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REMOVAL OF LEAD(II) FROM EFFLUENTS BY SORPTION ON PEAT USING SECOND-ORDER KINETICS

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ABSTRACT

The sorption of lead ions from aqueous solution onto peat has been studied. The kinetics of sorption of lead ion are described by a pseudo-second-order model modified with a new parameter, t_0, included to account for an initial resistance due to the film boundary layer. Analysis of this model has been carried out at various experimental conditions to study the effect of initial lead ion concentration, peat particle size, solution temperature, and agitation speed in an agitated batch system. The pseudo-second-order rate constant, initial sorption rate, and sorption capacity, together with time constant, t_0, also have been determined and correlated as a function of the system variables.

Key Words: Sorption; Second order; Lead; Peat

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INTRODUCTION

The health hazards due to the presence of lead in water are of extreme concern to the public, government and industry. Lead is known to have a toxic effect on the neuronal system (1) and on the function of brain cells (2). The health hazards due to the toxicity of lead in waters have been reported in many journals (3,4) and emphasize the need to identify effective lead sorption systems.

Numerous kinetic models have been investigated for the sorption of contaminants from wastewater by sorbent materials. The mechanism of sorption often involves the chemical reaction between functional groups on the sorbent and the metal ions, thus forming metal–organic complexes or a cation exchange reaction, due to the high cation exchange capacity of the sorbent. In addition, other mechanisms may be involved as well as mass-transport processes, such as transport in the bulk of the liquid phase, diffusion across the liquid film surrounding the solid particles, and diffusion in macropores or micropores. Sorption kinetics have been extensively studied, and it has been commonly observed that the sorption rate is very rapid at the beginning of the process, then the rate becomes slower as equilibrium is approached. Such kinetics are often described by a first-order kinetic reaction (5–10).

A limited number of studies have looked at the sorption of lead(II) on peanut hull (11), on bottom ash (12), and waste biogas residual (13).

The sorption of metal ions from aqueous solution plays an important role in water pollution control, and in recent years there has been considerable interest in the use of low-cost sorbents such as peat for this purpose. Batch metal removal by sphagnum moss peat has been studied by workers such as Rock et al. (14), Sharma and Forster (15) and Ho et al. (16). Column studies using moss peat for the removal of heavy metals from industrial and municipal leachates (17) as well as from wastewaters (18) have also been investigated.

Several groups of workers have described the reaction order of sorption in metal–peat systems using various kinetic models. Traditionally, the kinetics have been described by the first-order equation typical of that derived by Lagergren (19). However, Gosset et al. (20), Sharma and Forster (15), Low and Lee (21), as well as Ho et al. (22) have used a second-order equation to describe metal–peat sorption and Tien and Huang (23) have presented a second-order expression for metal sorption onto sludge solids.

The sorption of lead ions onto peat has been studied in this paper, and the effects of peat particle size, initial lead ion concentration, solution temperature, and agitation speed have been investigated. A modified pseudo-second-order model has been developed and used to analyze the data for the sorption of lead ions onto peat. The degree of correlation of this new model has been compared with the correlation coefficients of other lead–peat sorption models reported in the literature.

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. Exchange sorption between the hydrogen ions of peat and copper has been proposed by Coleman et al. (24) The peat–copper reaction may be represented in two ways (24) as shown in Equations (1) and (2). It is possible that divalent lead ion sorption onto peat may follow a similar mechanism:

$$2P^- + Pb^{2+} \Leftrightarrow PbP_2 \tag{1}$$

and

$$2HP + Pb^{2+} \Leftrightarrow PbP_2 + 2H^+ \tag{2}$$

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

In an attempt to present the equation representing sorption of divalent metals onto sphagnum moss peat in agitated batch sorbers, it has been assumed that the process may be pseudo-second-order and the rate-limiting step may be chemisorption. The mechanism may involve valency forces by sharing or through the exchange of electrons between sorbent and sorbate as covalent forces.

The rate expression for the sorption described by Equations (1) and (2) is:

$$\frac{d(P)_t}{dt} = k_2[(P)_0 - (P)_t]^2 \tag{3}$$

or

$$\frac{d(HP)_t}{dt} = k_2[(HP)_0 - (HP)_t]^2 \tag{4}$$

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 equations can therefore be rewritten as follows:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{5}$$

Where

k_2 is the pseudo-second-order rate constant of sorption, (g/mgmin),
q_e is the amount of divalent metal ion sorbed at equilibrium, (mg/g),
q_t is amount of divalent metal ion on the surface of the sorbent at any time, t, (mg/g).

Separating the variables in Equation (5) gives:

$$\frac{dq_t}{(q_e - q_t)^2} = k_2\,dt \tag{6}$$

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

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \tag{7}$$

which is the integrated rate law for a pseudo-second-order reaction. Equation (7) can be rearranged to obtain:

$$q_t = \frac{t}{\frac{1}{k_2 {q_e}^2} + \frac{t}{q_e}} \tag{8}$$

which has a linear form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{9}$$

This form of normalized plot has been used by several workers studying equilibrium processes (25–28).

The initial sorption rate, h, as $t \to 0$ is defined as:

$$h = k_2 q_e^2 \tag{10}$$

The initial sorption rate, h, the equilibrium sorption capacity, q_e, and the pseudo-second-order rate constant, k_2, can be determined experimentally from the slope and intercept of a plot of t/q_t against t.

However, in order to fit the pseudo-second-order equation to experimental data, the equilibrium sorption capacity, q_e, is required, and this can be obtained from the isotherm (29) or the slope of plot of t/q_t against t. Ritchie (30) developed a differential nth order equation, which can also be solved to derive Equation (8).

MATERIALS AND METHODS

The experiments were conducted with sphagnum peat obtained from Germany. The peat as supplied was dried at a temperature of 105 ± 5°C for 24 hours and then screened to obtain constant particle size range fractions of 150–250, 250–355, 355–500 and 500–710 microns. The peat was a sphagnum moss peat and an element analysis was carried out; the results, on a dry basis, are carbon, 57.2%; hydrogen, 5.7%; oxygen, 36.0%; and nitrogen, 0.7%.

The lead nitrate used in the experiments was supplied by Aldrich Chemicals (St. Louis, MO). Stock solutions of lead nitrate (analytical grade $Pb(NO_3)_2$) (3.26 g/dm^3) were prepared in distilled water.

A standard set of experimental conditions is described in this section. To study an experimental "variable" all parameters were set at the values specified in this section except the experimental variable. The ranges of variables are presented in Table 1.

Table 1. Experimental Variables

Variable	Parameter Value
Initial lead concentration C_0 (mg/dm^3)	101, 209, 309, 410, 504
Solution temperature T (°K)	279, 288, 298, 308, 318
Particle size (mean) d_p (microns)	200, 300.25, 425.25, 605
Agitation speed S (r.p.m.)	280, 350, 390, 430, 470, 510

RESULTS AND DISCUSSION

General

The main objective of this research is to develop a kinetic model that describes the sorption mechanism of lead ions onto peat and provides a high correlation factor to the experimental data. Due to the complex chemical structure of peat (31,32), the specification of an exact mechanism is likely to be very difficult. Therefore, the few solution models proposed adopt a fairly global approach to the mechanism of metal ion sorption on peat based on simplifying assumptions. One of the first main selection criteria is whether to apply a kinetic or diffusion-controlled model. Because the sorption of metal ions onto peat is complete within three or four hours, analysis of contact time data requires a different approach from the method used for long-time diffusional controlled processes, which take several days to reach equilibrium. The uptake of metal ion onto peat has been studied (33) for the initial 30-minute period of the sorption process. Gosset et al. (20) developed a kinetic model for the sorption of copper, zinc, cadmium, and nickel on peat, but a very restricted range of parameters was used. In particular, extensive studies by Bunzl et al. (34–35) on the adsorption and desorption of metal ions onto peat suggested that the cations participate in an ion exchange with protons from the humic acids. Bunzl carried out interruption tests and concluded that film diffusion was the rate-limiting step. Therefore, there are only a limited number of detailed kinetic analyses reported in the literature for the sorption of metal ions onto peat under carefully controlled experimental conditions for the entire sorption period.

In a previous paper (36), two pseudo-first-order models (Lagergren pseudo-first-order model, LPFOM and the Modified Lagergren pseudo-first-order model, MLPFOM) were developed and used to describe the peat–lead ions' contact time date. The models had only very limited success.

The results of this analysis give only limited success (36). The experimental data could only be correlated for the initial 20 minutes of the sorption process although all the linear correlation coefficients, r^2, were >0.991. However, when the theoretical q_e values were compared with the equilibrium q_e values very poor correlation was obtained and differences of up to 25% were observed in the values.

The present paper will develop two pseudo-second-order models, namely, the pseudo-second-order model, PSOM and the modified-pseudo second-order model, MPSOM, and compare these results with the modified pseudo-second-order model r^2 results. The PSOM kinetic equation was developed in the theory section and the modification, MPSOM, will be developed in the next section. Each of the four system variables will be compared and discussed in turn.

Effect of Particle Size

A series of experiments were performed using peat particle size range of 150–250, 250–355, 355–500, and 500–710 μm with the initial lead(II) concentration of 300 mg/dm^3 and an agitation speed of 400 rpm. Figure 1 shows an increase in the rate of lead(II) uptake as the mean diameter of the peat decreases. The pseudo-second-order model can describe the whole range of sorption reaction time because there is high correlation coefficient. For the early sorption phase

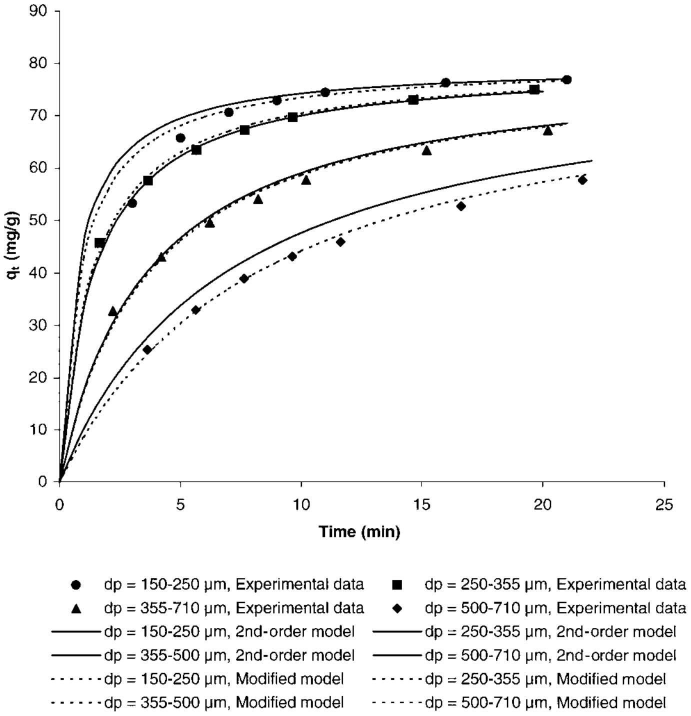

Figure 1. Plot of amount of lead sorbed versus time at various particle sizes.

comprising the first 20 minutes of the total reaction time of 4 h, there is a small error between the experimental data and model. Therefore a time constant, t_0, has been considered and can be defined as an imaginary negative time at which the rate of sorption is infinity (37). Other possibilities to explain t_0 is that some time is required to wet the adsorbent before sorption can commence uniformly through the liquid–solid interface or there is a boundary layer resistance to the chemisorption of lead ions on the peat surface and this imposes itself as an initial time resistance to the reaction process. After the first few minutes of the sorption process in well-agitated systems, this initial film resistance will become negligible as described in the analysis of diffusional mass transport mechanisms (38–43). A modified pseudo-second-order model can thus be obtained by incorporating t_0 into the second-order equation as follows:

$$q_t = \frac{t + t_0}{\frac{1}{k_2' {q_e}^2} + \frac{t+t_0}{q_e}} \tag{11}$$

which has a linear form:

$$\frac{t + t_0}{q_t} = \frac{1}{k_2' {q_e}^2} + \frac{1}{q_e}(t + t_0) \tag{12}$$

An alternative kinetic equation, which also incorporates a time constant, is the Elovich developed for the heterogeneous sorption of gases on solids (44) and applied to a limited number of soil sorption/desorption systems (29,37,45,46). More recently the model has been successfully applied to the sorption of pollutants from aqueous solutions onto a number of sorbents (36,47). This model is not analyzed in the present work due to the fact there are three dependent constants, whereas in Equation (11) there are only two dependent constants, namely, k_2' and t_0. The equilibrium capacity, q_e, can be obtained from the equilibrium isotherm or independently from the equilibrium isotherm and the slope of the system operating line.

Figure 1 illustrates the comparison between the pseudo-second-order model, Equation (5), the modified model described by Equation (11), and the experimental data. Figure 2 also shows the comparison between the pseudo-second-order model, in linear form as Equation (9), the modified model in a linear form as Equation (12), and the experimental data. From the contact time results the pseudo-second-order rate constant, k_2', initial sorption rate, h, and sorption capacity, q_e, together with time constant, t_0, and the correlation coefficients, r^2, are obtained from the slope and intercept of Equation (12) and are shown in Table 2. The influence of error obtained in the first 20 minutes increases with increasing mean diameter of the peat but not for the particle size less than 355 μm. The influence of particle size on sorption capacity, q_e, is very slight.

The variation in t_0 implies that wetting of the peat and/or the fluid film resistance varies with peat particle size. Both are possible, the larger the particle

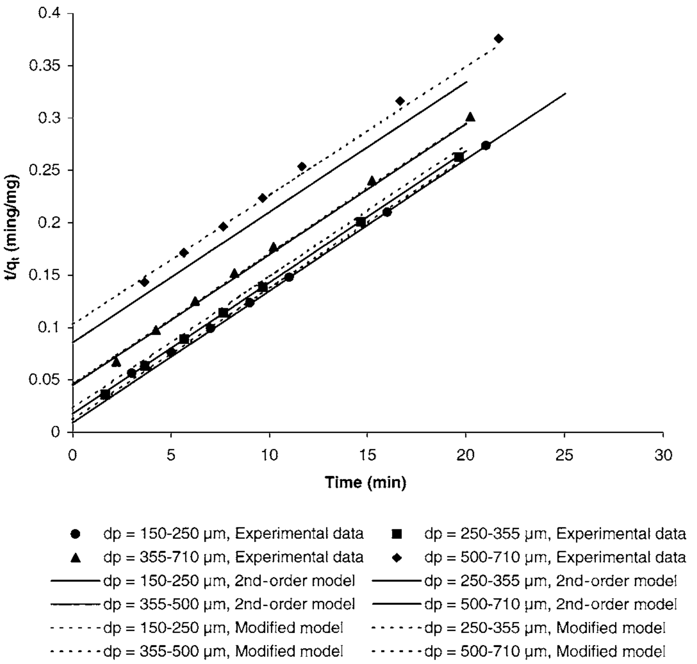

Figure 2. Comparison pseudo-second-order model and modified model at various particle sizes.

the longer the wetting time. The last three points show this trend. The particle momentum and buoyancy in the fluid will change with particle size and influence the film boundary layer with opposite trends possibly explaining the variation in the four sets of data.

The corresponding linear plots of the values of k'_2 and h against peat particle size, d_p, were regressed to obtain expressions for these values in terms of the peat particle size with high correlation coefficients of 0.986 and 0.985, respectively.

Table 2. Kinetic Parameters for the Sorption of Lead(II) on Peat at Various Peat Particle Sizes

d_p (μm)	q_e (mg/g)	k'_2 (g/mg min)	h (mg/g min)	r^2	t_0 (min)
200	79.6	1.47×10^{-2}	93.3	1.000	1.00
305	79.8	9.40×10^{-3}	59.8	1.000	0.036
428	80.2	3.38×10^{-3}	21.8	1.000	0.203
605	81.2	1.47×10^{-3}	9.69	1.000	1.63

Table 3. Correlation Coefficient for Effect of Particle Size on the Four Models

	Model r^2 Values			
Variable d_p (micron)	LPFOM	MLPFOM	PSOM	MPSOM
150–250	0.997	0.990	1.000	1.000
250–355	0.995	1.000	1.000	1.000
355–500	0.998	0.997	1.000	1.000
500–710	0.998	0.999	1.000	1.000

Therefore it is further considered that k'_2 and h can be expressed as a function of d_p as follows:

$$k'_2 = \frac{4.92 \times 10^{-2}}{\exp(5.89 \times 10^3 d_p)} \tag{13}$$

$$h = \frac{3.50 \times 10^2}{\exp(5.80 \times 10^3 d_p)} \tag{14}$$

Table 3 compares the correlation coefficients for the four models. The data for models LPFOM and MLPOM were determined previously (36) and were valid for 0–20 minutes (LPFOM) and 20–90 minutes (MLPFOM). The second-order model, PSOM, correlates the experimental data perfectly for 10–240 minutes, whereas model MPSOM is valid for 0–240 minutes.

Effect of Initial Concentration

The experimental results demonstrating the effect of initial lead(II) concentration with time is shown in Figures 3 and 4 for the sorption of lead(II) on peat with modified pseudo-second order model. When the initial lead(II) concentration is 101 mg/dm^3, saturation was obtained in less than 15 minutes and in the case of 209 mg/dm^3, saturation occurred in less than 120 minutes. The linearity of the plots of the modified pseudo-second-order model indicates that chemical reaction is the main rate-controlling step throughout most of the sorption process. Table 4 shows the influence of the time constant, t_0, obtained in the first 20 minutes, which increased with the increasing initial lead(II) concentration. A plot of lead(II) initial concentration versus t_0 is shown in Figure 5. A mass of 6.8 g peat (500–710 μm) has been used for all studies. A linear empirical correlation can be determined to describe the relationship between t_0 and C_0 in the following form:

$$t_0 = aC_0 + b \tag{15}$$

where a and b are constants.

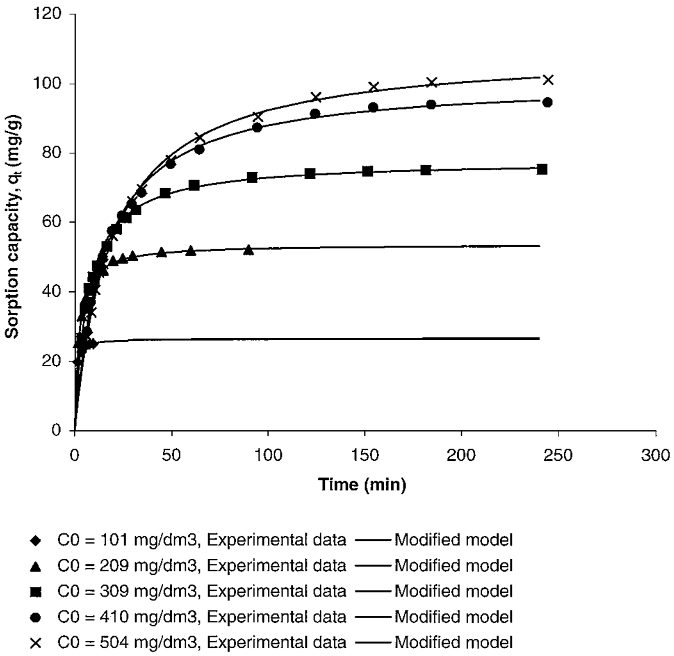

Figure 3. Plot of sorbed amount versus time for lead at various initial concentrations.

Substituting the numerical values from Figure 5 gives:

$$t_0 = 0.0145C_0 - 1.599 \qquad (16)$$

and the correlation coefficient, $r^2 = 0.915$.

However the equilibrium sorption capacity changes with initial lead(II) concentrations. This effect can be confirmed quantitatively by plotting the operating lines for the five initial lead(II) concentration tests on the lead equilibrium isotherm. Figure 6 shows the experimental equilibrium data points and the best fit Langmuir isotherm representing the experimental data. The five operating lines are shown on the Figure 6 demonstrating the different q_e values.

The t_0 values increase with increasing C_0 and a higher C_0 produces a higher driving force across the film, which should result in a more rapid change to kinetic control; however, a higher limiting q_e (at the surface) is required as C_0 increases, and this is the main factor controlling kinetics. This takes a longer time to stabilize.

Table 5 shows the correlation coefficients for the four models. The LPFOM and MLPFOM are subject to the same time constraints as the d_p results. The effect of C_0 is only perfectly modeled by the MPSOM.

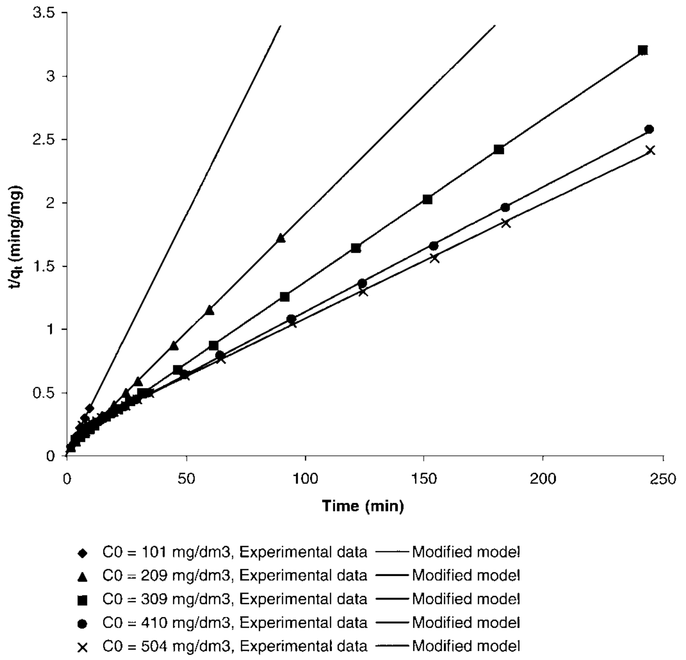

Figure 4. Modified pseudo-second-order sorption kinetics of lead(II) onto peat at various initial concentrations.

Effect of Temperature

Increasing the temperature is known to increase the rate at which chemisorption and diffusion processes occur. A series of experiments was undertaken at temperatures of 6, 15, 25, 35, and 45°C. Figure 7 shows plots of q_t against time for

Table 4. Kinetic Parameters for the Sorption of Lead(II) on Peat at Various Initial Lead(II) Concentrations

C_0 (mg/dm^3)	q_e (mg/g)	k_2' (g/mg min)	h (mg/g min)	r^2	t_0 (min)
101	26.5	7.27×10^{-2}	51.2	1.000	0.458
209	53.5	8.71×10^{-3}	24.9	1.000	0.684
309	77.8	1.90×10^{-3}	11.5	1.000	2.39
410	101	6.58×10^{-4}	6.73	1.000	5.19
504	110	4.78×10^{-4}	5.77	1.000	5.48

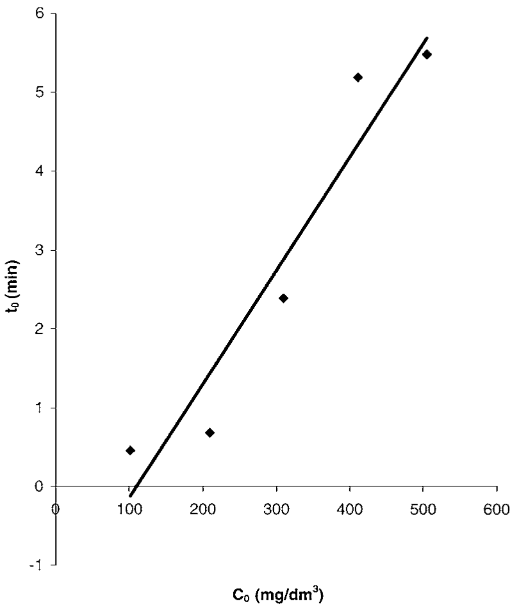

Figure 5. The relationship between initial concentration and t_0.

the modified pseudo-second-order model for the sorption of lead(II) on peat. The kinetic parameters are shown in Table 6 together with time constant t_0. The initial sorption rate, h, increases from 4.50 to 33.3 mg/gmin, and the rate constant, k_2', increases from 7.27×10^{-4} to 5.60×10^{-3} g/mgmin with the increase of solution temperature from 279 to 318°K. However the influence of solution temperature on sorption capacity, q_e, is very slight. The results show a decrease in t_0 as the temperature is increased. Figure 8 shows a plot of $\ln(k_2')$ against $1/T$ is linear, and the activation energy of the process has been determined as 37.7 kJ/mol using an Arrhenius equation of the type:

$$k_2' = 1.002 \exp^{\frac{-37700}{RT}} \tag{17}$$

where A and E are the Arrhenius constant and activation energy of sorption (kJ/mol), respectively. Physisorption processes usually have energies in the range of 5–20 kJ/mol, the value of 37.7 kJ/mol in the present studies indicates a chemical sorption process.

The decrease in t_0 is almost certainly due to the decrease in water viscosity and slightly due to a decrease in water density with increasing temperature. Both these phenomena will lower the film resistance round the particle.

Table 7 gives the four model correlation coefficients. Model (ii) is in good agreement with experimental data for the 20–90 minute period, except for the first

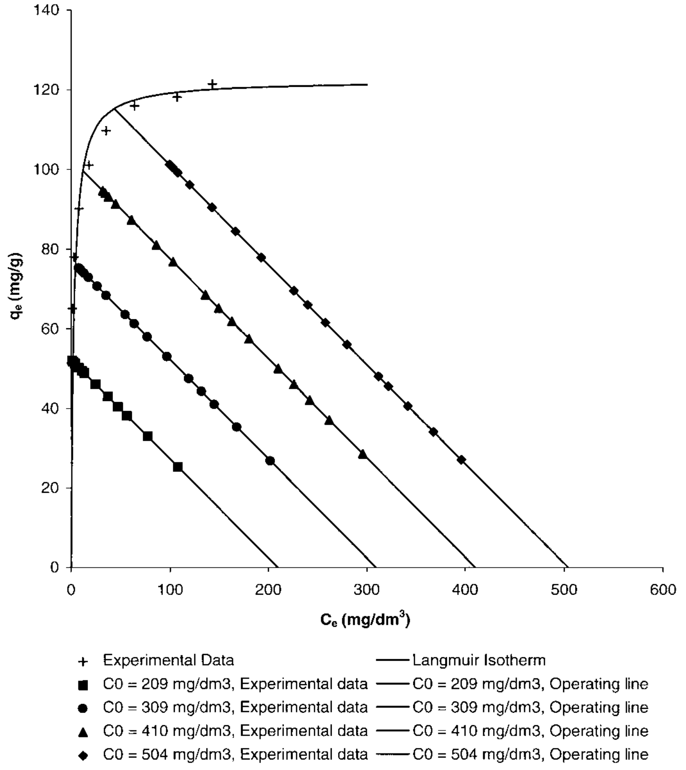

Figure 6. Langmuir isotherm for the sorption of lead of initial lead concentration.

data point. However, the t_0 value for this point is 33.4 minutes, well outside the $\cong$20 minutes t_0 values for the other four temperature systems. The model PSOM again correlates all five sets of experimental temperature data perfectly with the PSOM model correlating four out of the five systems perfectly.

Table 5. Correlation Coefficient for Effect of Initial Concentration on the Four Models

Variable C_0 (mg/dm^3)	Model r^2 Values			
	LPFOM	MLPFOM	PSOM	MPSOM
101	0.997	0.999	1.000	1.000
209	0.992	0.999	1.000	1.000
309	0.994	1.000	1.000	1.000
410	0.999	0.999	0.999	1.000
504	0.998	0.999	0.998	1.000

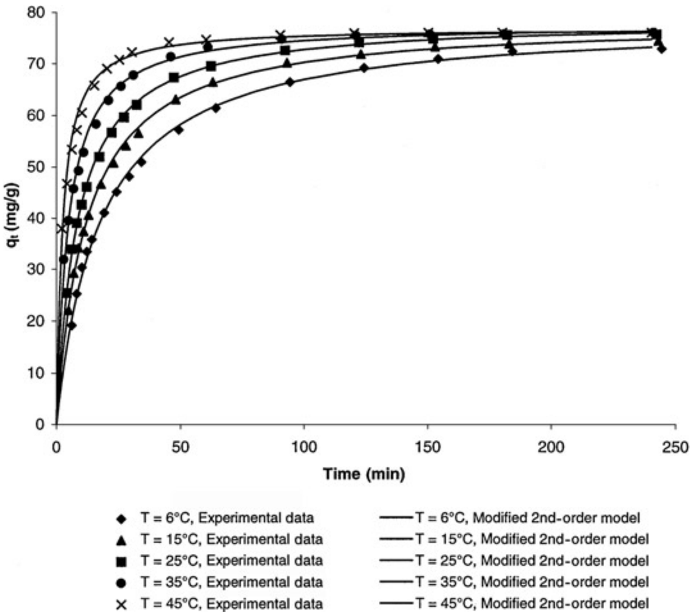

Figure 7. Plot of amount of lead versus time at various temperatures.

Effect of Agitation

The effect of varying the agitation speed is shown in Figure 9 for the sorption of lead(II) onto peat for the modified pseudo-second-order model. The theoretical curves give a good prediction of experimental results. The corresponding linear plots of the values of k_2' and h against agitation speed, S, were regressed to obtain expressions for these values in terms of the agitation speed with high correlation coefficients of 0.996 and 0.997, respectively. It is possible to correlate k_2' and h as

Table 6. Kinetic Parameters for the Sorption of Lead(II) on Peat at Various Solution Temperatures

T (°K)	q_e (mg/g)	k_2' (g/mg min)	h (mg/g min)	r^2	t_0 (min)
279	78.7	7.27×10^{-4}	4.50	1.000	4.02
288	78.6	$1.07 \times 10{-}3$	6.62	1.000	2.72
298	78.8	1.52×10^{-3}	9.47	1.000	1.96
308	77.9	2.78×10^{-3}	16.9	1.000	0.762
318	77.1	5.60×10^{-3}	33.3	1.000	5.00×10^{-3}

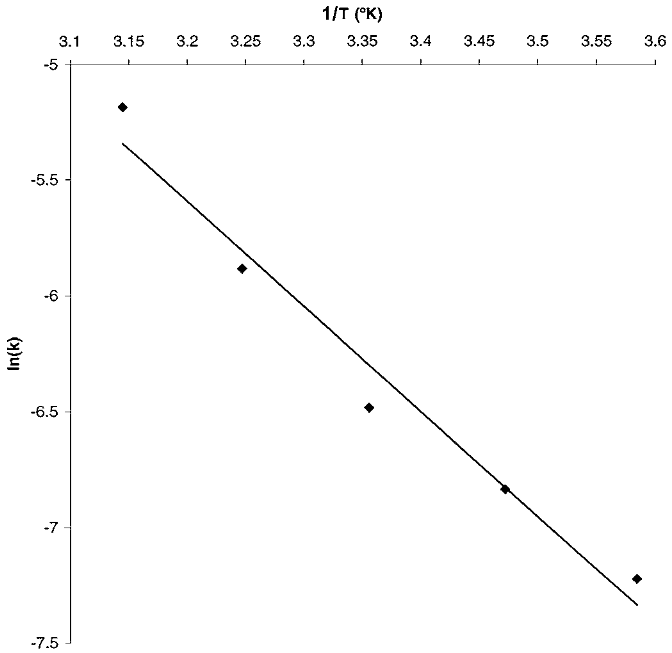

Figure 8. The relationship between temperature and t_0.

a function of S as follows:

$$k_2' = \frac{1}{1.44 \times 10^3 - 2.11S} \tag{18}$$

$$h = \frac{1}{0.218 - 3.12 \times 10^{-4}S} \tag{19}$$

Table 7. Correlation Coefficient for Effect of Temperature on the Four Models

	C Model r^2 Values			
Variable T (°K)	LPFOM	MLPFOM	PSOM	MPSOM
279	0.999	0.991	0.999	1.000
288	0.997	1.000	1.000	1.000
298	0.997	0.998	1.000	1.000
308	0.999	1.000	1.000	1.000
318	0.997	1.000	1.000	1.000

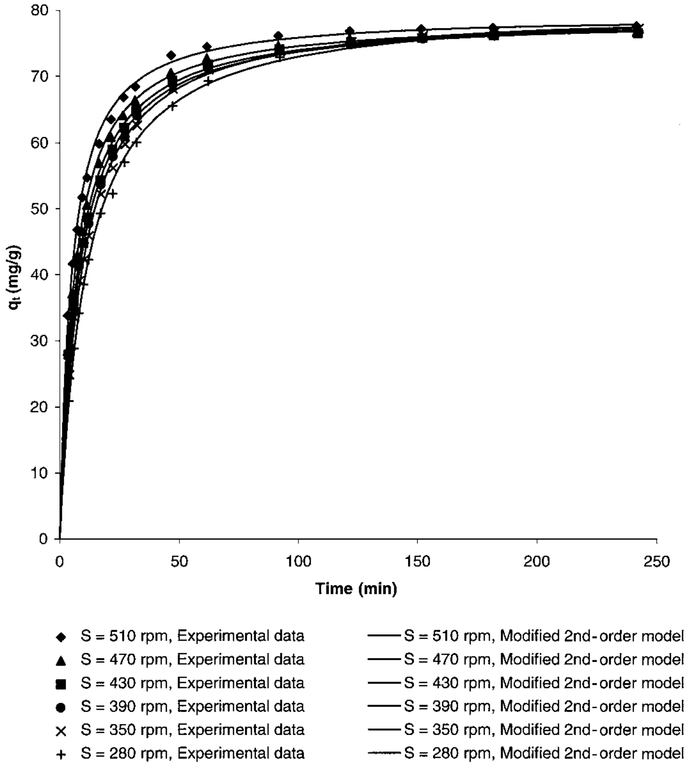

Figure 9. Plot of sorbed amount versus time for lead at various agitation speeds.

However, the influence of agitation speed on sorption capacity, q_e, is small. Figure 10 shows a plot of agitation speed against t_0, and the values of k_2' and t_0 are shown in Table 8.

At low agitation, the peat particles are not completely mixed and the t_0 value is approximately constant until 390 rpm because there is no influence on the boundary film. At 390 rpm the peat particles are fully suspended and completely mixed. From 390 rpm to 470 rpm, increasing agitation increases the shear force on the boundary film and decreases the boundary layer of fluid surrounding the suspended particle. At 470 rpm and above the t_0 are becoming fairly constant, indicating that a limiting thickness of the boundary layer fluid film surrounding the particle is being approached at $t_0 = 1.03 \pm 0.03$. However, the influence of increasing agitation on the boundary layer, resistance is still effective, as can be seen from the changing k_2' values with 5 rpm in Table 8. The correlation coefficients, r^2, for the four models are shown in Table 9. None of the LPFOM systems are correlated perfectly, and only half the MLPFOM systems

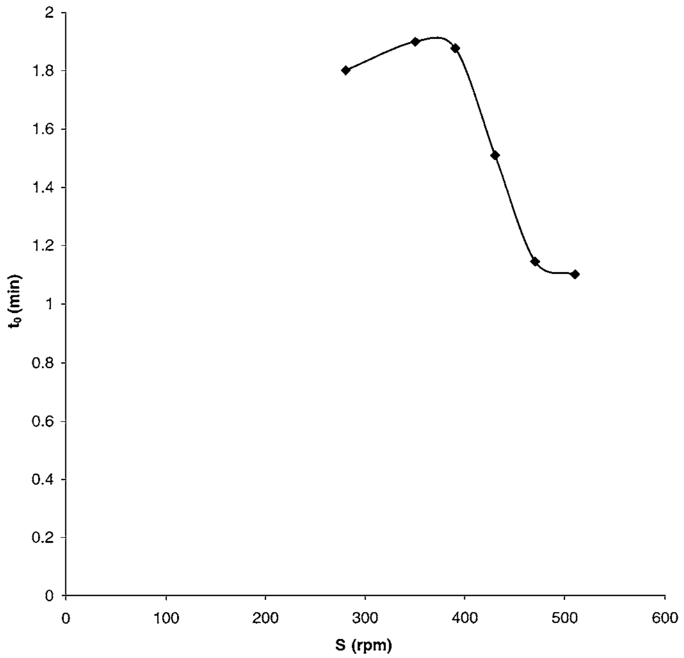

Figure 10. The relationship between agitation speed and t_0.

have a correlation coefficient at 1.000. A similar trend is observed with Model (iii), PSOM, as only two sets of data are fully correlated. Consequently, only the MPSOM provides a really satisfactory correlation of the experimental data, thus confirming a second-order chemisorption mechanism with some initial boundary layer film resistance as the most appropriate description of the sorption of lead(II) ions onto peat.

Table 8. Kinetic Parameters for the Sorption of Lead(II) on Peat at Various Agitation Speeds

S (rpm)	q_e (mg/g)	k'_2 (g/mg min)	h (mg/g min)	r^2	t_0 (min)
280	80.8	1.16×10^{-3}	7.57	1.000	1.80
350	80.3	1.43×10^{-3}	9.24	1.000	1.90
390	79.3	1.67×10^{-3}	10.5	1.000	1.88
430	79.0	1.86×10^{-3}	11.6	1.000	1.51
470	78.9	2.20×10^{-3}	13.7	1.000	1.01
510	79.4	2.71×10^{-3}	17.1	1.000	1.05

Table 9. Correlation Coefficient for Effect of Variable Agitation on the Four Models

Variable S (r.p.m)	Model r^2 Values			
	LPFOM*	MLPFOM**	PSOM	MPSOM
280	0.998	0.999	0.999	1.000
350	0.998	1.000	0.999	1.000
390	0.997	0.999	1.000	1.000
430	0.997	1.000	1.000	1.000
470	0.999	1.000	0.999	1.000
510	0.998	0.996	0.998	1.000

* Valid for initial 20 minutes only[36]

** Valid for 20–90 minute sorption period only[36]

Correlation of Pseudo-Second-Order Rate Constant

A general correlation for the second-order rate constant, k_2', for the best fit model namely, the MPSOM, has been developed as shown in Equation (20):

$$k_2' = \frac{3.42T^{0.93}S^{1.4}}{C_0^{3.2}d_p^{2.1}} \tag{20}$$

The correlation coefficient for Equation (20) is 0.903. Therefore, k_2' can be predicted for any set of process system variables.

CONCLUSION

The kinetics of sorption of lead ions onto peat have been studied on the basis of a modified pseudo-second-order rate model (MOPM). A number of conclusions can be made:

- The equilibrium sorption capacity is affected by the initial lead(II) concentration, particle size, and solution temperature. These phenomena suggest that the process of sorption of lead(II) on peat includes chemisorption. However, a simple Lagergren first-order model (LPFOM) and a pseudo-second-order model (PSOM) were not sufficient to correlate the experimental data particularly after the initial 30 minutes.
- Therefore, it was necessary to consider an additional contributing factor or resistance to explain the mechanism:
    - The degree of swelling
    - The rate of wetting the particle
    - Film diffusion may be a factor responsible for t_0

- The degree of swelling was low and took up to 30 minutes to reach equilibrium (48), and therefore this is probably not responsible for the t_0 effect in this work.
- The variation of t_0 with agitation speed could be explained by either film diffusion resistance or the rate of particle wetting or a combination of both processes. The fact that t_0 increases with initial lead concentration does suggest that the rate of wetting is the responsible cause. The ionic strength of the solution changes with C_0, which is more likely to affect the rate of bulk liquid wetting of the particle rather than the resistance of the boundary film. The variation in t_0 did not show a definite trend with d_p but it did decrease with both increasing temperature and agitation speed.

These other trends with both d_p and S strongly support a mechanism initially controlled by the thickness of the fluid boundary layer surrounding the particle, followed by a second-order sorption kinetic control step. It seems reasonable to assume that the t_0 effect is due, in part, to particle wetting and, in part, to boundary layer resistance.

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NOMENCLATURE

A	Arrhenius constant
C_0	initial solution phase metal ion concentration (mg/dm^3)
d_p	peat particle size (μm)
E	activation energy of sorption (kJ/mol)
h	initial metal ion sorption rate (mg metal/g peat min)
HP^-	polar sites on the peat surface
$(HP)_0$	number of equilibrium sites (polar) occupied on the peat at time t
$(HP)_t$	number of active sites (polar) occupied on the peat at time t
k_1	pseudo-first-order rate constant in LPFOM model (min^{-1})
k_1'	pseudo-first-order rate constant in MLPFOM model (min^{-1})
k_2	pseudo-second-order rate constant (g peat/mg metal min)
LPFOM	Lagergren pseudo-first-order model
MLPFOM	modified Lagergren pseudo-first-order model
MPSOM	modified pseudo-second-order model
P^-	polar sites on the peat surface

P_0	number of equilibrium sites (polar) occupied on the peat at time t
PSOM	pseudo-second-order model
P_t	number of active sites occupied on the peat at time t
q_e	mass of metal ion sorbed at equilibrium (mg metal ion/g peat)
q_t	mass of metal ion sorbed at time t (mg metal ion/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)
S	agitation speed (revolutions/minute)
t	contact time (min)
t_0	contact time at zero (min)
T	temperature (K, °C)

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