentration on the sorption of copper onto peat.

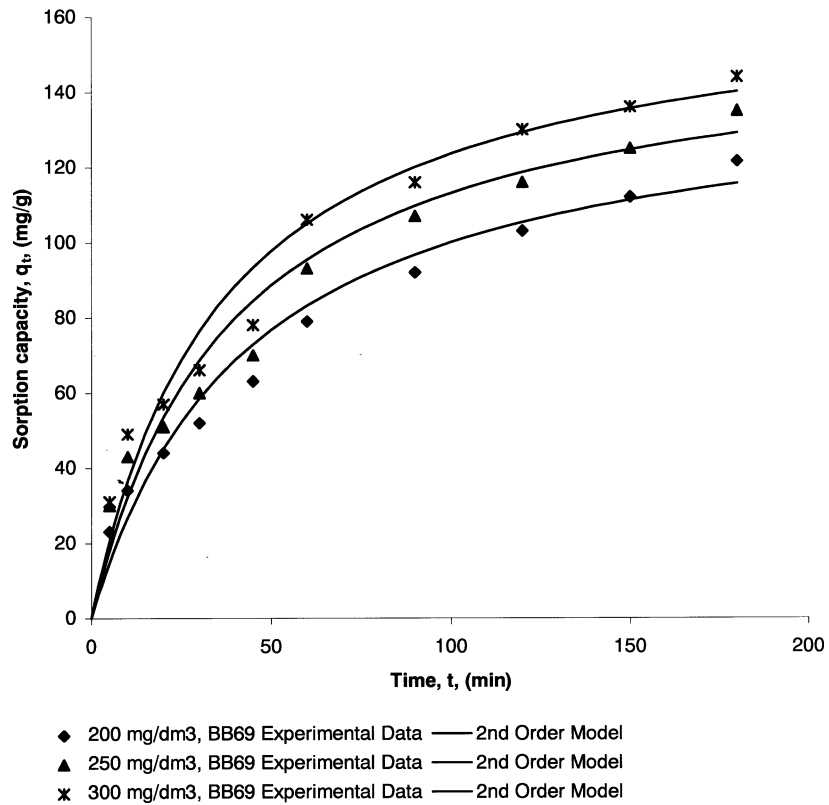


Fig. 2. Effect of initial concentration on the sorption of BB69 onto pith.

Table 2
Effect of initial concentration of copper, AB25 and BB69

	C_0 (mg/dm ³)	r^2	q_e (mg/g)	k (g/(mg min))	h (mg/(g min))	R_c (%)	r_i^2	k_i (mg/(g min ^{0.5}))
Cu	25	1.00	5.75	9.64×10^{-2}	3.19	92.0	0.630	0.147
	50	0.999	8.87	1.68×10^{-2}	1.32	70.9	0.865	0.429
	100	0.998	12.4	1.13×10^{-2}	1.73	49.5	0.818	0.634
	200	0.996	14.3	8.91×10^{-3}	1.81	28.5	0.874	0.720
BB69	200	0.974	1.44×10^2	1.59×10^{-4}	3.29	71.8	0.995	8.86
	250	0.972	1.57×10^2	1.66×10^{-4}	4.07	62.7	0.986	9.55
	300	0.978	1.68×10^2	1.65×10^{-4}	4.67	56.0	0.976	10.3
AB25	100	0.979	11.2	1.83×10^{-3}	0.232	22.5	0.986	0.700
	129	0.963	12.1	1.86×10^{-3}	0.270	18.7	0.978	0.744
	166	0.954	14.4	1.19×10^{-3}	0.246	17.3	0.983	0.881

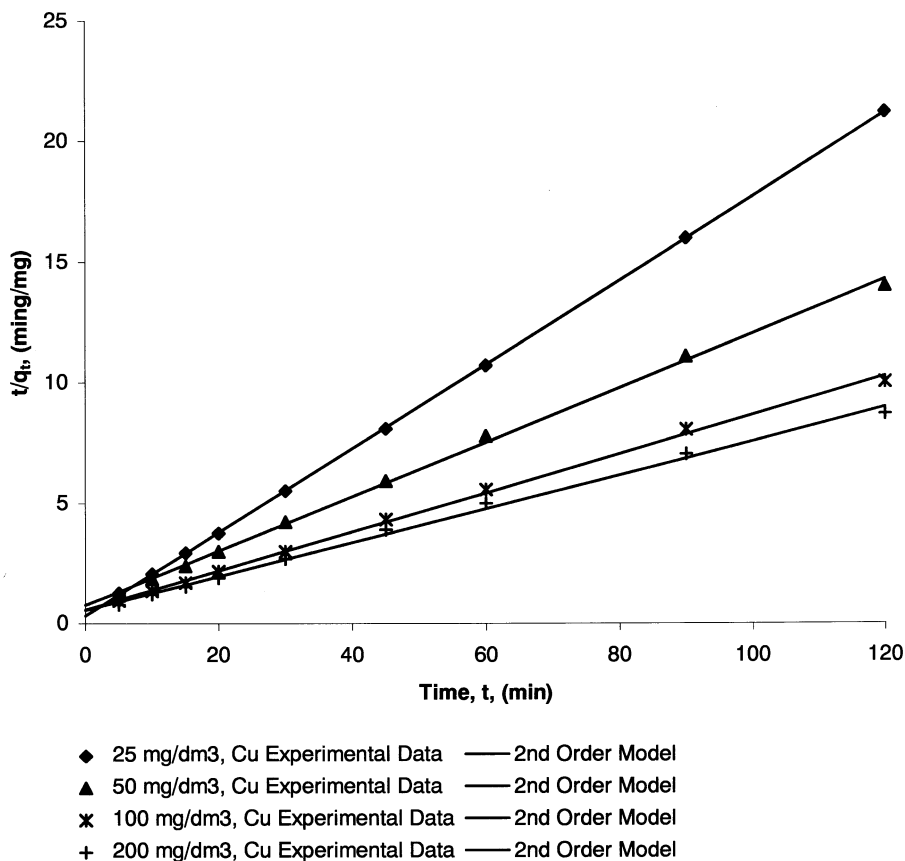


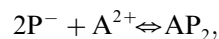
Fig. 3. Plot of amount of sorption versus time for copper sorption onto peat at various initial concentrations.

3. Results and discussion

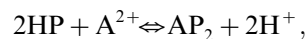
The sorption of pollutants from aqueous solutions plays a significant role in water pollution control. It is therefore important to be able to predict the rate at which contamination is removed from aqueous solutions in order to design an appropriate adsorption treatment plant.

Pith is the name commonly given to parenchyma cells which have the character of fibres and peat contains polar functional groups such as aldehydes, ketones,

acids, and phenolics. These characters of biomaterials can be involved in chemical bonding and are responsible for the cation exchange capacity. Thus, the reaction may be expressed by the following two relationships:



and



where P^- and HP are polar sites on the biosorbent surface and A^{2+} is soluted sorbates.

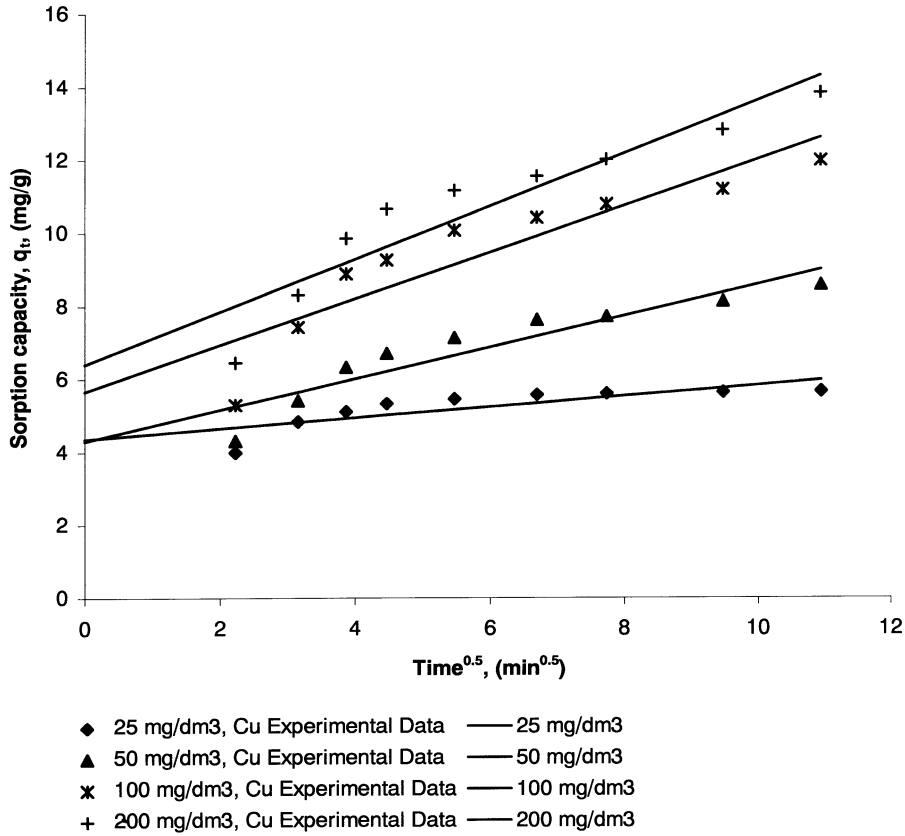


Fig. 4. Plot of sorption capacity versus square root of time for copper sorption onto peat.

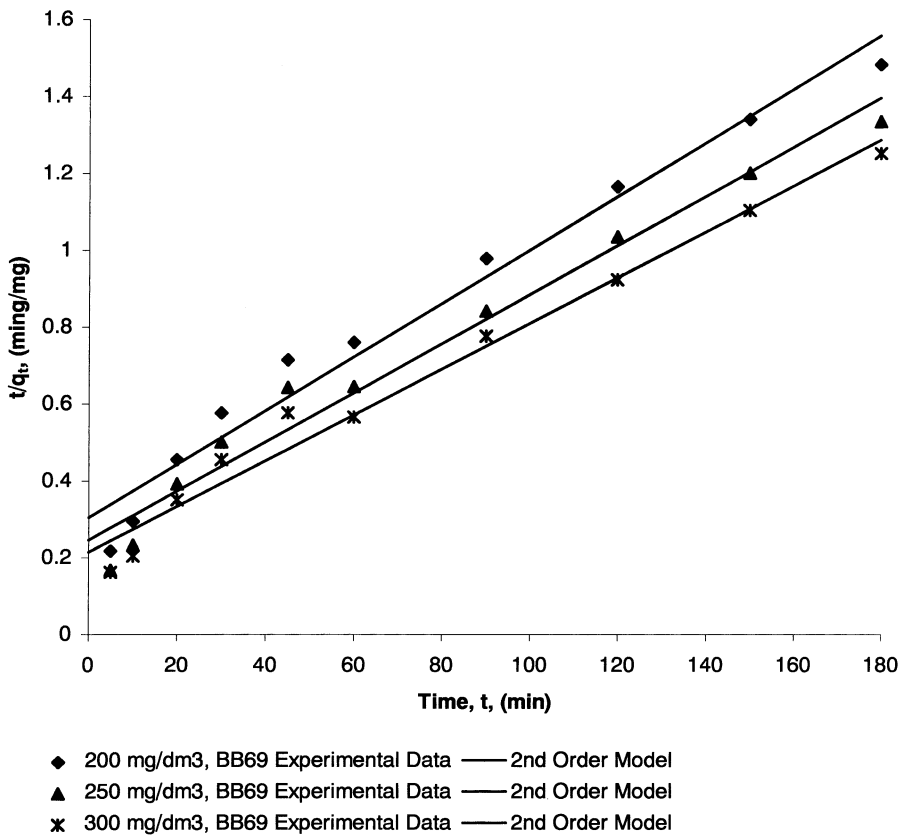


Fig. 5. Plot of amount of sorption versus time for BB69 sorption onto pith at various initial concentrations.

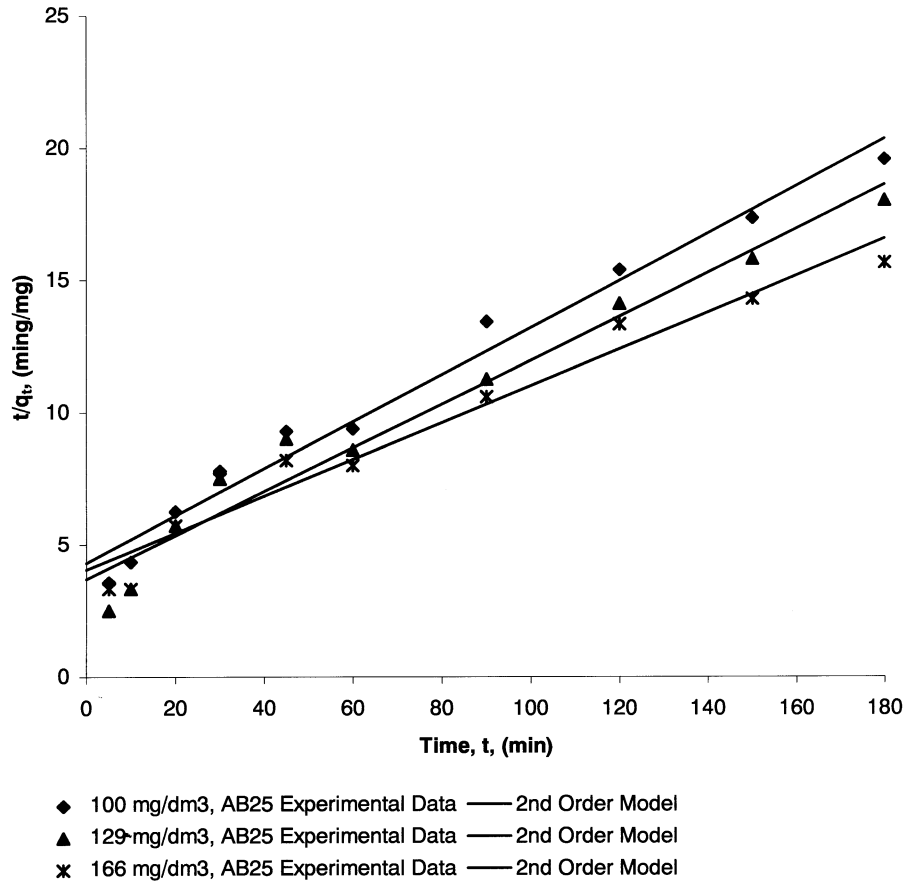


Fig. 6. Plot of amount of sorption versus time for AB25 sorption onto pith at various initial concentrations.

The rate of pseudo-second-order reaction may be dependent on the amount of solute sorbed on the surface of biosorbent and the amount sorbed at equilibrium. The sorption equilibrium, q_e , is a function of, e.g., the temperature, the initial metal ion concentration, the biosorbent dose, particle size and the nature of solute–sorbent interaction.

The rate expression for the sorption described is

$$\frac{d(P)_t}{dt} = k[(P)_0 - (P)_t]^2,$$

or

$$\frac{d(HP)_t}{dt} = k[(HP)_0 - (HP)_t]^2,$$

where $(P)_t$ and $(HP)_t$ are the number of active sites occupied on the biosorbent at time t and $(P)_0$ and $(HP)_0$ are the number of equilibrium sites available on the biosorbent.

The kinetic rate equations can be rewritten as follows:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2,$$

where k is the rate constant of sorption ($g/(mg \text{ min})$), q_e the amount of soluted sorbate at equilibrium (mg/g) and q_t the amount of soluted sorbate on the surface of the biosorbent at any time t (mg/g).

Separating the variables in the equation above gives

$$\frac{dq_t}{(q_e - q_t)^2} = k dt,$$

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

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + kt, \quad (1)$$

which is the integrated rate law for a pseudo-second-order reaction.

The kinetics of sorption of copper, BB69 and AB25 on biosorbents (peat and pith) were studied on the basis of the pseudo-second-order rate equation (1) and

$$h = kq_e^2, \quad (2)$$

where h is the initial sorption rate ($mg/(g \text{ min})$).

Eq. (1) can be rearranged to Eq. (3) which provides a linearised form for plotting as q_t/t versus time t :

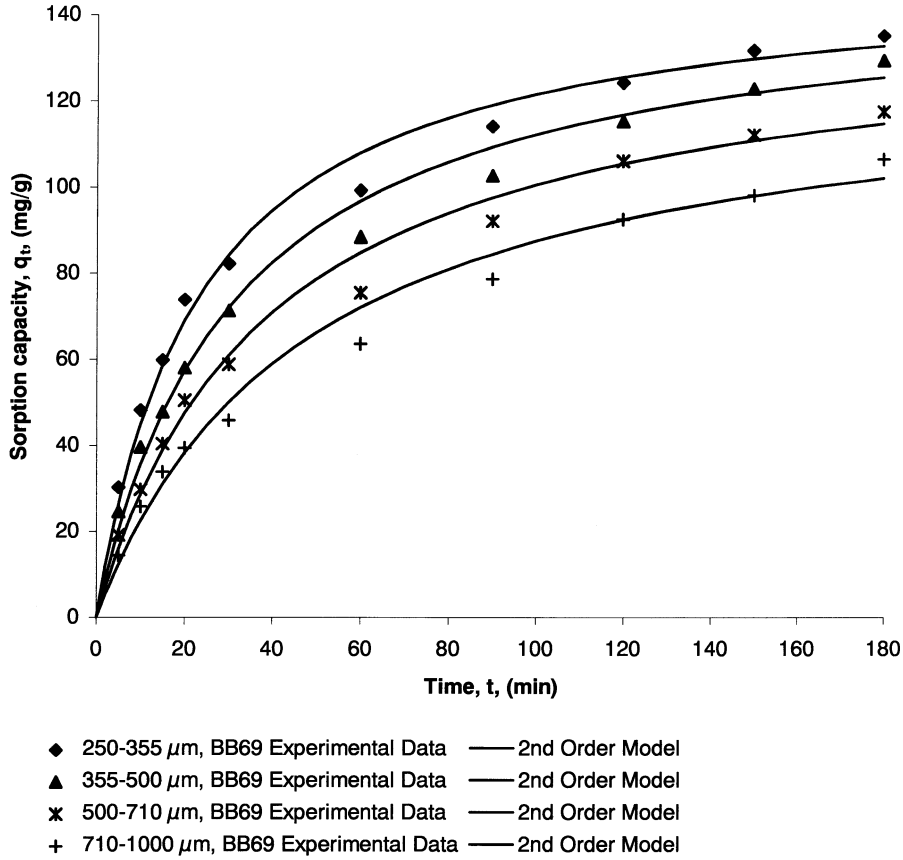


Fig. 7. Effect of pith particle size on the sorption of BB69 onto pith.

Table 3
Effect of particle size of BB69 and AB25

	d_p (μm)	r^2	q_c (mg/g)	k (g/(mg min))	h (mg/(g min))	R_c (%)	r_i^2	k_i (mg/(g min ^{0.5}))
BB69	250–355	0.997	1.50×10^2	2.86×10^{-4}	6.43	74.9	0.956	8.91
	355–500	0.993	1.47×10^2	2.17×10^{-4}	4.70	73.6	0.980	9.12
	500–710	0.991	1.39×10^2	1.87×10^{-4}	3.61	69.6	0.985	8.77
	710–1000	0.984	1.29×10^2	1.65×10^{-4}	2.73	64.3	0.995	8.07
AB25	250–355	0.999	14.3	3.78×10^{-3}	0.769	28.0	0.926	0.820
	355–500	0.997	12.8	3.64×10^{-3}	0.599	25.2	0.926	0.745
	500–710	0.998	11.6	3.13×10^{-3}	0.419	22.7	0.934	0.722
	710–1000	0.995	10.0	2.57×10^{-3}	0.259	19.7	0.968	0.636

$$\frac{t}{q_t} = \frac{1}{kq_c^2} + \frac{1}{q_c} t. \tag{3}$$

3.1. Effect of contact time and initial concentration

Figs. 1 and 2 show the effect of agitation time on the removal of copper ions by peat and BB69 by pith. The results show that an increase in the initial copper and dye concentrations produces a reduction in the percentage removal of copper ions and dyestuff from the

water. The removal of copper decreases from 92.0 to 28.5% with the increase of initial copper ion concentration from 25 to 200 mg/dm³ at pH 5, showing the process to be highly dependent on the initial concentration. The percentage removal of BB69 and AB25 also decreases with an increase in the initial dye concentrations. The removal of BB69 decreases from 71.8 to 56.0% with the increase of initial concentration from 200 to 300 mg/dm³ and for AB25 from 22.5 to 17.3% with the increase of initial dye concentration from 100 to 166 mg/dm³. However, it may be shown that the adsorption capacity varies from 5.75 to 14.3 mg/g, as C_0 varies from

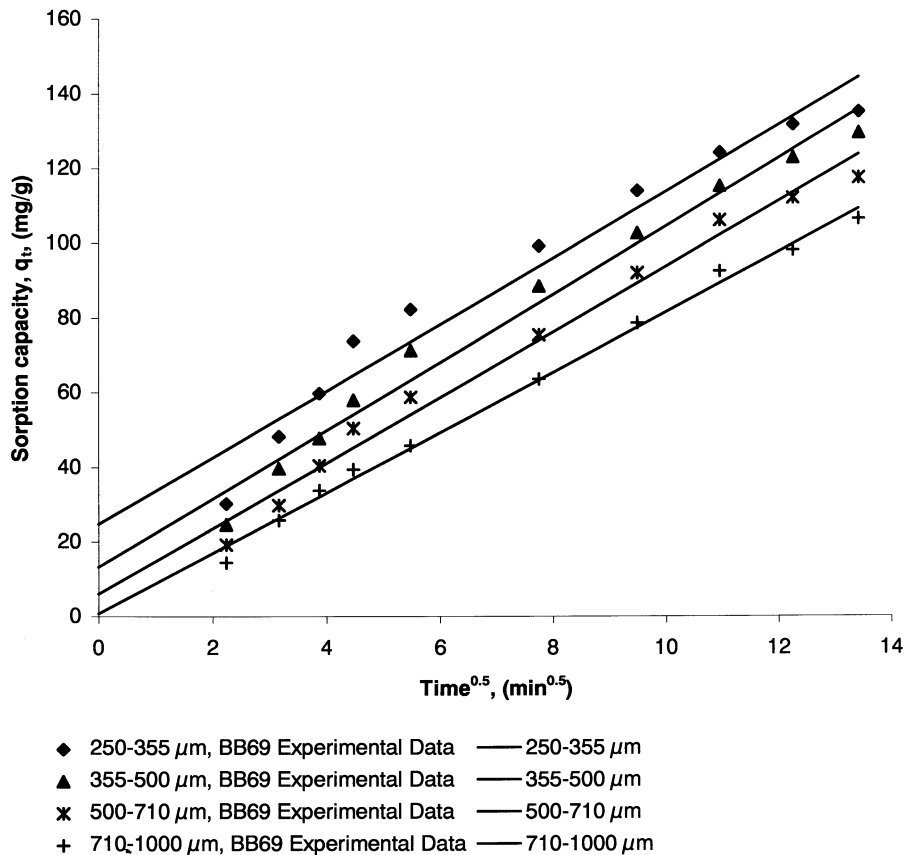


Fig. 8. Plot of sorption capacity versus square root of time for BB69 sorption onto pith.

25 to 200 mg/dm³ for copper; from 144 to 168 mg/g, as C_0 varies from 200 to 300 mg/dm³ for BB69 and from 11.2 to 14.4 mg/g, as C_0 varies from 100 to 166 mg/dm³ for AB25. It is clear that the sorption capacity of basic dye is always much higher than acid dye in the pith sorption system. The rate constants, k , obtained from the plots of Eq. (3), are shown in Table 2. Fig. 3 shows a plot of the linearised form of the model in Eq. (3) for the sorption of copper ions onto peat at different initial copper ion concentrations. Table 2 also indicates that the regression coefficients for the linear plots from the pseudo-second-order equation are better than 0.954 for all systems. The correlation coefficient of the two dye/pith sorption systems are lower than the copper/peat system as shown from data in Table 2.

The nature of the rate-limiting step in a batch system can be assessed from the properties of the solute and sorbent. Weber and Morris [22] stated that if intraparticle diffusion is the rate-controlling factor, uptake of the sorbate varies with the square root of time. Thus, rates of sorption are usually measured by determining the change in concentrations of sorbate with the sorbent as a function of the square root of time. Fig. 4 shows the amount of sorption against square root of time and the straight lines do not pass through the origin; therefore,

intraparticle diffusion also may not be the sole rate-limiting factor [14]. Poots et al. [13] proposed that during the early stages of sorption, some boundary layer resistance was involved. However, for the sorption of copper ions onto peat, the linearised plots of Eq. (3) have a good correlation of the data as shown in Fig. 3. The correlation coefficients, r^2 , for the pseudo-second-order kinetic model are much greater than the intraparticle diffusion coefficients for the sorption/reaction of copper ions onto peat, strongly suggesting a chemical reaction mechanism. In the case of the sorption of the two dyes on pith, the reaction correlation coefficients and the intraparticle diffusion coefficients are all high (>0.95) with most of the r_i^2 -values being slightly higher. This suggests that for dye sorption onto pith, the mechanism is predominantly intraparticle diffusion but the distinction is not completely clear. The overall rate of the sorption process appears to be controlled by the chemical process in the case of copper in accordance with the pseudo-second-order reaction mechanism. For the two dyes, there could be a combination of mechanisms. Eq. (3) has been plotted to show the effect of initial dye concentration for the sorption of BB69 and AB25 in Figs. 5 and 6 respectively.

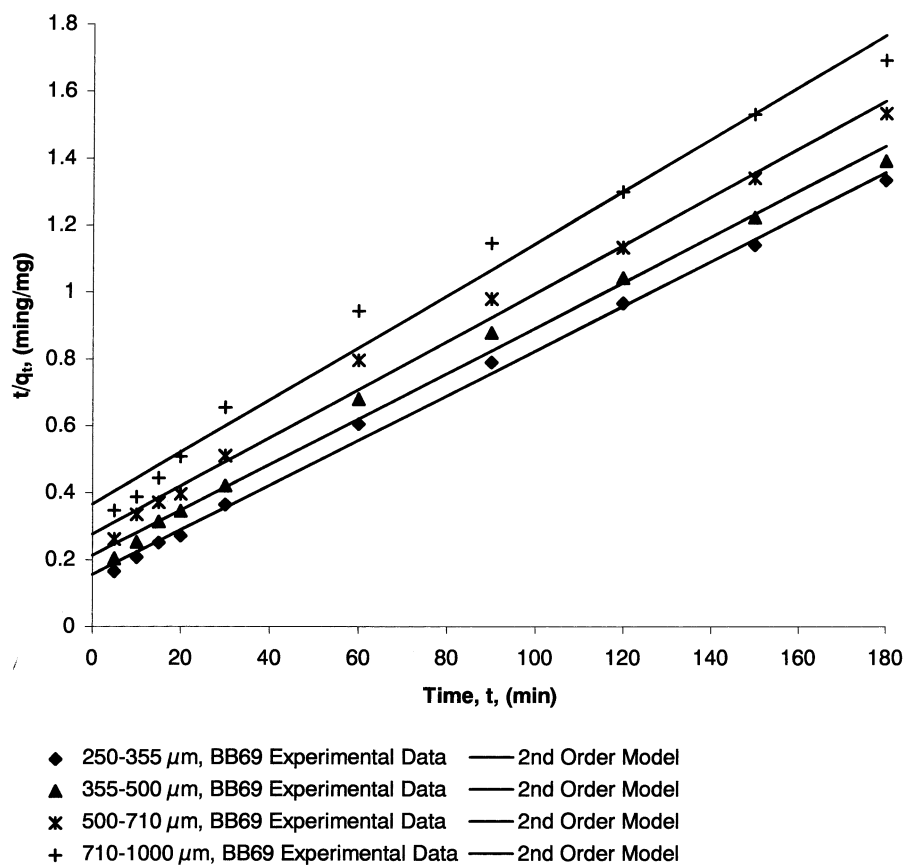


Fig. 9. Plot of amount of sorption versus time for BB69 sorption onto pith at various particle sizes.

3.2. Effect of contact time and particle size of BB69 and AB25

Fig. 7 shows a series of contact time curves with sorbent size ranging from 250–355 to 710–1000 μm of BB69. The removal of BB69 increases from 64.3 to 74.9% and for AB25 the increase in sorption capacity is from 19.7 to 28.0% with the decrease of the pith particle size ranging from 250–355 to 710–1000 μm . This indicates that the smaller the sorbent particle size, then for a given mass pith, more surface area is made available and therefore the number of sites increases. The results are shown in Table 3 for BB69 and AB25. The correlation coefficients, r^2 , and 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. The data show a good compliance with the pseudo-second-order equation and the regression coefficients for the linear plots were higher than 0.984 for all the systems in these studies. The correlation coefficients of the intraparticle diffusion model are given in Table 3 for the effect of contact time and particle size of BB69 and AB25 also and although they are all greater than 0.926, they are significantly lower than the coefficients obtained for the second-order kinetic model.

Fig. 8 shows that plotting the amount sorbed per unit weight of sorbent against square root of time generates best-fit straight lines that do not pass through the origin again indicating that there is an initial boundary layer resistance which decreases as the available external surface area also decreases. Fig. 9 shows a plot of t/q_t against time, t , for the sorption of BB69 onto pith based on the assumption of a pseudo-second-order mechanism. In Table 3, all correlation coefficients are extremely high. The second-order r^2 are decreasing with increasing particle size and the intraparticle correlation coefficients r_i^2 are increasing with increasing particle size. This suggests that if the sorption is a combination of reaction and diffusion-controlled processes, there is a trend towards diffusion control with increasing d_p . This would be expected since the amount of external surface area available for rapid reaction decreases with increasing particle size for constant sorbent mass. Therefore, the reaction has to wait longer for diffusion into the less accessible pores within the particle bonding as the pith particle size increases. A similar, although less pronounced trend can be observed for the effect of increasing particle size on r^2 and r_i^2 for the sorption of AB25 onto pith. The intraparticle diffusion is more likely to be affected by larger dye ions than copper ions, which in size are smaller and more mobile than dye ions.

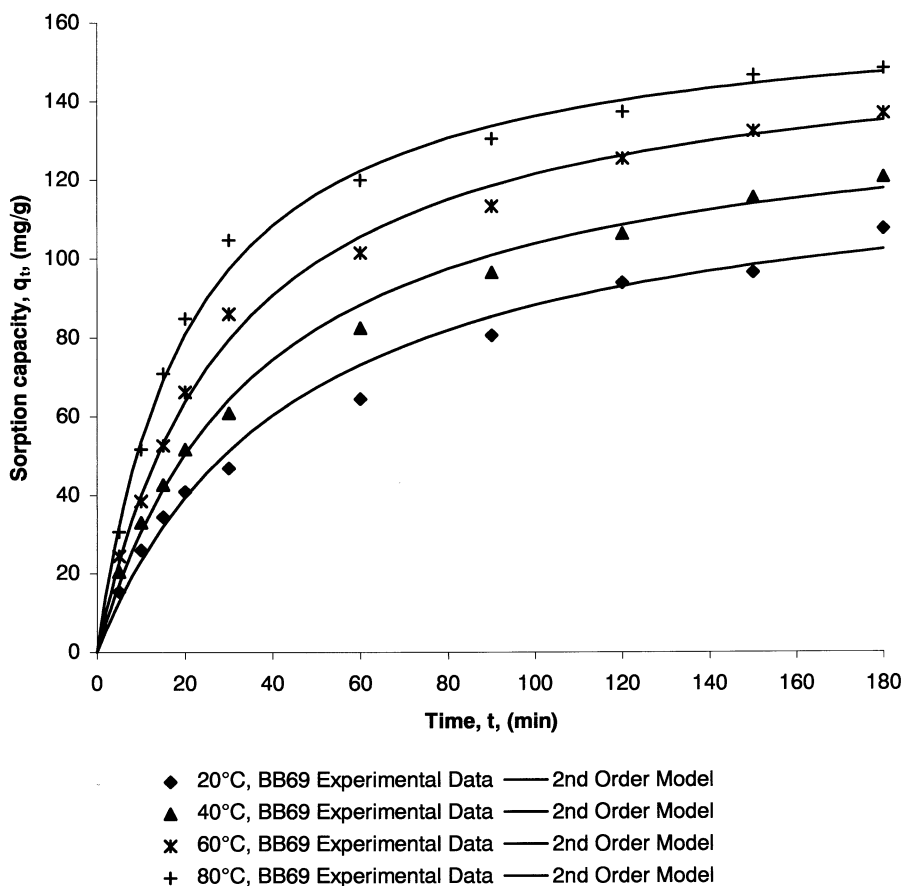


Fig. 10. Effect of temperature on the sorption of BB69 onto pith.

The correlation coefficients of the relation between time/amount sorption and time as defined by Eq. (3) is high for the effect of particle size for the sorption of the two dyes on pith. The sorption process may involve a chemical reaction process and demonstrates that the pseudo-second-order rate constant, k , is a function of surface area of the sorbent.

3.3. Effect of temperature of BB69 and AB25

A series of contact time experiments has been carried out with a constant initial dye concentration of 200 mg/dm³, pith dose 1 g/dm³ with various temperatures of reaction sorption. The increase in the equilibrium sorption of dye with temperature indicates that a high temperature favours dye removal by adsorption on pith. This effect is shown in Figs. 10 and 11. Obviously, the exothermic nature of the reaction in the present process can be explained by this behaviour of the system [23,24]. The sorption of dye by pith may involve not only physical but also chemical adsorption. This effect may be due to the fact that at higher temperatures, an increase in free volume occurs due to increased movement of the solute [25]. This may be due to a relative increase in the tendency of dye molecules to escape from

the solid phase to the bulk phase with increasing temperature of the solution [26]. It may also be due to the dissolution of the sorbing species, changes in the size of the pores, and enhanced rate of intraparticle diffusion of adsorbent [27]. This effect could be explained by assuming that at higher values of temperature, the total energy of the sorbate molecules is increased and consequently their escaping tendency is also increased; therefore, the sorption of lead species is lowered [28]. Thus, on increasing the temperature of the reaction from 20 to 80 °C, the removal of the dye increased from 64.0 to 82.2% for BB69 and 19.7 to 28.7% for AB25. Consequently, it is clear that adsorption equilibrium is temperature-dependent.

Figs. 10 and 11 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 are shown in Table 4.

The results in Table 4 also show the sorption rate constant, k , initial sorption rate, h , and equilibrium sorption capacity, q_e , as a function of solution temperature. Thus, on increasing the temperature from 20 to 80 °C, the specific sorption at equilibrium, q_e , increased

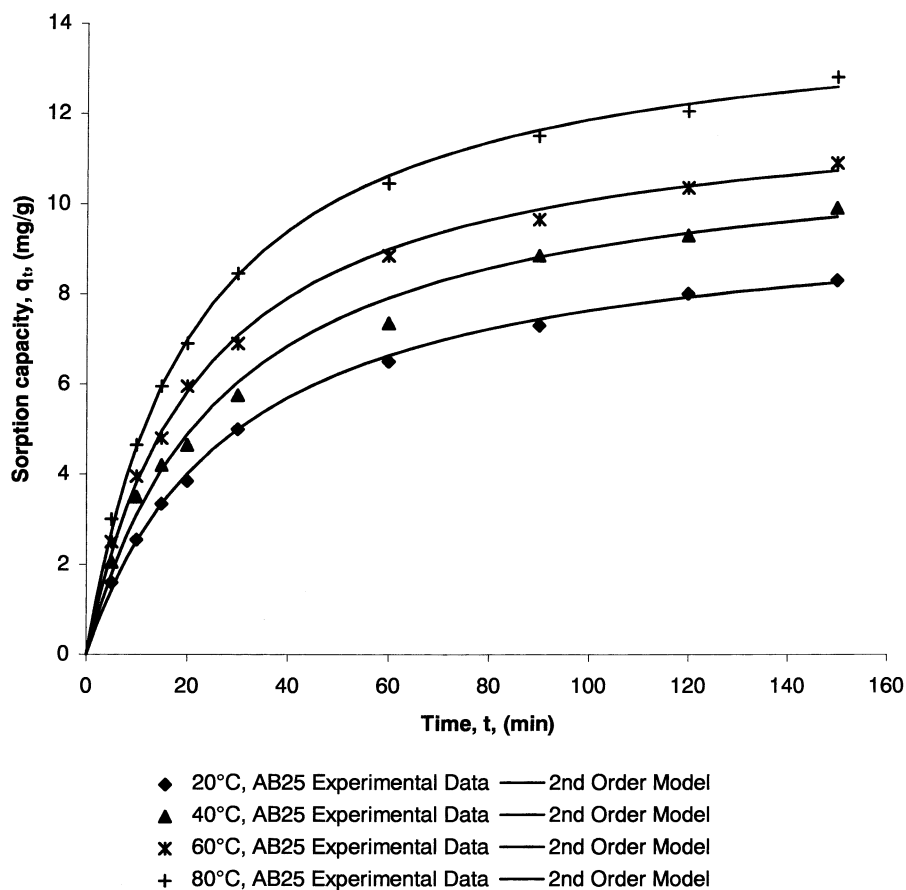


Fig. 11. Effect of temperature on the sorption of AB25 onto pith.

Table 4
Effect of temperature of BB69 and AB25

	T (°C)	r^2	q_e (mg/g)	k (g/(mg min))	h (mg/(g min))	R_c (%)	r_i^2	k_i (mg/(g min ^{0.5}))
BB69	20	0.984	1.28×10^2	1.74×10^{-4}	2.84	64.0	0.992	8.05
	40	0.995	1.41×10^2	1.97×10^{-4}	3.93	70.7	0.984	8.90
	60	0.998	1.57×10^2	2.17×10^{-4}	5.37	78.6	0.946	9.81
	80	0.999	1.64×10^2	2.94×10^{-4}	7.96	82.2	0.900	9.76
AB25	20	0.999	9.84	3.50×10^{-3}	0.339	19.7	0.966	0.671
	40	0.995	11.4	3.27×10^{-3}	0.427	22.9	0.976	0.765
	60	0.999	12.3	3.65×10^{-3}	0.554	24.6	0.952	0.811
	80	0.999	14.4	3.31×10^{-3}	0.682	28.7	0.943	0.940

Table 5
Empirical parameters for predicted q_e and h from T

	A_q	B_q (mg/(g K ^(A_q)))	r^2	A_h	B_h (mg/(g min K ^(A_h)))	r^2
BB69	1.39	4.89×10^{-2}	0.981	5.47	9.07×10^{-14}	0.994
AB25	1.94	1.61×10^{-4}	0.983	3.80	1.46×10^{-10}	0.999

from 128 to 164 mg/g for BB69 and 9.84 to 14.4 mg/g for AB25. The initial sorption rate increases with an increase in the temperature. Table 4 shows that h varies from 2.84 to 7.96 mg/(g min) for BB69 and h varies from

0.339 to 0.682 mg/(g min) for AB25, respectively, for a temperature variation from 20 to 80 °C. Both dye/pith systems show extremely high reaction correlation coefficients, r^2 , which are all greater than 0.995. The

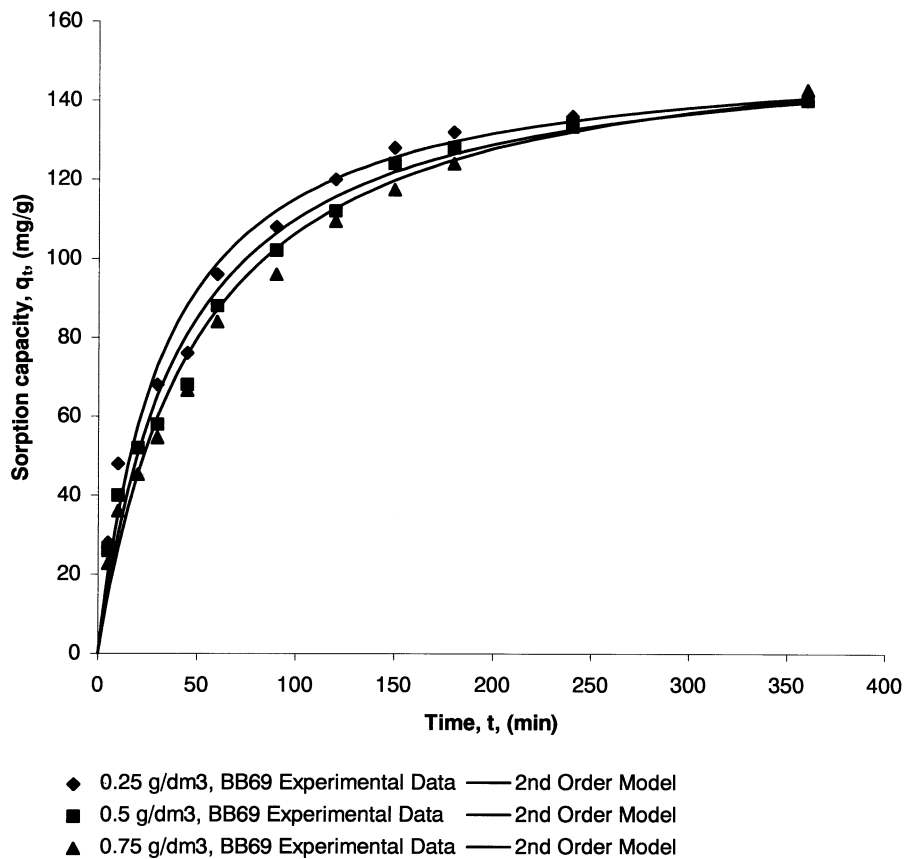


Fig. 12. Effect of pith dose on the sorption of BB69 onto pith.

intraparticle coefficients, r_i^2 , are also high, being greater than 0.900 in all cases, but they are all consistently decreasing with increasing temperature. This trend would tend to indicate 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 pith system show a steady increase with temperature whereas the k -values for AB25 on pith are constant and equal to 3.45 ± 0.20 g/(mg min). Despite the high r^2 -values, this suggests that the AB25/pith system may not be an activated or chemisorption process.

An examination of the effect of temperature on both the equilibrium capacity, q_e , and initial sorption rate, h , produces best-fit correlation of the types shown by Eqs. (4) and (5) with high correlation coefficients shown in Table 5.

$$q_e = B_q T^{A_q}, \quad (4)$$

and

$$h = B_h T^{A_h}. \quad (5)$$

Substituting the values of q_e and h from Table 5 into Eqs. (4) and (5) and then into Eq. (1), the rate law for a

pseudo-second-order and the relationship of q_t , T and t can be represented as follows:

for BB69:

$$q_t = \frac{t}{9.07 \times 10^{14} T^{-5.47} + (4.89 \times 10^2 T^{-1.39})t}, \quad (6)$$

for AB25:

$$q_t = \frac{t}{1.46 \times 10^{10} T^{-3.80} + (1.61 \times 10^4 T^{-1.94})t}. \quad (7)$$

These equations can then be used to derive the amount of dye sorbed at any given temperature and the reaction time.

The values of rate constant, k , were found to increase from 1.74×10^{-4} to 2.94×10^{-4} g/(mg min), for an increase in the solution temperature from 293 to 353 K for the sorption of BB69. There is a linear relationship between the pseudo-rate constant and temperature with correlation coefficient of 0.903. The sorption rate constant is usually expressed as a function solution of temperature by the following relationship:

$$k = k_0 \exp\left(\frac{-E}{RT}\right), \quad (8)$$

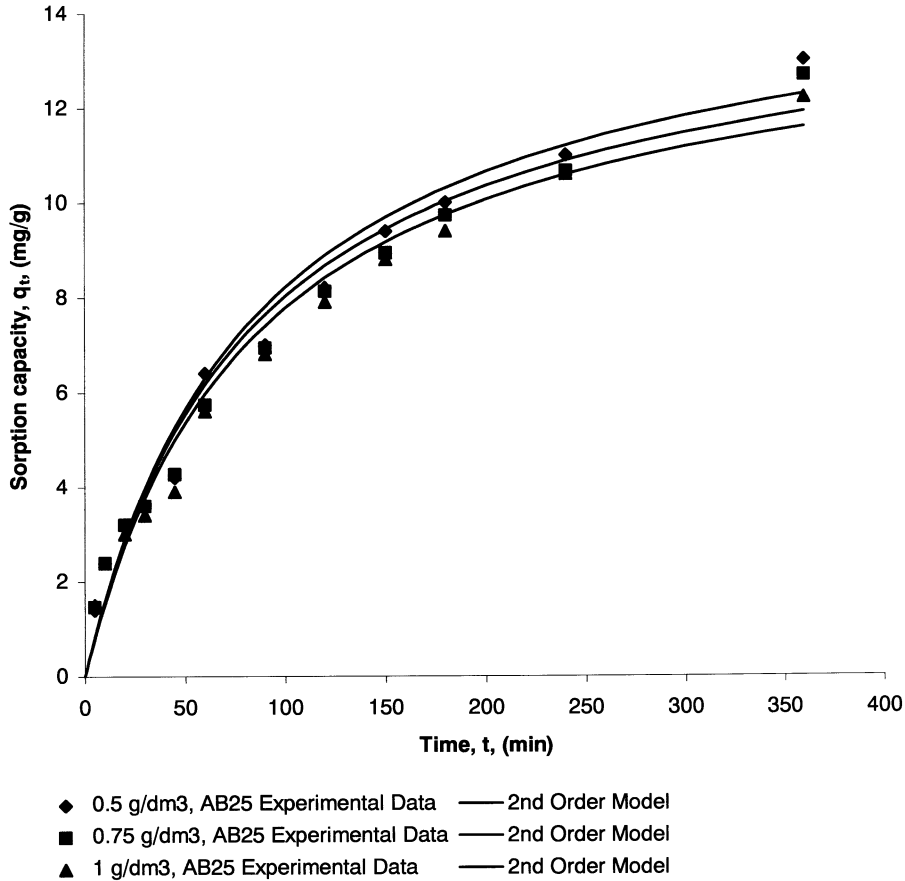


Fig. 13. Effect of pith dose on the sorption of AB25 onto pith.

Table 6
 Effect of pith dose of BB69 and AB25

	m_s (g/dm ³)	r^2	q_c (mg/g)	k (g/(mg min))	h (mg/(g min))	R_c (%)	r_i^2	k_i (mg/(g min ^{0.5}))
BB69	0.25	0.996	1.54×10^2	1.96×10^{-4}	4.61	19.2	0.903	7.13
	0.5	0.993	1.56×10^2	1.55×10^{-4}	3.75	38.9	0.933	7.38
	0.75	0.992	1.60×10^2	1.25×10^{-4}	3.19	59.9	0.955	7.65
AB25	0.5	0.962	15.2	7.81×10^{-4}	0.179	7.58	0.985	0.716
	0.75	0.963	14.6	8.33×10^{-4}	0.178	11.0	0.991	0.690
	1.0	0.959	14.3	8.37×10^{-4}	0.171	14.3	0.987	0.674

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

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

$$k = 3.12 \times 10^{-3} \exp\left(\frac{-7.13 \times 10^3}{8.314T}\right).$$

From this equation, the rate constant of sorption, k_0 , is 3.12×10^{-3} g/(mg min) and activation energy of sorption, E , is 7.13 kJ/mol for the sorption system of BB69/pith. Since sorption is an exothermic process, it would be expected that an increased solution temperature would result in decreased sorption capacity. However, Weber [29] has stated that, since diffusion is an endothermic process, the rate of sorption will increase with increased solution temperature when intraparticle transport (pore diffusion) is the rate-limiting step. The results of this study on the effect of temperature indicate

that for the sorption of BB69 dye on pith involves some chemical sorption. The values of k at different temperatures for the sorption of AB25 onto pith are shown in Table 5 and for a temperature range of 60 K, the values may be considered as relatively constant. This suggests a non-activated sorption process such as physical sorption for AB25 sorption on pith. It is possible that this pseudo-second-order model could act as a methodology for discriminating between sorption mechanisms on this basis.

3.4. Effect of pith dose of BB69 and AB25

Figs. 12 and 13 show a series of contact time curves with sorbent dose ranging from 0.25 to 0.75 g/dm³ of BB69 and 0.5 to 1 g/dm³ of AB25. The removal of BB69 increases from 19.2 to 59.9% and for AB25 the increase in removal is from 7.58 to 14.3% with the increase of the pith dose ranging from 0.25 to 0.75 g/dm³ for BB69 and 0.5 to 1 g/dm³ for AB25, respectively. However, the sorption capacity increases slightly and varies from 154 to 160 mg/g, as m_s varies from 0.25 to 0.75 g/dm³ for BB69 and from 15.2 to 14.3 mg/g, as m_s varies from 0.5 to 1 g/dm³ for AB25, respectively. 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 intraparticle diffusion-based model (Table 6). The data show a good compliance with the pseudo-second-order equation and the regression coefficients for the linear plots were higher than 0.959 for all the systems in these studies. However, in the case of AB25, the effect of contact time and pith dose the r_1^2 values are all greater than 0.985 and are significantly greater than the coefficients obtained for the second-order kinetic model.

4. Conclusion

The kinetics of sorption of copper, BB69 and AB25 on biosorbents (peat and pith) 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 by pith is an exothermic, activated process whereas the sorption of AB25 on pith appears to be a non-activated process. For both dye/pith systems, intraparticle diffusion and chemical reactions seem significant in the rate-controlling step but for the sorption of copper ions onto peat the pseudo-second-order chemical reaction kinetics provide the best correlation of the data.

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