RESEARCH NOTE

THE SORPTION OF LEAD(II) IONS ON PEAT

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Abstract—The sorption of lead ions from aqueous solution onto peat has been studied. Kinetic studies have been carried out using an agitated batch and the effect of varying process parameters has been investigated; these include initial lead ion concentration, peat particle size, solution temperature and agitation speed. The data were analyzed using a pseudo-first order Lagergren equation and the data were correlated using a two-step first order reaction mechanism. © 1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

The first order rate equation of Lagergren (1898) has long been widely applied. The earlier application of the first order rate equation of Lagergren to the sorption of cellulose triacetate from chloroform on calcium silicate was undertaken by Trivedi *et al.* (1973). Numerous studies report first order Lagergren kinetics for the sorption of metals, such as the sorption of nickel(II) from aqueous solutions by Wollastonite and China clay (Sharma *et al.*, 1990, 1991), the sorption of chromium(VI) traces by bismuth trioxide (Bhutani and Kumari, 1994) and the sorption of lead(II) onto kaolinitic clay (Orumwense, 1996). However, it is often incorrect to apply simple kinetic models such as first- or second-order rate equations to a sorption system with solid surfaces which are rarely homogeneous and because the effects of transport phenomena and chemical reactions are often experimentally inseparable (Sparks, 1989). Singh *et al.* (1996) reported that the sorption of mercury(II) by kaolinite obeyed multiple first order kinetics.

This investigation studies the kinetics of the sorption of lead(II) by peat under various initial lead (II) concentrations, solution temperatures, peat particle size ranges and agitation speeds.

THEORY

The Lagergren rate equation (Lagergren, 1898) was the first rate equation for the sorption of

liquid/solid system based on solid capacity. The Lagergren rate equation is one of the most widely used sorption rate equations for the sorption of a solute from a liquid solution. It may be represented:

$$\frac{dq_t}{dt} = k(q_e - q_t) \tag{1}$$

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

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

which is the integrated rate law for a pseudo-first order reaction, where q_e is the amount of dye sorbed at equilibrium (mg/g); q_t is amount of dye sorbed at time t (mg/g); k is the equilibrium rate constant of pseudo-first sorption (1/min).

Equation 2 can be rearranged to obtain a linear form

$$\log(q_e - q_t) = \log(q_e) - \frac{k}{2.303}t \tag{3}$$

The equation applicable to experimental results generally differs from a true first order equation two ways (Aharoni and Sparks, 1991).

● The parameter $k(q_e - q_t)$ does not represent the number of available sites.
● The parameter $\log(q_e)$ is an adjustable parameter, often it is found not equal to the intercept of a plot of $\log(q_e - q_t)$ against t, whereas in a true first order process $\log(q_e)$ should be equal to the intercept of a plot of $\log(q_e - q_t)$ against t.

In order to fit equation 3 to experimental data, the equilibrium sorption capacity, q_e, must be

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known. In most cases in the literature, the pseudo-first order equation of Lagergren does not fit well for the whole range of contact time. In equation 3, one has to find some means of extrapolating the experimental data to $t = \infty$, or treat q_e as an adjustable parameter to be determined by trial and error. For this reason, it is necessary to use a trial and error method to obtain the equilibrium sorption capacity, q_e.

The results of the equilibrium sorption capacity, q_e, from equation 3 using a trial and error method cannot agree with the value determined from intercept of equation 3, $\log(q_e)$ in this study. A time constant, t_0, therefore can be considered for a pseudo-first order process as shown in equation 4:

$$\log(q_e - q_t) = \log(q_e) - \frac{k}{2.303}(t + t_0) \qquad (4)$$

where t_0 is an adjustable parameter that makes the equilibrium sorption capacity, q_e, suitable for use in the kinetic expression. Its value may be determined by plotting equation 4, the intercept gives q_e with an extremely high correlation coefficient in all studies.

EXPERIMENTAL PROCEDURE

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 analyzed with an inductively coupled plasma atomic emission spectrophotometer (ICP-AES) for all of studies. Unless a process parameter was the system variable, the following conditions were used a 6.8 g sample of peat (500–710 μm) was added to each 1.7 dm³ volume of lead(II) solution using an agitation speed of 400 rpm at room temperature ($24 \pm 2°C$).

DISCUSSION AND RESULTS

Equilibrium isotherm

The equilibrium isotherm for the sorption of lead(II) on peat was determined by agitating 0.25 gm peat (500–710 μm) with 50×10^{-3} dm³ of lead(II) solutions of various concentrations. The systems were agitated in a constant temperature shaking water bath for seven days. The experimental points are shown in Fig. 1 and compared with a solid Langmuir isotherm line, having a correlation coefficient 0.99 and equation:

$$q_e = \frac{45.6C_e}{1 + 0.374C_e}. \qquad (5)$$

Effect of initial concentration

Several experiments were undertaken to study the effect of varying the initial lead(II) concentration on the rate of lead(II) removal from solution. A range of lead(II) concentrations from 100 to 500 mg/dm³ were used and agitation was carried out for four hours.

The effect of initial concentration on the sorption of lead(II) on peat is shown in Fig. 2. The curves
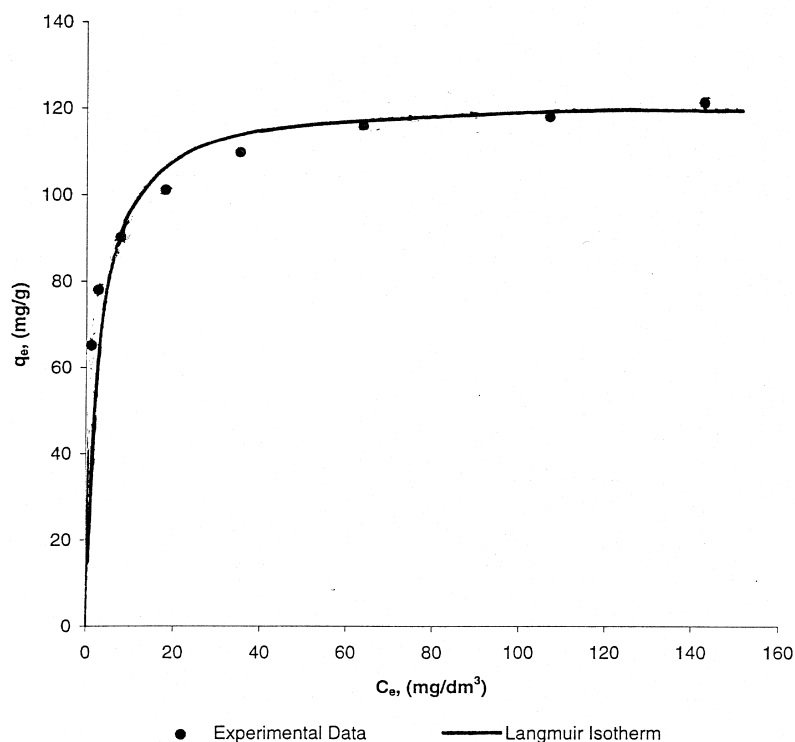

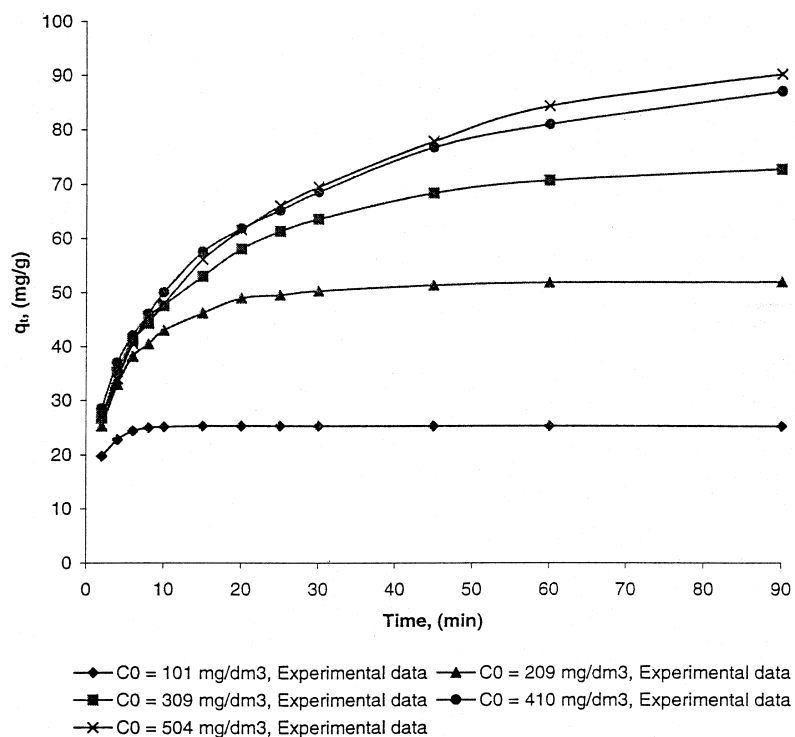Fig. 1. Isotherm for the sorption of lead(II) using peat.

Fig. 2. Effect of concentration on the sorption of lead(II) by peat at various initial concentrations.

indicate that the rate of sorption is very fast initially and reaches a plateau at equilibrium. When the initial lead(II) concentration is 209 mg/dm³, saturation was obtained in less than 120 min. The change in the sorption capacity with time is found to fit the first order relationship as defined by
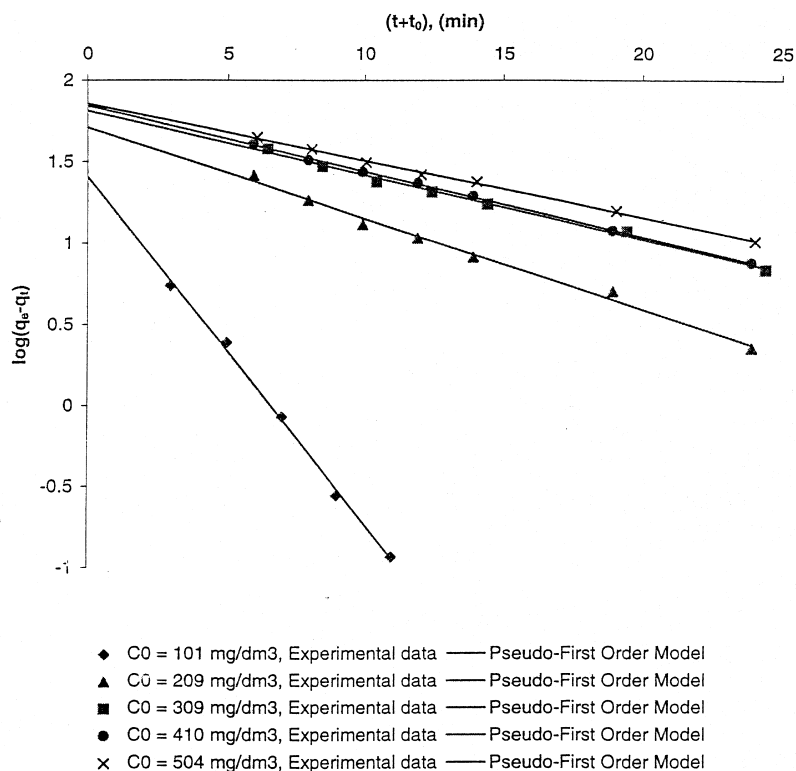

Fig. 3. Pseudo-first order sorption kinetics of lead(II) onto peat at various initial concentrations.

Table 1. Kinetic parameters for the sorption of lead(II) on peat at 0–20 min

C_0 (mg/dm^3)	k_1 (1/min)	q_e (mg/g)	t_0 (min)	r^2	q_{20} (mg/g)	q_{240} (mg/g)
504	8.08×10^{-2}	71.7	4.03	0.998	61.5	101
410	9.29×10^{-2}	69.3	3.90	0.999	61.8	94.6
309	9.12×10^{-2}	64.8	4.42	0.994	58.0	75.3
209	0.129	51.2	3.91	0.992	48.9	52.3
101	0.494	25.2	0.947	0.997	25.3	–

Table 2. Kinetic parameters for the sorption of lead(II) on peat at 20–90 min

C_0 (mg/dm^3)	k_2 (1/min)	q_e (mg/g)	t_0 (min)	r^2	q_{240} (mg/g)
504	2.79×10^{-2}	95.2	17.0	0.999	101
410	2.52×10^{-2}	92.6	23.7	0.999	94.6
309	4.09×10^{-2}	93.4	18.2	1.00	75.3
209	5.99×10^{-2}	52.1	25.8	0.999	52.3

equation 4 and the results indicate that the lead(II) sorption in these systems obeyed a two-step first order kinetics, because the regression analysis of equation 4 revealed two distinct rate curves. The values of the rate constants for the first two steps can be obtained from the slopes of the lines in Fig. 3. The constants of k_1, k_2, t_0 and equilibrium sorption capacity, q_e, evaluated from equation 4 for the four different initial concentrations are presented in Tables 1 and 2.

The rate constants for the first step, k_1, is higher than the second step for each initial concentration of lead(II).

Effect of temperature

A series of experiments were undertaken to study of effect of temperature by performing experiments at 6, 15, 25, 35 and 45°C. In all the experiments the particle size range of peat was 500–710 μm, the initial lead(II) concentration was 300 mg/dm^3 and an agitation speed of 400 rpm was used. The influence of temperature on the sorption of lead(II) is shown in Fig. 4. The rate of sorption increased with decreasing temperature and the constants from equation 4 are shown in Tables 3 and 4.

The effect of temperature on the sorption rate in the first and second regions is shown in Fig. 5. The values of k_1 and k_2 increase with decreasing temperature. The activation energy for the sorption of lead(II) was calculated and for the first step it is 6.39 kJ/mol and for the second step is 11.4 kJ/mol using the Arrhenius equation.
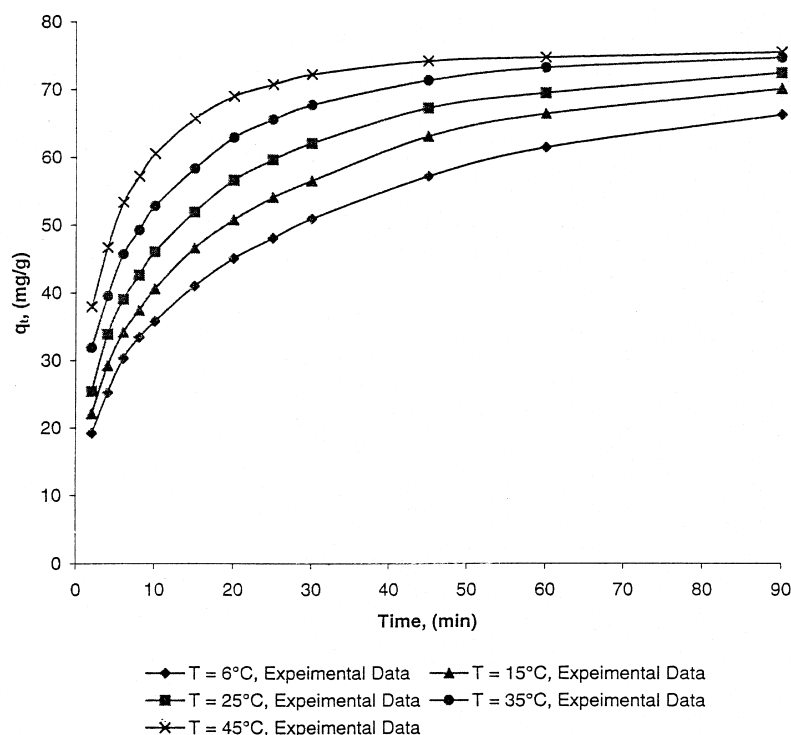

Fig. 4. Effect of temperature on the sorption of lead(II) by peat at various temperatures.

Table 3. Kinetic parameters for the sorption of lead(II) on peat at 0–20 min

T (°K)	k_1 (1/min)	q_e (mg/g)	t_0 (min)	r^2	q_{20} (mg/g)	q_{240} (mg/g)
279	0.129	72.2	4.04	0.999	69.0	76.2
288	9.72×10^{-2}	68.9	4.72	0.997	62.9	76.2
298	9.23×10^{-2}	63.4	4.01	0.997	56.6	75.8
308	8.97×10^{-2}	57.5	3.71	0.999	50.7	74.6
318	8.85×10^{-2}	51.2	3.65	0.997	45.0	73.0

Table 4. Kinetic parameters for the sorption of lead(II) on peat at 20–90 min

T (°K)	k_2 (1/min)	q_e (mg/g)	t_0 (min)	r^2	q_{240} (mg/g)
279	4.67×10^{-2}	75.8	33.4	0.991	76.2
288	4.36×10^{-2}	75.3	21.8	1.00	76.2
298	3.41×10^{-2}	74.1	22.9	0.998	75.8
308	3.27×10^{-2}	72.4	17.0	1.00	74.6
318	2.53×10^{-2}	70.8	20.0	1.00	73.0

Table 5. Kinetic parameters for the sorption of lead(II) on peat at 0–20 min

| d_p (µm)	k_1 (1/min)	q_e (mg/g)	t_0 (min)	r^2	q_{20} (mg/g)	q_{240} (mg/g)
500–710	8.77×10^{-2}	65.5	3.91	0.998	57.6	78.2
355–500	0.125	70.9	3.34	0.998	67.1	78.8
250–355	0.179	75.9	3.72	0.995	74.9	79.3
150–240	0.261	77.0	3.08	0.997	76.8	79.3

Effect of particle size

The influence of contact time on four particle size ranges of peat was investigated using the size ranges listed in Table 5. The effect of uptake was studied using an initial lead(II) concentration of 300 mg/dm^3, an agitation speed of 400 rpm, a solution temperature of room temperature (24 ± 2°C) and 1.7 dm^3 volume lead(II) solution with 6.8 g of peat. The influence of particle size on the sorption of lead(II) is shown in Fig. 6. The measured values of sorption capacity at time of 20 and 240 min, q_{20} and q_{240}, are listed in Tables 5 and 6. The equilibrium sorption capacities, q_e, and first order rate constants, k_1, k_2, were determined from the equation 4.

Effect of agitation

A series of experiments were performed using agitation speeds of 280, 350, 390, 430, 470 and
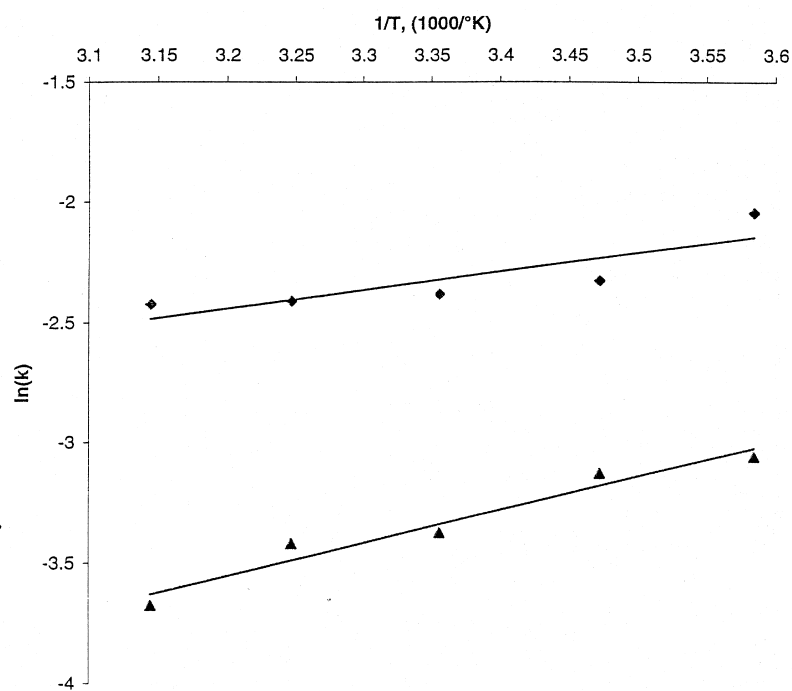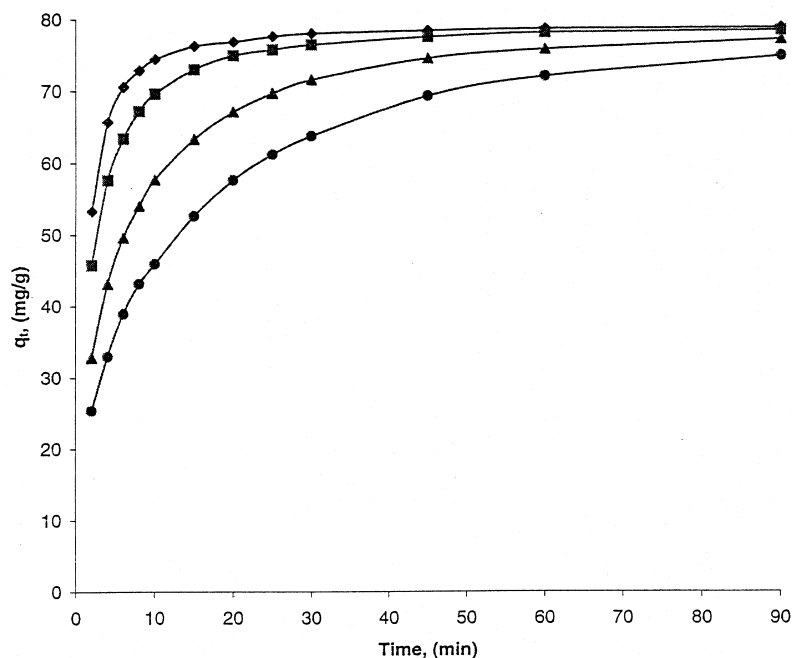
Fig. 5. Plot of In(k) against ($1/T$).

Fig. 6. Effect of particle size on the sorption of lead(II) by peat at various particle sizes.

510 rpm, and a particle size range of 500–710 μm. The initial lead(II) concentration was 300 mg/dm^3. From the contact time results the first order rate constant, k_1 and k_2 can be obtained using equation 4. The k_1 and k_2 values and equilibrium sorption capacity, q_e, determined using trial and error method are compared in Tables 7 and 8. Figure 7 illustrates a plot of sorption capacity against time. The constants of k_1, k_2, t_0 and equili-brium sorption capacity, q_e, evaluated from equation 4 for the six different agitation speeds are presented in Tables 7 and 8. The influence of agitation speed on the rate constant, k, is very slight.

Since t_0 has been considered as a pre-sorption time, the equilibrium sorption capacity, q_e, can be evaluated by equation 4 using a trial and error method were closer to the experimental data (q_{240}) which are shown in Tables 1–8.

Table 6. Kinetic parameters for the sorption of lead(II) on peat at 20–90 min

d_p (μm)	k_1 (1/min)	q_e (mg/g)	t_0 (min)	r^2	q_{240} (mg/g)
500–710	3.66×10^{-2}	76.3	18.8	0.999	78.2
355–500	4.15×10^{-2}	77.9	29.0	0.997	78.8
250–355	4.40×10^{-2}	78.6	48.7	1.00	79.3
150–240	4.18×10^{-2}	78.7	67.4	0.990	79.3

Table 7. Kinetic parameters for the sorption of lead(II) on peat at 0–20 min

S (rpm)	k_1 (1/min)	q_e (mg/g)	t_0 (min)	r^2	q_{20} (mg/g)	q_{240} (mg/g)
510	0.115	67.5	4.24	0.998	63.5	77.7
470	0.108	66.1	3.45	0.999	60.8	76.8
430	9.37×10^{-2}	65.6	4.33	0.997	59.0	76.6
390	9.89×10^{-2}	63.7	4.05	0.997	57.9	76.7
350	0.102	61.7	3.38	0.998	56.2	77.2
280	0.120	56.5	1.80	0.998	52.3	77.0

Table 8. Kinetic parameters for the sorption of lead(II) on peat at 20–90 min

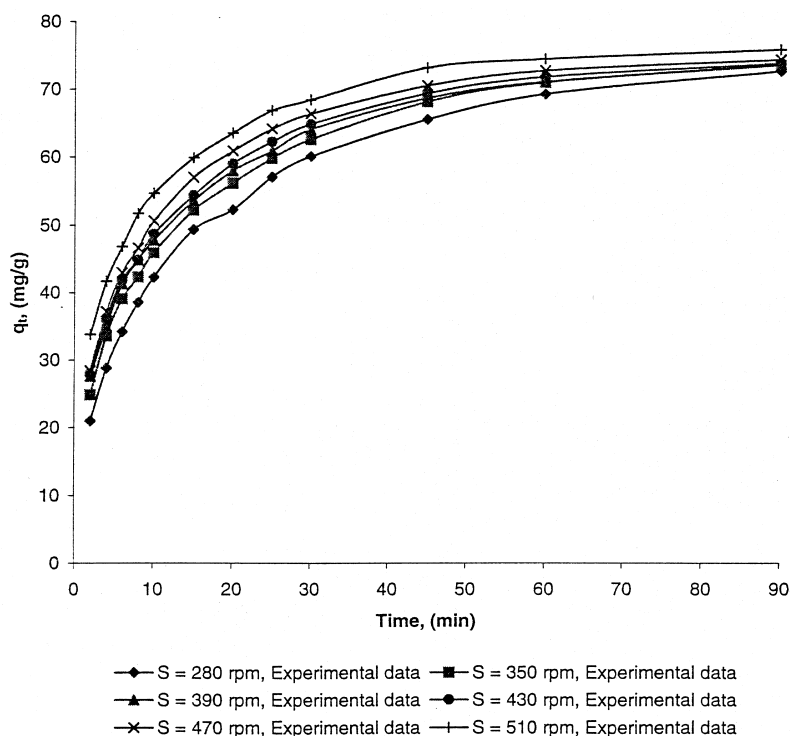| S (rpm)	k_2 (1/min)	q_e (mg/g)	t_0 (min)	r^2	q_{240} (mg/g)
510	4.77×10^{-2}	76.5	17.7	0.996	77.7
470	4.27×10^{-2}	75.0	19.2	1.00	76.8
430	4.03×10^{-2}	75.0	18.9	1.00	76.6
390	3.69×10^{-2}	74.9	20.6	0.999	76.7
350	3.89×10^{-2}	74.8	15.9	1.00	77.2
280	3.43×10^{-2}	74.8	16.2	0.999	77.0

Fig. 7. Effect of agitation speed on the sorption of lead(II) by peat at various agitation speeds.

CONCLUSION

The kinetics of sorption of lead ions onto peat has been well correlated by a pseudo-first order two step reaction mechanism. The first reaction stage appears to be diffusion controlled and the second stage is chemisorption controlled. The two disadvantages of the model are firstly, that a value for the equilibrium sorption capacity, q_e, has to be incorporated into the kinetic equation and solved by trial and error.

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