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Kinetic Model for Lead(II) Sorption on to Peat

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ABSTRACT: The kinetics of lead sorption on to peat have been investigated. 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 lead(II) concentration, peat particle size and temperature. An equilibrium capacity of sorption has been evaluated with the pseudo-second order rate equation. In addition, an activation energy of sorption has also been determined based on the pseudo-second order rate constants.

INTRODUCTION

The removal of metal ions from wastewaters has received considerable attention in recent years (Lalancette and Coupal 1972; Tummavuori and Aho 1980; Green *et al.* 1994; Xie *et al.* 1996). Extensive investigations are being carried out to identify suitable relatively cheap sorbents capable of removing significant quantities of metal ions. A number have already been identified, including fly ash (Nonavinakere and Reed 1996), lignite (Allen and Brown 1995), wollastonite (Yadava *et al.* 1991), biogas residue (Namasivayam and Yamuna 1995) and peat (Viraraghavan and Dronamraju 1993).

The present paper reports on the sorption of lead ions on to peat. The health hazards due to the toxicity of lead have been documented in many journals (Goldstein 1990; Crocetti *et al.* 1990; Aldrich *et al.* 1993) and justify the intensive search for effective lead sorption systems.

The capacity of peat for lead ions has been studied in the present paper by determining the equilibrium isotherm. In addition, kinetic studies have been carried out using an agitation batch sorber to study the effects of initial lead ion concentration, peat particle size and temperature. A kinetic analysis has been carried out to correlate the experimental data based on a pseudo-second order kinetics equation.

MATERIALS AND METHODS

The experiments were conducted with peat obtained from Germany. The peat, as supplied, was dried at a temperature of $90 \pm 2^\circ\text{C}$ for 24 h and then screened.

The lead nitrate used in the experiments was supplied by Aldrich Chemicals. Stock solutions of lead nitrate [Analytical grade $\text{Pb}(\text{NO}_3)_2$ (3.26 g/dm^3)] were prepared in distilled water. All solutions used in this study were diluted with distilled water as required.

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Effect of initial concentration

A range of lead(II) concentrations from 100 to 500 mg/dm³ was used and agitation was carried out for 4 h. All contact investigations were carried out using a baffled, agitated 2 dm³ sorber vessel. Samples (3 ml) were withdrawn at suitable time intervals, filtered through a 0.45 µm membrane filter and then analysed with an inductively coupled plasma atomic emission spectrophotometer (ICP-AES). A 6.8 g sample of peat (500–710 µm) was added to each 1.7 dm³ volume of lead(II) solution and an agitation speed of 400 rpm was used for all experiments. The temperature was maintained at room temperature (24 ± 2°C) throughout all studies.

Effect of temperature

A range of temperatures from 6°C to 45°C was used and agitation was carried out for 4 h. A 6.8 g sample of peat (500–710 µm) was added to each 1.7 dm³ volume of lead(II) solution with an initial concentration of 300 mg/dm³ and an agitation speed of 400 rpm was employed.

Effect of particle size

A range of particle sizes from 150–250 µm to 500–710 µm was used and agitation was carried out for 4 h. A 6.8 g sample of peat was added to each 1.7 dm³ volume of lead(II) solution using an initial concentration of 300 mg/dm³ and an agitation speed of 400 rpm.

THEORETICAL

Peat contains polar functional groups such as aldehydes, ketones, acids and phenolics. These groups can be involved in chemical bonding and are responsible for the cation-exchange capacity of the peat. Thus, the peat/copper reaction may be represented in two ways (Coleman *et al.* 1956), and it seems possible that divalent lead could follow a similar mechanism:



and



where P⁻ and HP are polar sites on the peat surface.

In an attempt to present the equation representing sorption of divalent metals on to sphagnum moss peat during agitation, the assumption has been made that the process may be pseudo-second order and the rate-limiting step may be chemical sorption or chemisorption (generally termed sorption throughout this paper) involving valency forces through sharing or the exchange of electrons between sorbent and sorbate as covalent forces.

The rate of the pseudo-second order reaction may be dependent on the amount of divalent metal ion on the surface of the peat and the amount of divalent metal ion sorbed at equilibrium. The amount of lead(II) ion sorbed at sorption equilibrium, q_e , is a function of, for example, the temperature, the initial metal ion concentration, the peat dose, particle size and the nature of the solute-sorbent interaction.

The rate expression for the sorption described by equations (1) and (2) 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 peat at time t , and $(P)_0$ and $(HP)_0$ are the number of equilibrium sites available on the peat.

The kinetic rate equation can be rewritten as follows:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \quad (3)$$

where:

k = the rate constant of sorption (g/mg min)

q_e = the amount of lead ion sorbed at equilibrium (mg/g)

q_t = the amount of lead ion on the surface of the sorbent at any time t (mg/g).

Separating the variables in equation (3) gives:

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

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

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + kt \quad (4)$$

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

Equation (4) can be rearranged to obtain:

$$q_t = \frac{t}{\frac{1}{kq_e^2} + \frac{t}{q_e}} \quad (5)$$

which has a linear form:

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

If the initial sorption rate is:

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

then equations (5) and (6) become:

$$q_t = \frac{t}{\frac{1}{h} + \frac{t}{q_e}} \quad (8)$$

and

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \quad (9)$$

Thus, the initial sorption capacity, h , the equilibrium sorption capacity, q_e , and the rate constant, k , can be determined experimentally from the slope and intercept by plotting t/q_t against t .

In many cases, the equilibrium sorption capacity, q_e , is unknown as chemisorption tends to become immeasurably slow while the amount sorbed is still significantly smaller than the equilibrium amount (Ungarish and Aharoni 1981). However, in the proposed pseudo-second order model, by fitting equation (9) to the experimental data the equilibrium sorption capacity, q_e , can be obtained from the slope of the plot of t/q_t against t .

RESULTS AND DISCUSSION

Effect of initial concentration of lead(II)

The rate of lead(II) sorption on to peat was determined as a function of the initial lead(II) concentration using initial concentrations of 101, 209, 309, 410 and 504 mg/dm³. The sorption rate was rapid at the beginning of the period and lead(II) was completely removed from the 101 mg/dm³ solutions in 10 min and from the 209 mg/dm³ solutions in 120 min, but only partially removed from other higher initial concentrations within the contact time experiment in these studies. The initial rapid sorption of lead(II) could be attributed to ion exchange with surface cations on the peat followed by a gradual uptake which could be due to cation exchange at the inner surface (Low and Lee 1990).

Figure 1 shows the extremely linear variation of t/q_t with time, t , for a large initial fraction of the sorption period. The figure shows a good linearisation of the experimental data, thereby supporting the proposal that chemical sorption is the rate-limiting step and that the mechanism follows a pseudo-second reaction scheme. Table 1 lists the rate constant, k , the equilibrium sorption, q_e , and the initial sorption rate, h , of sorption at various initial concentrations of lead(II); these were calculated from the intercept and slope of the straight line plots of t/q_t versus t according to equation (6). The initial sorption rate increased with an increase in the initial concentration of lead(II). Thus, the initial sorption rate varied from 37.6 to 8.57 mg/g min as the initial concentration of lead(II) was varied from 101 to 504 mg/dm³. The values of the rate constants were found to decrease from 5.15×10^{-2} to 7.62×10^{-4} g/mg min with an increase in the initial concentration of lead(II) from 101 to 504 mg/dm³. The observed dependence of the rate on the initial

TABLE 1. Initial Lead(II) Concentration Dependence of Rate of Sorption

C_0 (mg/dm ³)	q_e (mg/g)	k (g/mg min)	h (mg/g min)	r^2
101	27.0	5.15×10^{-2}	37.6	1.000
209	53.6	8.11×10^{-3}	23.3	1.000
309	77.3	2.25×10^{-3}	13.5	1.000
410	98.5	1.01×10^{-3}	9.81	0.999
504	106	7.62×10^{-4}	8.57	0.998

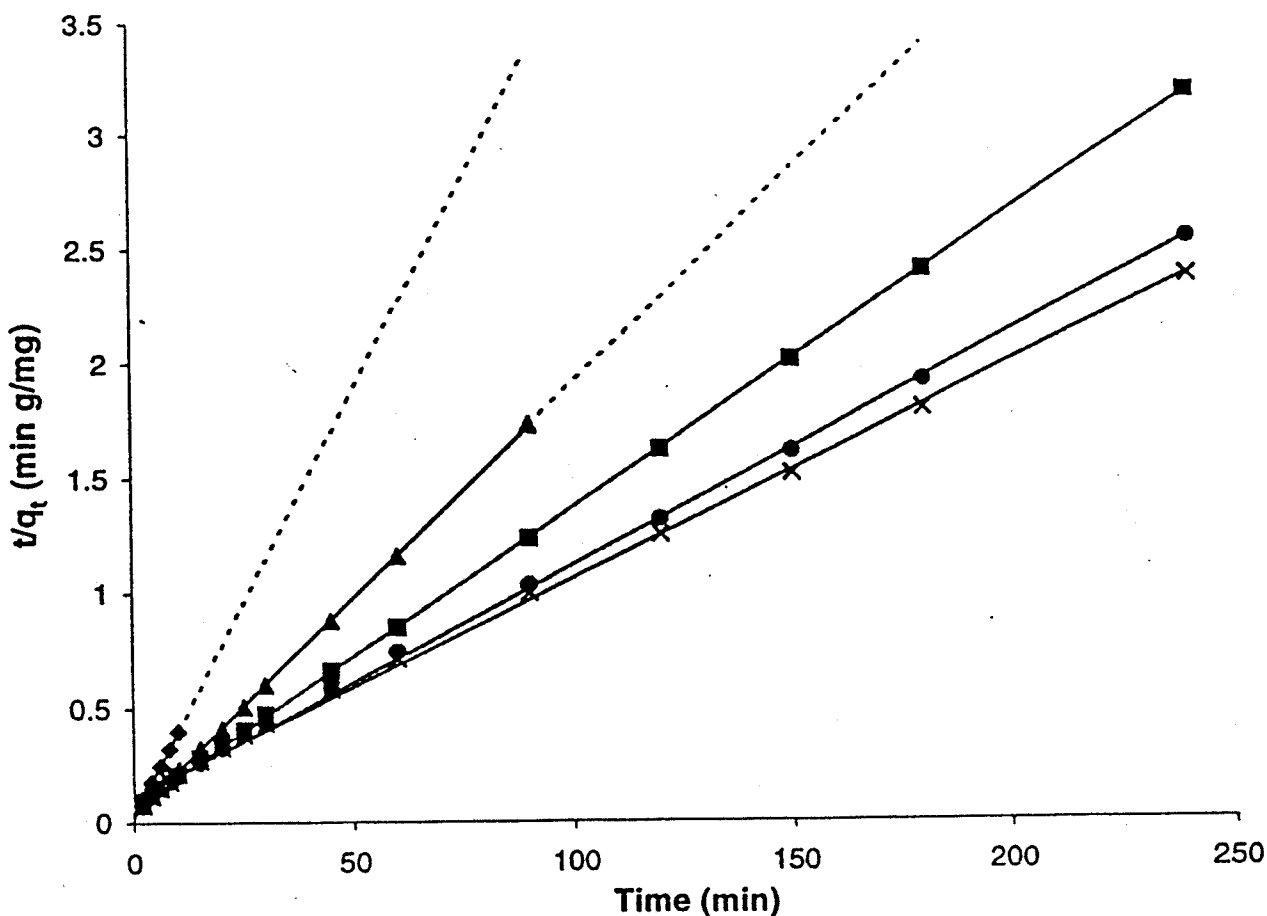


Figure 1. Pseudo-second order sorption kinetics of lead(II) on to peat at various initial concentrations. Experimental data: \blacklozenge , $C_0 = 101 \text{ mg/dm}^3$; \blacktriangle , $C_0 = 209 \text{ mg/dm}^3$; \blacksquare , $C_0 = 309 \text{ mg/dm}^3$; \bullet , $C_0 = 410 \text{ mg/dm}^3$; \times , $C_0 = 504 \text{ mg/dm}^3$. Full lines correspond to application of second-order model at the same initial concentration in each case.

concentration of lead(II) indicates that removal of lead(II) from dilute aqueous solution should present no great obstacle, since sorption relative to the initial concentration of lead(II) is more rapid the more dilute the solution, i.e. a greater fraction of the lead(II) present will be sorbed in a given period of time (Weber and Morris 1963).

Figure 2 shows a plot of the experimental data points for the sorption of lead(II) by peat as a function of time. In addition, the theoretical constants k and q_e have been used to generate theoretically predicted curves using equation (5). These curves are shown by the solid and dashed lines in Figure 2 and excellent fits are obtained between the predicted curves and the experimental data points.

The pseudo-second order rate constants, k , were found to decrease non-linearly with increasing initial concentrations of lead(II) within the range from 101 to 504 mg/dm^3 . Accordingly, a correlation has been made empirically of the pseudo-second order rate constant, k , as a function of the initial concentration of lead(II) as follows:

$$k = mC_0^n \quad (10)$$

McKay *et al.* (1983) reported that, in the case of adsorption of AB25 using chitin, n centred around the 0.5 value, confirming that intraparticle diffusion was a prominent factor in the adsorption process. The results from these studies suggest the relationship between the pseudo-second

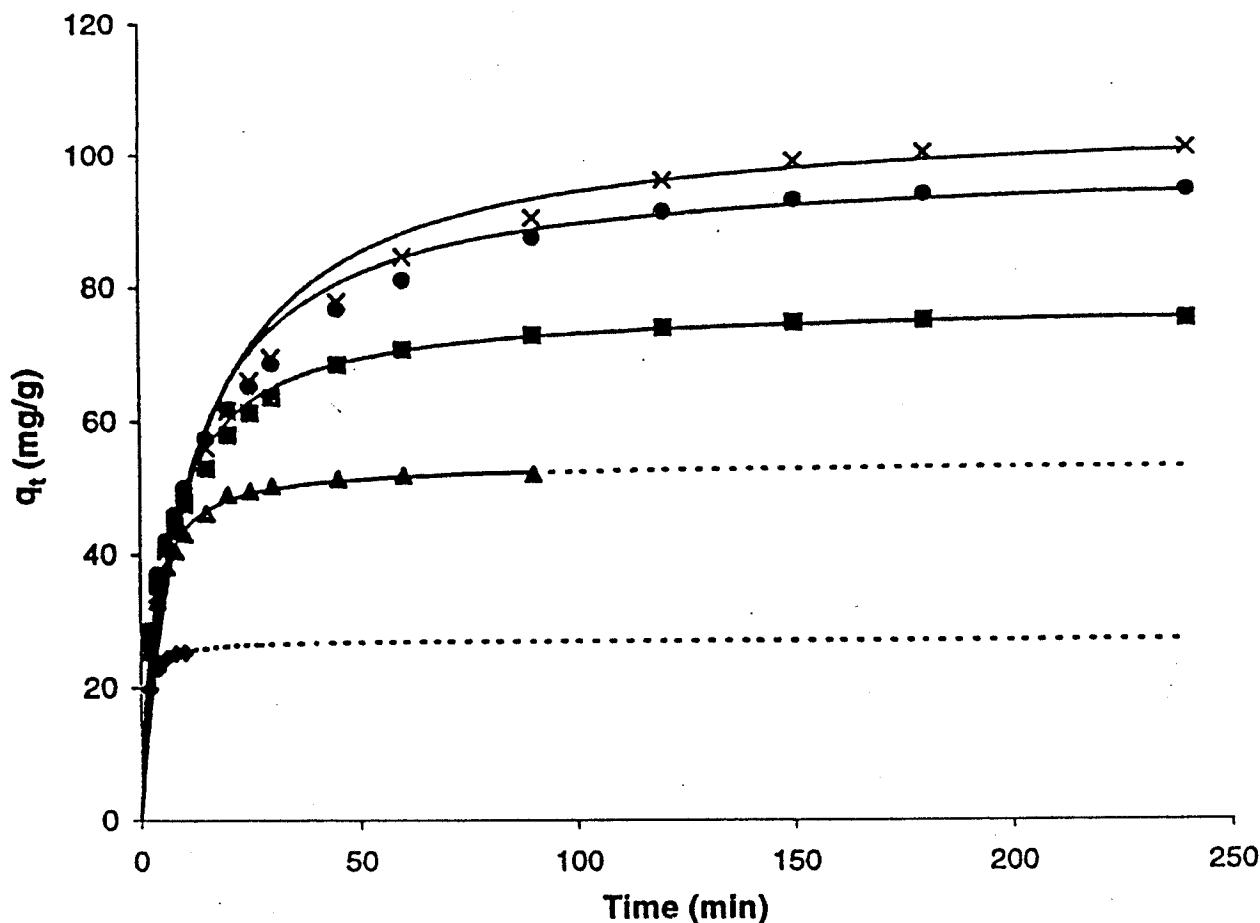


Figure 2. Plots of sorbed amounts versus time at various initial concentrations of lead(II). Experimental data: \blacklozenge , $C_0 = 101 \text{ mg/dm}^3$; \blacktriangle , $C_0 = 209 \text{ mg/dm}^3$; \blacksquare , $C_0 = 309 \text{ mg/dm}^3$; \bullet , $C_0 = 410 \text{ mg/dm}^3$; \times , $C_0 = 504 \text{ mg/dm}^3$. Full lines correspond to application of second-order model at the same initial concentration in each case.

order rate constant, k , and the initial lead(II) concentration follows equation (10) with a correlation coefficient of 0.995 as shown in the following equation:

$$k = 1.45 \times 10^4 C_0^{-2.72} \quad (11)$$

The value of n (-2.72) is different from the 0.5 based on intraparticle diffusion. This indicates that second-order chemisorption is important in the sorption of lead(II) using peat.

Effect of temperature

Further evidence that the rate of uptake of lead(II) by peat in these studies was controlled by a chemical sorption phenomenon and a pseudo-second order model is provided by the temperature dependence of the rate of sorption which had extremely high correlation coefficients. Figure 3 shows that the variation in temperature influenced the time required to reach saturation with excellent agreement existing between the experimental data and theoretical curves predicted using equation (8). The data listed in Table 2 show the rate constant, k , the equilibrium sorption, q_e , and the initial sorption rate, h , of sorption at different temperatures, calculated from the intercept and slope of the straight line plots of t/q_t versus t in accordance with equation (6). The initial sorption rate increased with an increase in the temperature. The initial sorption rate varied

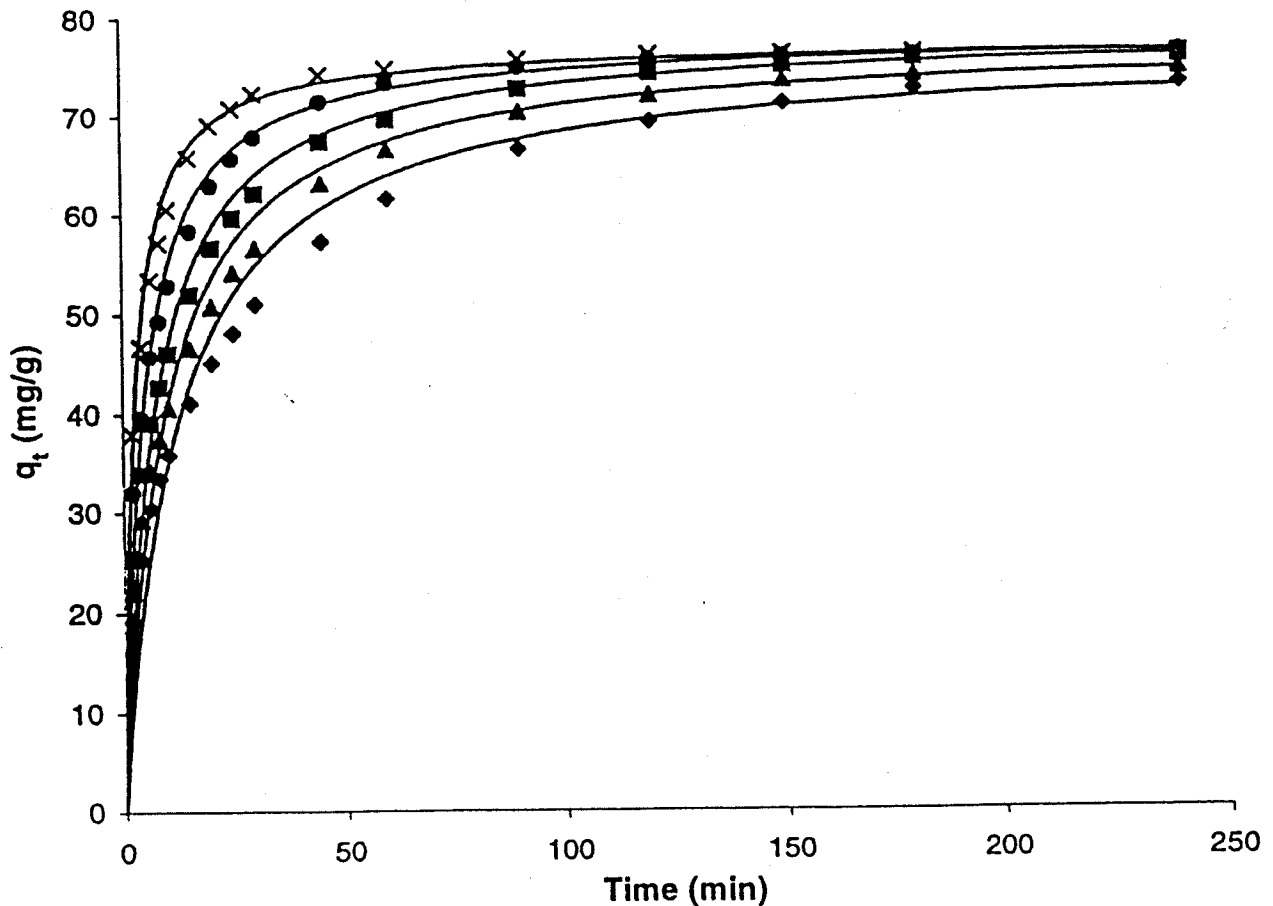


Figure 3. Plots of sorbed amounts versus time for lead(II) at various temperatures. Experimental data: \blacklozenge , 6°C; \blacktriangle , 15°C; \blacksquare , 25°C; \bullet , 35°C; \times , 45°C. Full lines correspond to application of second-order model at the same temperature in each case.

from 6.48 to 33.3 mg/g min as the temperature was varied from 279 K to 318 K. The values of the rate constants were found to increase from 1.11×10^{-3} to 5.60×10^{-3} g/mg min as the temperature increased from 279 K to 318 K.

TABLE 2. Temperature Dependence of Rate of Sorption

T (K)	q_e (mg/g)	k (g/mg min)	h (mg/g min)	r^2
279	76.3	1.11×10^{-3}	6.48	0.999
288	77.3	1.46×10^{-3}	8.71	1.000
298	78.0	1.92×10^{-3}	11.7	1.000
308	77.7	3.07×10^{-3}	18.6	1.000
318	77.1	5.60×10^{-3}	33.3	1.000

The increase in the pseudo-second order rate constants with increasing temperature may be described by the equation:

$$k = k_0 \exp\left(\frac{-E}{RT}\right) \quad (12)$$

where:

- k = 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)
- T = the solution temperature (K).

There is a linear relationship between the pseudo rate constant and the reciprocal absolute temperature with a correlation coefficient of 0.958. The values of k were plotted as a function of the reciprocal of the Kelvin temperature and the linear variation is shown in Figure 4. Hence, the relationship between k and T can be represented in an Arrhenius form as:

$$k = 3.75 \times 10^2 \exp\left(\frac{-29.8 \times 10^3}{8.314T}\right) \quad (13)$$

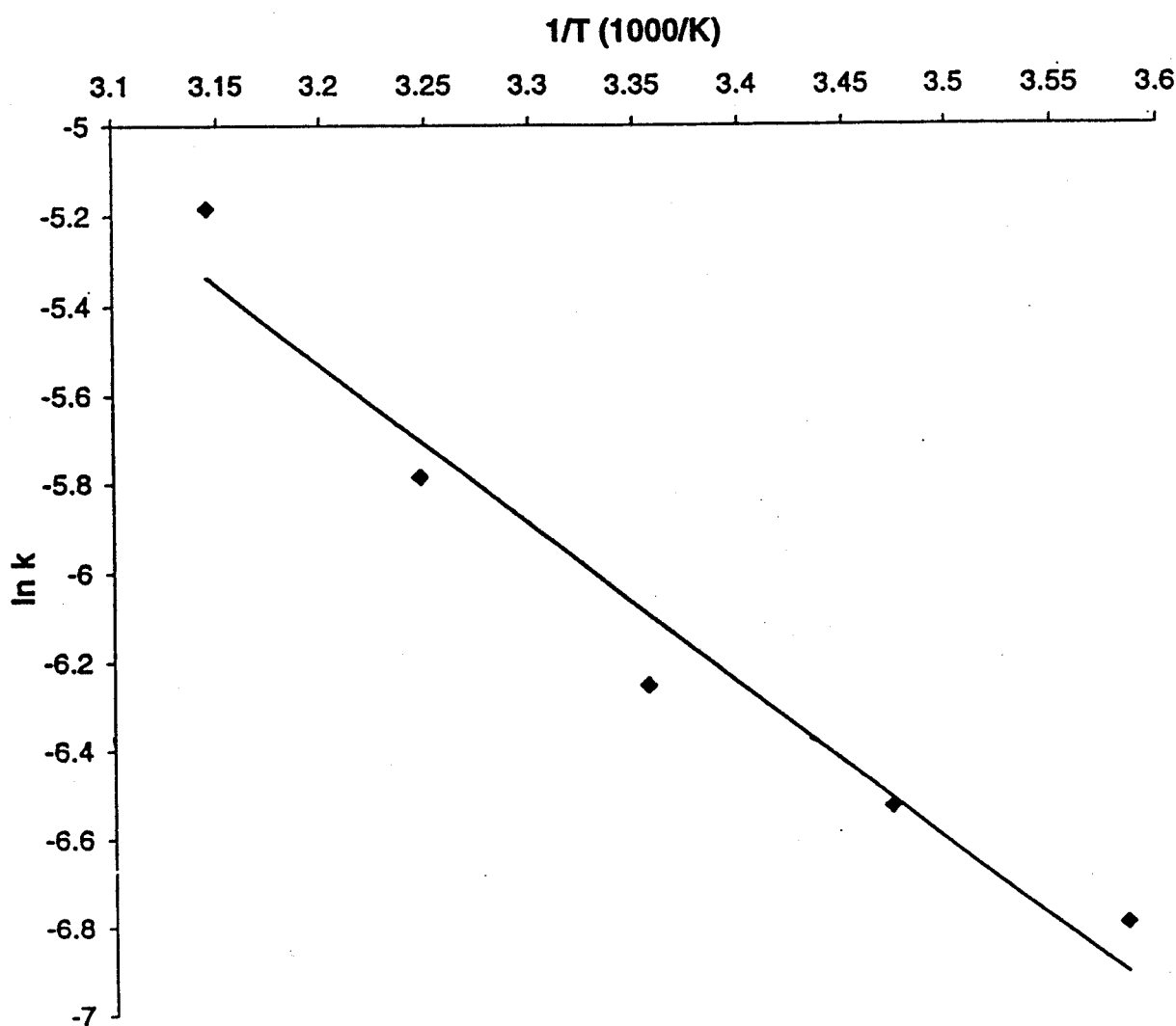


Figure 4. Plot of $\ln k$ versus reciprocal temperature for the sorption of lead(II) on to peat. Experimental data: \blacklozenge ; full line corresponds to application of Arrhenius equation.

From this equation, the rate constant for sorption, k_p , is 3.75×10^3 g/mg min and the activation energy for sorption, E , is 29.8 kJ/mol, which is outside the range of values of 8–22 kJ/mol for diffusion-controlled processes (Glasston *et al.* 1941). The rate-controlling step in a process can also be characterised in part by its activation energy. McKay *et al.* (1981) reported that the activation energy for the adsorption of Telon Blue dye on peat is 26.6 kJ/mol. Again, this value of the activation energy is higher than the normal range of 8–22 kJ/mol typical of physical adsorption processes and indicates that chemisorption is important.

Physical adsorption and chemisorption have not been discussed in detail; however, the difference between them is almost indistinguishable in certain situations. Physical adsorption applies to adsorption in which no electrons are transferred between or shared between the adsorbed molecules and the adsorbent surface. Compared with exchange forces, which are responsible for chemisorption, physical adsorption forces act over greater distances. Physical adsorption is almost independent of the nature of the adsorbent surface and at temperatures near the boiling point of the adsorbate this type of adsorption is reversible. According to spectroscopic measurements, mainly OH groups appear to act as centres for the preferential physical adsorption of oxygen and nitrogen-containing substances, but are also partly centres for the chemisorption of these substances. Active centres, acidic and basic centres are suitable for chemisorption. The sorption of lead(II) on to peat is an activated process in which the activation energy is higher than the range of values 8–22 kJ/mol for normal diffusion-controlled processes. Hence, the sorption of lead(II) on to peat involves chemisorption.

Effect of particle size

It is expected that the rate of sorption on to a solid surface will vary with the available surface area or, for a constant mass of sorbent, with the particle size. The particle diameters used in these studies, viz. 200, 303, 428 and 605 μm , were averages of the mesh sizes for the sieves through which the particles passed or were retained. Figure 5 shows the effect of peat particle size on the uptake of lead(II), with linearity being observed when the lead(II) uptake is plotted via the pseudo-second order equation (9). The data show an increase in the rate of lead(II) uptake as the mean diameter of the peat decreased. As the particle size decreased, the time required to achieve equilibrium also decreased. This effect is shown in Figure 6 and this trend is generally observed in adsorption studies (McKay *et al.* 1980; Lee and Low 1987). The results are different from those for the sorption of acid dye on to peat (Poots *et al.* 1976) where the variation in particle size appeared to have little influence on the time required to reach equilibrium. This process was considered to be a physisorption diffusion process.

The rate constant, k , the equilibrium sorption, q_e , and the initial sorption rate, h , of sorption at various particle sizes have been determined and are listed in Table 3. The initial sorption rate increased with a decrease in the particle size. The initial sorption rate varied from 11.6 to 109 mg/g min as the particle size was varied from 605 μm to 200 μm . The values of the rate constants were found to increase from 1.80×10^{-3} to 1.72×10^{-2} g/mg min with a decrease in the particle size from 605 μm to 200 μm .

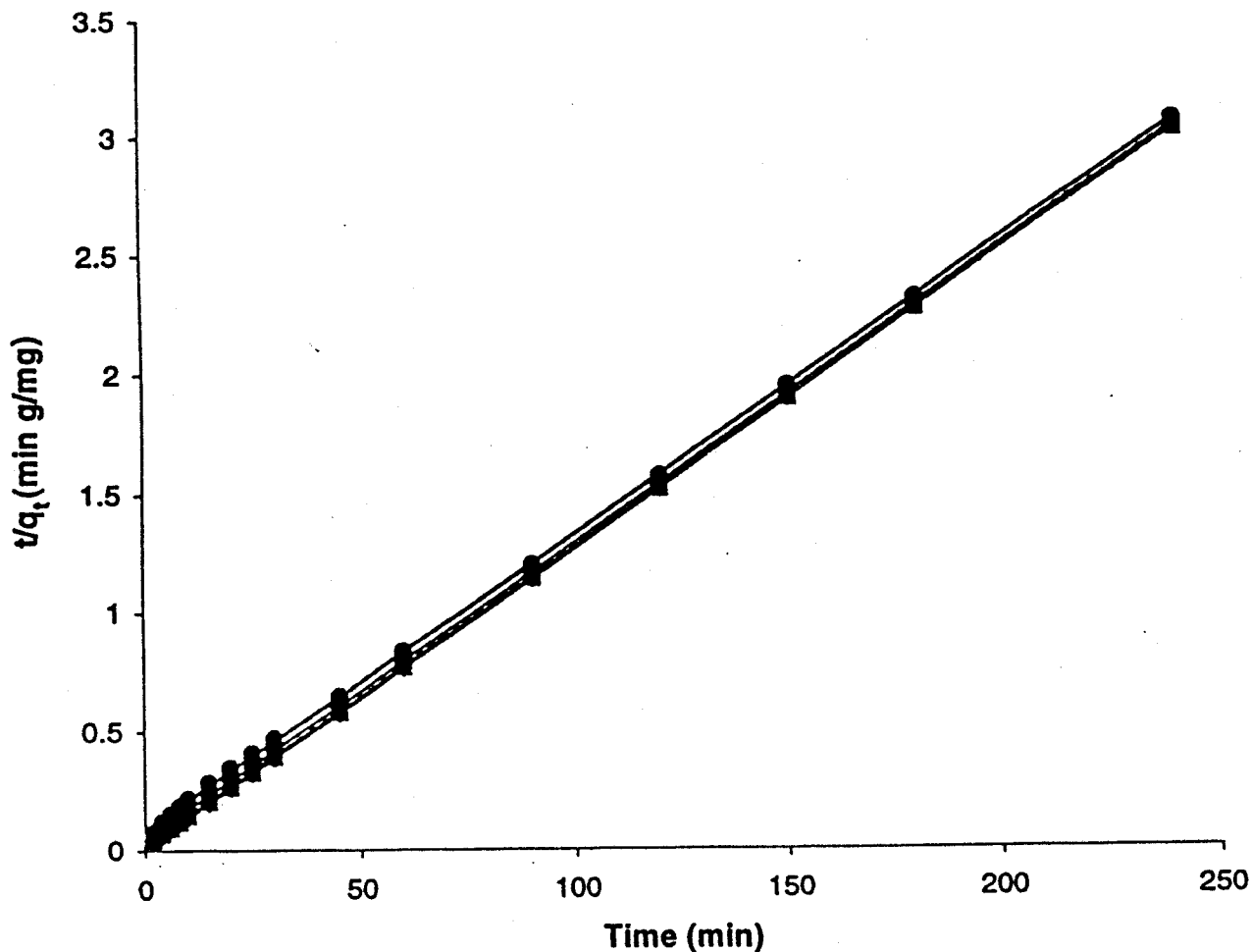


Figure 5. Pseudo-second order sorption kinetics of lead(II) on to peat of various particle sizes. Experimental data: \blacklozenge , $d_p = 150\text{--}250\ \mu\text{m}$; \blacktriangle , $d_p = 250\text{--}355\ \mu\text{m}$; \blacksquare , $d_p = 355\text{--}500\ \mu\text{m}$; \bullet , $d_p = 500\text{--}710\ \mu\text{m}$. Full lines correspond to application of second-order model for the same particle size range in each case.

TABLE 3. Particle Size Dependence of Rate of Sorption

d_p (μm)	q_e (mg/g)	k (g/mg min)	h (mg/g min)	r^2
605	80.5	1.80×10^{-3}	11.6	1.000
428	80.1	3.48×10^{-3}	22.4	1.000
303	79.8	8.88×10^{-3}	56.6	1.000
200	79.6	1.72×10^{-2}	109	1.000

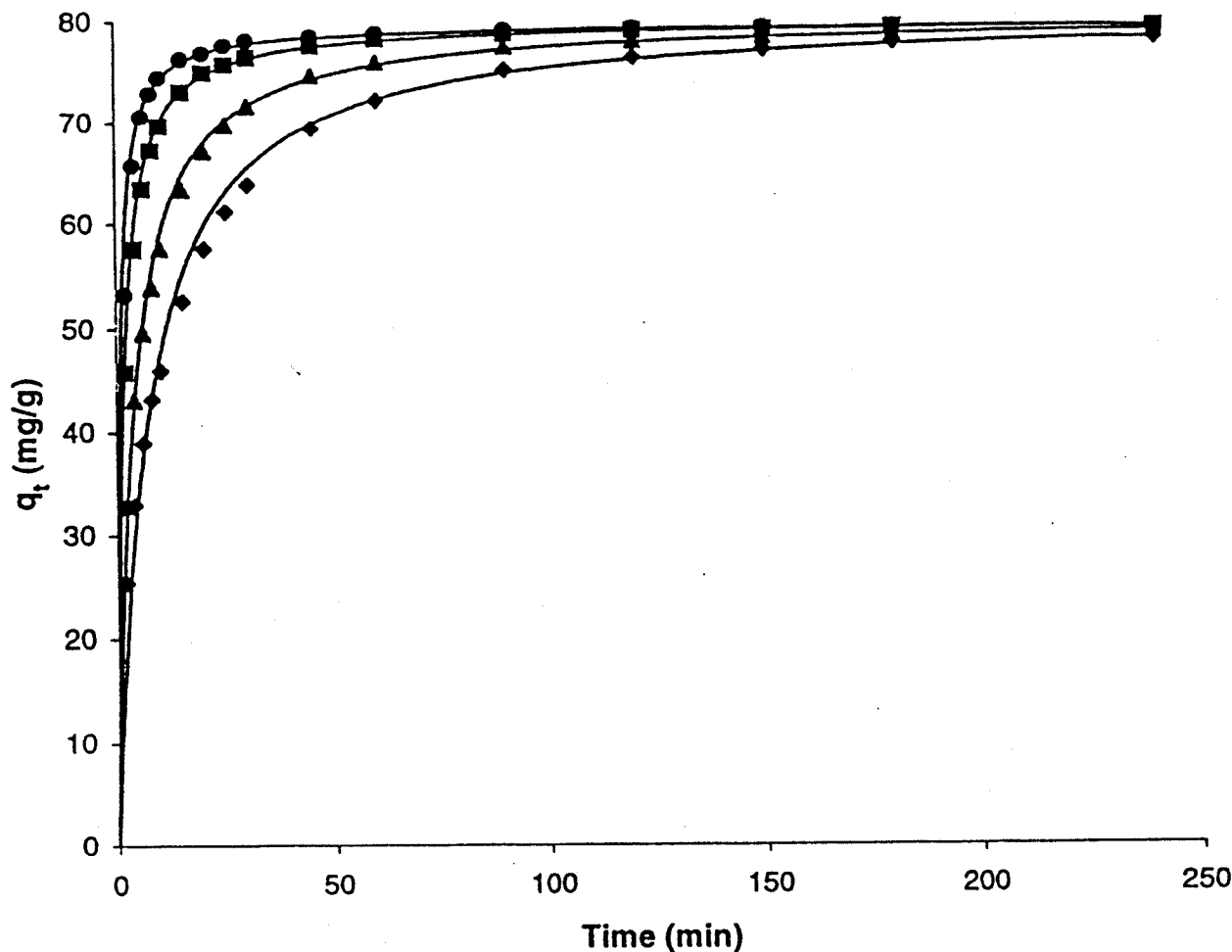


Figure 6. Plots of amount of lead(II) sorbed versus time for various particle sizes. Experimental data: \blacklozenge , $d_p = 500\text{--}710\ \mu\text{m}$; \blacktriangle , $d_p = 355\text{--}500\ \mu\text{m}$; \blacksquare , $d_p = 250\text{--}355\ \mu\text{m}$; \bullet , $d_p = 150\text{--}250\ \mu\text{m}$. Full lines correspond to application of second-order model for the same particle size range in each case.

Figure 6 compares the experimental points with the theoretically predicted sorption curves using equation (9) with good agreement being observed. Figure 7 shows the plot of $\log k$ against $\log d_p$. The relationship between k and d_p can be represented as:

$$k = 1.24 \times 10^3 d_p^{-2.10} \quad (14)$$

with a correlation coefficient of 0.990. The variation observed is in accord with the pseudo-second order equation. This trend is generally observed in the adsorption of dyestuffs from aqueous solutions using activated carbon in accordance with equations for intraparticle diffusion representing the main rate-controlling step (McKay *et al.* 1983) as well as in the adsorption of *p*-chlorophenol using activated carbon in accordance with an external mass-transfer coefficient (McKay *et al.* 1986).

CONCLUSIONS

The kinetics of lead(II) sorption on to peat were based on the assumption of a pseudo-second order mechanism with chemisorption being important. A pseudo-second order model has been developed to predict the rate constant of sorption, the equilibrium capacity and the initial sorption

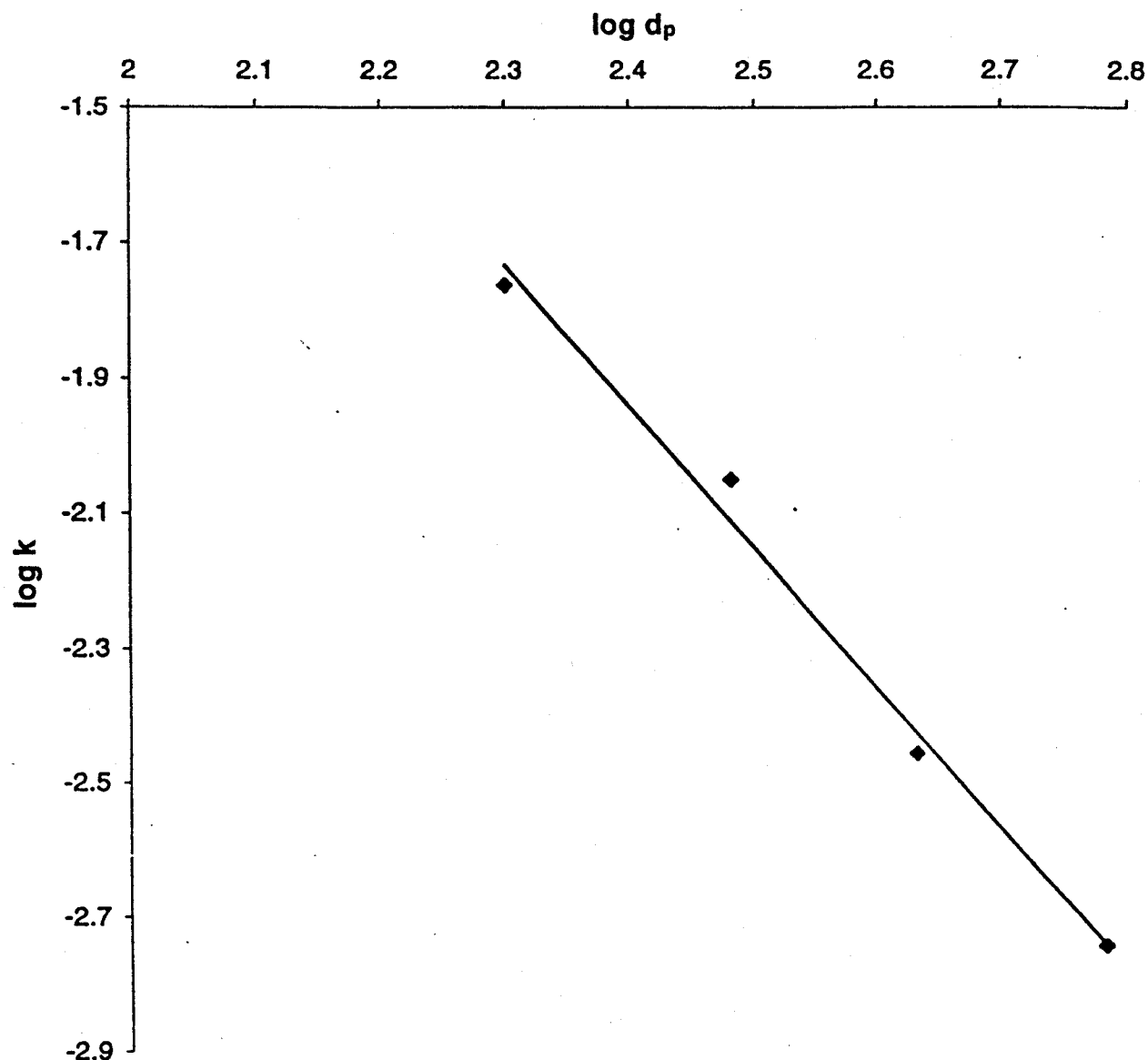


Figure 7. Plot of $\log k$ versus $\log d_p$.

rate. Using these constants to generate the theoretically predicted curves showed that the kinetic model equation had an extremely high degree of correlation with the experimental data points. The rate constant is a function of the initial lead(II) concentration, the temperature and the peat particle size. The activation energy for sorption was 29.8 kJ/mol.

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