

# BATCH LEAD(II) REMOVAL FROM AQUEOUS SOLUTION BY PEAT: Equilibrium and Kinetics

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The sorption of lead ions onto peat has been studied. Equilibrium isotherms have been measured and modelled. Kinetic studies have been carried out in a batch adsorber to study the effect of initial concentration, agitation and temperature. A pseudo-second order kinetic model has been proposed to correlate the experimental data.

*Keywords: kinetics; lead; peat; sorption.*

## INTRODUCTION

The hazards to human life from the effects of various metal ions have received extensive attention in the past twenty years. In particular, low levels of cadmium, lead and mercury have been the subject of considerable studies in the medical field. The effects of lead on neurobehavioural development<sup>1</sup> and brain cell function<sup>2</sup> have been investigated. The accumulation of lead in river beds<sup>3</sup> has been detected and gives cause for concern. Consequently, methods to remove lead and other metal ion species from drinking waters and wastewaters have been the subject of several research papers.

The removal of lead from drinking water has been studied using activated carbon in batch systems<sup>4,5</sup> and fixed bed column systems<sup>6</sup>. Since activated carbon is the most widely used adsorbent in industry, several studies<sup>7-11</sup> have reported on its use to sorb metal ions from wastewaters. However, activated carbon is an expensive adsorbent material despite its ability for regeneration, when appropriate. Therefore in recent years extensive studies have been undertaken to find cheaper sorbent materials to remove lead and other metal ions from aqueous effluents.

In the case of lead removal these include water hyacinth<sup>12</sup>, *Eichhornia crassipes*<sup>13</sup>, marine algae biomass<sup>14,15</sup>, wood and fungal biosorbents<sup>16</sup>, olive stone based carbon<sup>17</sup>, bottom ash<sup>18</sup>, blast furnace sludge<sup>19</sup>, penicillium biomass<sup>20</sup>, groundnut husks<sup>21</sup>, kaolinitic clay<sup>22</sup>, *Cladophora crispata*<sup>23</sup>, oxidized anthracite<sup>24</sup>, goethite<sup>25</sup>, *Zoogloea ramigera*<sup>26</sup>, waste tea leaves<sup>27</sup>, china clay and wollastonite<sup>28</sup>. Furthermore, the use of peat, a humic based material, for a wide range of pollution applications has been reviewed<sup>29</sup>. The application of peat and humic acid for lead sorption has received limited attention.<sup>30-32</sup> There is only limited information available on the kinetics and mechanism of lead sorption onto peat. The current research presents an equilibrium model and a pseudo-second order kinetic model for the sorption of lead ions onto peat in batch sorption systems.

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

### Equilibrium Studies

The sorption isotherm was obtained by shaking a fixed weight (0.5 g) of peat with 125 ml of lead(II) solution of known initial lead(II) concentration. Shaking was carried out for five days, and after this time the solution was filtered and analysed with an inductively coupled plasma atomic emission spectroscope (ICP-AES).

#### *Effect of initial concentration*

A range of lead(II) concentrations from 200 to  $500 \text{ mg dm}^{-3}$  were used and agitation was carried out for four hours. All contact investigations were carried out using a baffled agitated  $2 \text{ dm}^3$  sorber vessel. Samples (3 ml) were withdrawn at suitable time intervals, filtered through a  $0.45 \mu\text{m}$  membrane filter and then analysed with an inductively coupled plasma atomic emission spectroscope (ICP-AES) for all studies. A 6.8 g sample of peat ( $500-710 \mu\text{m}$ ) was added to each  $1.7 \text{ dm}^3$  volume of lead(II) solution using an agitation speed of 400 rpm at  $24 \pm 2^\circ\text{C}$ .

### Kinetic Studies

#### *Effect of agitation*

A range of agitation speeds from 280 to 510 rpm were used and agitation was carried out for four hours. A 6.8 g sample of peat ( $500-710 \mu\text{m}$ ) was added to each  $1.7 \text{ dm}^3$

volume of lead(II) solution with initial concentration  $300 \text{ mg dm}^{-3}$ .

#### Effect of temperature

A range of temperatures from 6 to  $45^\circ\text{C}$  were used and agitation was carried out for four hours. A 6.8 g sample of peat (500–710  $\mu\text{m}$ ) was added to each  $1.7 \text{ dm}^3$  volume of lead(II) solution with initial concentration  $300 \text{ mg dm}^{-3}$  using an agitation speed of 400 rpm.

### Kinetic Model Theory

The sorption kinetics can be described by a pseudo-second order model and the differential equation is as follows:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \quad (1)$$

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

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + kt \quad (2)$$

which is the integrated rate law for a pseudo-second order reaction.  $q_e$  is the amount of metal ion sorbed at equilibrium ( $\text{mg g}^{-1}$ ) and  $k$  is the equilibrium rate constant of pseudo-second order sorption ( $\text{g mg min}^{-1}$ ).

Equation (2) can be rearranged to obtain a linear form:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t \quad (3)$$

and

$$h = kq_e^2 \quad (4)$$

where  $h$  is the initial sorption rate ( $\text{mg g min}^{-1}$ ) and equation (2) can be rearranged to obtain:

$$q_t = q_e \left[ 1 - \frac{1}{(1 + kq_e t)} \right] = \frac{q_e^2 kt}{(1 + q_e kt)} \quad (5)$$

## RESULTS AND DISCUSSION

### Equilibrium Studies

The analysis of the isotherm data is important to develop an equation which accurately represents the results and which could be used for design purposes. In order to investigate the sorption isotherm, three equilibrium models were analysed. These included the Langmuir, the Freundlich and the Redlich-Peterson isotherm equations. The Langmuir sorption isotherm<sup>33</sup> is perhaps the best known of all isotherms describing sorption. The Langmuir sorption isotherm is often used to describe sorption of a solute from a liquid solution as:

$$q_e = \frac{KC_e}{1 + a_L C_e} \quad (6)$$

where:

$K = X_m a_L (\text{dm}^3 \text{g}^{-1})$ ;

$q_e$  is the sorption density at the equilibrium solute concentration  $C_e$  ( $\text{mg g}^{-1}$ );

$C_e$  is the concentration of sorbate in solution ( $\text{mg dm}^{-3}$ );

$X_m$  is the maximum sorption capacity corresponding to complete monolayer coverage ( $\text{mg g}^{-1}$ );

$a_L$  is a Langmuir constant related to energy of sorption ( $\text{dm}^3 \text{mg}^{-1}$ ).

The Freundlich isotherm<sup>34</sup> is the earliest known relationship describing the sorption equation and is most frequently used to describe the adsorption of organic components in solution. This fairly satisfactory empirical isotherm can be used for nonideal sorption that involves heterogeneous sorption and is expressed by the following equation:

$$q_e = K_F C_e^{1/n} \quad (7)$$

where:

$q_e$  is the sorption density ( $\text{mg g}^{-1}$ );

$C_e$  is the concentration of sorbate in solution ( $\text{mg dm}^{-3}$ );

$K_F$  and  $1/n$  are empirical constants dependent on several environmental factors and  $n$  is greater than one.

The Redlich-Peterson isotherm<sup>35</sup> contains three parameters and incorporates the features of the Langmuir and the Freundlich isotherms. It can be described as follows:

$$q_e = \frac{K_F C_e}{1 + a_R C_e^{b_R}} \quad (8)$$

It has three isotherm constants, namely  $K_R$ ,  $a_R$  and  $b_R$ . These can be evaluated from the linear plot represented by equation (9) using a trial and error optimization method:

$$\ln \left( K_R \frac{C_e}{q_e} - 1 \right) = b_R \ln(C_e) + \ln(a_R) \quad (9)$$

The distribution of lead(II) between the sorbent and the lead(II) solution, when the system is in a state of equilibrium, is of fundamental importance in determining the maximum sorption capacity of the peat for the lead ion from the isotherm. Figure 1 shows the isotherm plots for three isotherms—the Langmuir, the Freundlich and the Redlich-Peterson isotherm. The graph is plotted in the form of lead(II) sorbed per unit mass of peat,  $q_e$ , against

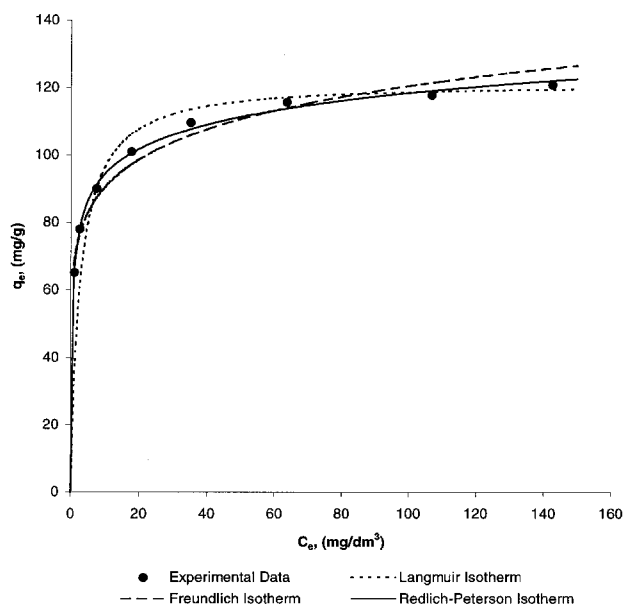


Figure 1. Isotherms for the sorption of lead(II) using peat.

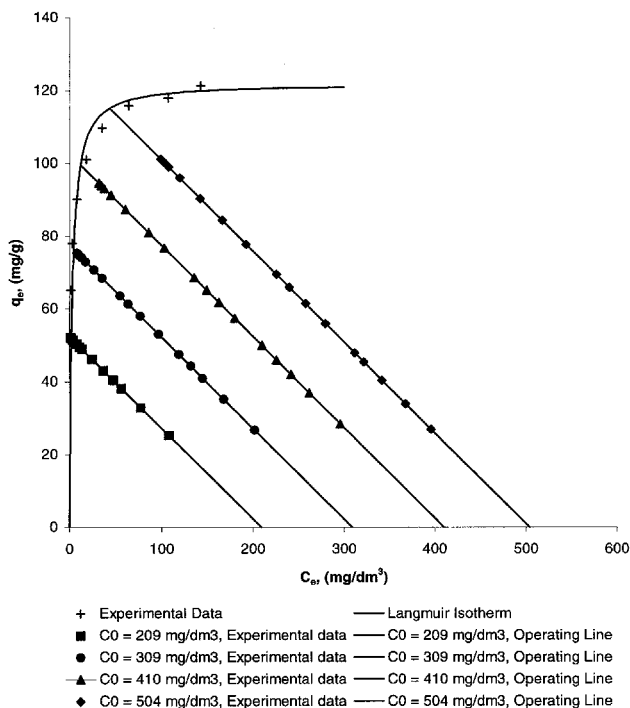


Figure 2. Langmuir isotherm for the sorption of lead at various initial lead concentrations.

the concentration of lead(II) remaining in solution,  $C_e$ . The correlation coefficients are 1.000, 0.999 and 0.972 for the Redlich-Peterson, the Langmuir and the Freundlich sorption isotherm, respectively. The equilibrium sorption of lead(II),  $X_m$ , and constant,  $a_L$ , were determined from the slope and intercept of the Langmuir equation and found to be  $122 \text{ mg g}^{-1}$  and  $0.374 \text{ dm}^3 \text{ mg}^{-1}$ , respectively. The Freundlich sorption isotherm constant  $K_F$  is  $67.8 \text{ mg g}^{-1}$  and  $1/n$  is 0.126. The Redlich-Peterson isotherm constant  $K_R$  is  $289 \text{ dm}^3 \text{ g}^{-1}$ ,  $a_R$  is 3.61 and  $b_R$  is 0.913.

Figure 2 shows the lead(II) sorption isotherm and certain operating lines for the contact time investigations. A series of parallel operating lines are generated with a slope of solution volume/peat mass. The final solution concentration is predicted from the point of intersection of the operating lines on the sorption isotherm. The equation of the operating line can be expressed as follows:

$$q_m = \frac{C_0 - C_e}{m_s} \quad (10)$$

The equilibrium sorption capacity,  $q_m$ , can be obtained from the operating line and the Langmuir equation (Figure 2). The results are in reasonable agreement with the equilibrium sorption capacity,  $q_e$ , which were obtained from the pseudo-second order model as described in the theory section. In Table 1 a comparison is made between the equilibrium sorption capacity evaluated from the Langmuir equation and the pseudo-second order model. It shows that both equilibrium sorption capacities evaluated are reasonable in all cases. The  $q_e$  values are determined from a regression analysis of equation (3).

A number of sorbents have been tested for their ability to sorb lead(II). It has already been shown that there are wide variations between the amounts of lead taken up by various sorbents from differing sources. Table 2 shows

Table 1. Comparison of the equilibrium sorption capacity, evaluated from the Langmuir equation ( $q_m$ ) and the pseudo-second order model ( $q_e$ )

$C_0, \text{ mg dm}^{-3}$	$Q_m, \text{ mg g}^{-1}$	$q_e, \text{ mg g}^{-1}$
209	51.8	53.6
309	76.1	77.3
410	99.6	98.5
504	115	106

the Langmuir constant,  $X_m$ , for the sorption of lead(II) onto various substances. The data in Table 2 show that agricultural slurry and several types of biomass have the largest sorption capacity for lead ions. These are in the range from 100 to  $1380 \text{ mg Pb g}^{-1}$  biomass. The practical problems with the biomass systems are cultivation, harvesting and designing the adsorption contacting system. Peat can be readily dried, crushed and sieved to obtain a discrete particle size range for fixed bed column sorbers or agitated batch sorbers. Amberlite IR-120<sup>14</sup> shows a significant sorption capacity of  $1039 \text{ mg Pb g}^{-1}$  resin but this ion exchange resin is over one hundred times more expensive than peat. Apart from the lead capacity of peat, reported as  $30.7 \text{ mg g}^{-1}$ <sup>30</sup>, the sorption capacity of the sphagnum peat moss in the present study of  $122 \text{ mg Pb g}^{-1}$  peat lies between the two capacities of  $150 \text{ mg g}^{-1}$  and  $61.9 \text{ mg g}^{-1}$  reported by Majid *et al.*<sup>37</sup> and Allen *et al.*<sup>40</sup> This range of peat sorption capacities is not surprising due to the multitude of types and ages of peat found naturally throughout the world. It is obvious from some preliminary testing that peats with a capacity  $>100 \text{ mg Pb g}^{-1}$  peat can be identified and used in industrial applications. The only other two sorbents with lead sorption capacities greater than  $100 \text{ mg g}^{-1}$  are spruce sawdust<sup>16</sup> and anthracite<sup>24</sup>, having lead capacities of 224 and  $259 \text{ mg g}^{-1}$  respectively. However, both these materials require chemical pretreatment, increasing process complexity and product cost. Therefore, carefully selected sphagnum peat moss appears to be one of the more attractive sorbents for lead removal.

#### Effect of agitation speed

Kinetic investigations are necessary for determining the rate of reaction and mechanism. The influence of varying the agitation speed,  $S$ , range was investigated for sorption of lead(II) using peat. The other process variables were kept constant while a series of experiments was undertaken with different agitation speeds of 510, 470, 430, 390, 350 and 280 rpm. Figure 3 shows a plot of lead(II) uptake against time at various agitator speeds for the sorption of lead(II) on peat. The variation in agitation speed appears to have only a small influence on the time required to reach equilibrium. The pseudo-second order rate constant,  $k$ , is determined from equation (3) by plotting  $t/q_t$  against  $t$ . The solid curves in Figure 3 are the theoretical plots of equation (5) and they show good agreement with the experimental data points. The rate parameters for six agitation speeds were determined and are shown in Figure 4 as a plot of  $\ln(k)$  versus  $S$ . The  $k$  values can be correlated by an equation as follows:

$$k = \exp(3.16 \times 10^{-3} S - 7.43) \quad (11)$$

where  $S$  is agitation speed (rpm). The individual values of

Table 2. Lead(II) sorption by sorbents: a selection of Langmuir constant,  $X_m$ , of various related substances from the literature.

$X_m$ , mg g <sup>-1</sup>	Material	Reference
1380	Waste slurry	Srivastava <i>et al.</i> (1989) <sup>36</sup>
1039	Amberlite IR-120	Holan and Volesky (1994) <sup>14</sup>
600	<i>Fucus vesiculosus</i>	Holan and Volesky (1994) <sup>14</sup>
478	<i>Ascophyllum nodosum</i>	Holan and Volesky (1994) <sup>14</sup>
378	<i>Sargassum fluitans</i>	Leusch <i>et al.</i> (1995) <sup>15</sup>
351	<i>Absidia orchidis</i>	Holan and Volesky (1995) <sup>16</sup>
259	Oxidized anthracite	Petrov <i>et al.</i> (1992) <sup>24</sup>
257	<i>Ascophyllum nodosum</i>	Leusch <i>et al.</i> (1995) <sup>15</sup>
251	Algae	Özer <i>et al.</i> (1994) <sup>23</sup>
224	Spruce sawdust (phosphorylated)	Holan and Volesky (1995) <sup>16</sup>
166	<i>Rhizopus nigricans</i>	Holan and Volesky (1995) <sup>16</sup>
150	Peat	Majid <i>et al.</i> (1996) <sup>37</sup>
110	<i>Zoogloea ramigera</i>	Sag and Kutsal (1995) <sup>26</sup>
110	Resting cells	Chang <i>et al.</i> (1997) <sup>38</sup>
79.9	Blast furnace sludge	Lopez <i>et al.</i> (1995) <sup>19</sup>
79.5	Inactivated cells	Chang <i>et al.</i> (1997) <sup>38</sup>
78.7	Tea leaves	Tan and Abd. Rahman (1988) <sup>27</sup>
71.8	Montmorillonite clay	Farrah <i>et al.</i> (1980) <sup>39</sup>
63	<i>Penicillium chrysogenum</i>	Holan and Volesky (1995) <sup>16</sup>
61.9	Sphagnum peat moss	Allen <i>et al.</i> (1992) <sup>40</sup>
55	<i>Rhizopus arrhizus</i>	Holan and Volesky (1995) <sup>16</sup>
55.0	High carbon content sludge	López-delgado <i>et al.</i> (1996) <sup>41</sup>
39.4	Groundnut husks	Okieimen <i>et al.</i> (1991) <sup>21</sup>
30.7	Sphagnum moss peat	Ho <i>et al.</i> (1996) <sup>30</sup>
19.1	Coke	López-delgado <i>et al.</i> (1996) <sup>41</sup>
15	Spruce sawdust	Holan and Volesky (1995) <sup>16</sup>
14.1	Illite clay	Farrah <i>et al.</i> (1980) <sup>39</sup>
12.6	Soil	Majid <i>et al.</i> (1996) <sup>37</sup>
12	Linden sawdust	Holan and Volesky (1995) <sup>16</sup>
9.37	Kaolinitic clay	Majone <i>et al.</i> (1993) <sup>42</sup>
6.46	Kaolinitic clay	Orumwense (1996) <sup>22</sup>
3.93	Kaolinitic clay	Farrah <i>et al.</i> (1980) <sup>39</sup>
1.68	Wollastonite	Yadava <i>et al.</i> (1991) <sup>28</sup>
0.411	China clay	Yadava <i>et al.</i> (1991) <sup>28</sup>
0.368	Fly ash	Yadava <i>et al.</i> (1989) <sup>43</sup>
122	Peat	This study

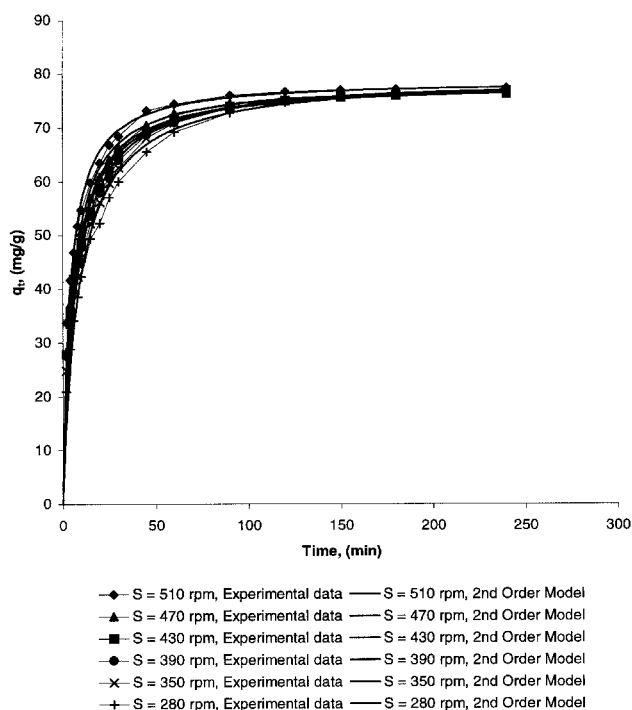


Figure 3. Plot of sorbed amount versus time for lead(II) at various agitation speeds.

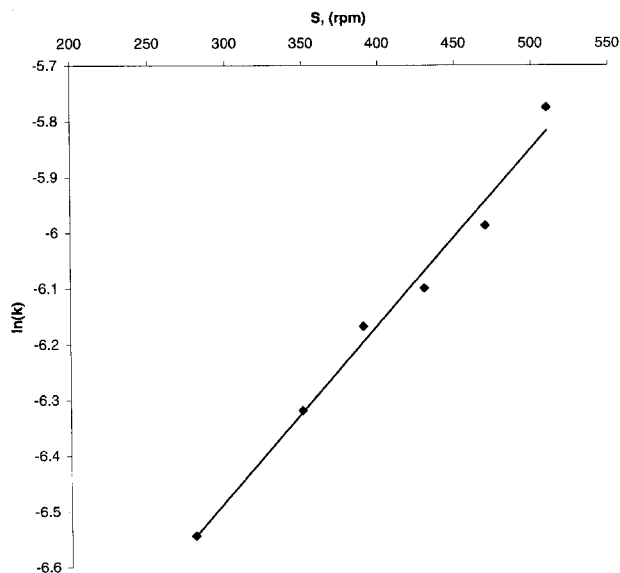


Figure 4. Pseudo-second order sorption kinetics of lead(II) onto peat at various agitation speeds.

Table 3. Pseudo-second order rate constant.

$k, \text{g mgmin}^{-1}$	Agitation, rpm	$r^2$	$k, \text{g mgmin}^{-1}$	$C_0, \text{mg dm}^{-3}$	$r^2$	$k, \text{g mgmin}^{-1}$	$T, \text{K}$	$r^2$
$1.44 \times 10^{-3}$	280	0.999	$5.15 \times 10^{-2}$	101	0.999	$1.13 \times 10^{-3}$	279	0.999
$1.80 \times 10^{-3}$	350	0.999	$8.11 \times 10^{-3}$	209	0.999	$1.46 \times 10^{-3}$	288	0.999
$2.09 \times 10^{-3}$	390	0.999	$2.25 \times 10^{-3}$	309	0.999	$1.92 \times 10^{-3}$	298	0.999
$2.24 \times 10^{-3}$	430	0.999	$1.01 \times 10^{-3}$	410	0.999	$3.07 \times 10^{-3}$	308	0.999
$2.51 \times 10^{-3}$	470	0.999	$7.26 \times 10^{-4}$	504	0.998	$5.60 \times 10^{-3}$	318	0.999
$3.10 \times 10^{-3}$	510	0.999						

the pseudo-second order rate constants and the correlation coefficients,  $r^2$ , are shown in Table 3. The correlation coefficient on the agitation data was 0.985. The change in the  $k$  values with agitation is only small but it does increase slightly as the agitation speed increases. This could be due to the fact that better and more uniform mixing is achieved with increasing agitation or there may possibly be some boundary layer resistance to reaction which is decreased by increasing the agitation. The more agitation the greater is the shear on the boundary layer surrounding the particle.

Figure 5 shows the relationship between initial sorption rate,  $h$ , and agitation speed as a plot of  $h$  versus  $S$ . The  $h$  values can be correlated by an equation as follows:

$$h = \frac{1}{0.173 - 2.36 \times 10^{-4} S} \quad (12)$$

where  $h$  is the initial sorption rate ( $\text{mg gmin}^{-1}$ ). The correlation coefficient on the agitation data was 0.985.

Effect of initial concentration

The experimental results for the effect of initial concentration obtained from a series of contact time studies for the sorption of lead(II) onto peat in which the initial lead(II) concentration was varied (209, 309, 410 and  $504 \text{ mg dm}^{-3}$ ) are shown in Figure 6. In all runs the agitation speed was 400 rpm, the peat dose was  $4 \text{ g dm}^{-3}$ ,

the peat particle size range was  $500-710 \mu\text{m}$  and the solution temperature was  $24 \pm 2^\circ\text{C}$ .

The results have been analysed using the pseudo-second order model. The correlation coefficients,  $r^2$ , rate constant,  $k$ , initial sorption rate,  $h$ , and sorption capacity,  $q_e$ , are obtained from the slope and intercept of equation (3). The solid line curves in Figure 6 are the theoretical plots of equation (5), the values of  $r^2$  are all extremely high ( $>0.998$ ). The corresponding linear plots of the values of  $q_e$ ,  $k$  and  $h$  against  $C_0$  were regressed to obtain expressions for these values in terms of the initial lead ion concentration with high correlation coefficients ( $>0.981$ ). The individual values of the pseudo-second order rate constants and the correlation coefficients,  $r^2$ , are presented in Table 3. Therefore it is further considered that  $q_e$ ,  $k$  and  $h$  can be expressed (Figures 7 and 8) as a function of  $C_0$  for lead as follows:

$$q_e = 0.776 C_0^{0.798} \quad (13)$$

$$k = 1.81 \times 10^4 C_0^{-2.75} \quad (14)$$

$$h = \frac{1}{2.53 \times 10^{-4} C_0 - 6.68 \times 10^{-3}} \quad (15)$$

Substituting the values of  $q_e$  and  $h$  from equations (13) and (15) into equation (5), the rate law for a pseudo-second order and the relationship of  $q_t$ ,  $C_0$  and  $t$  can be represented

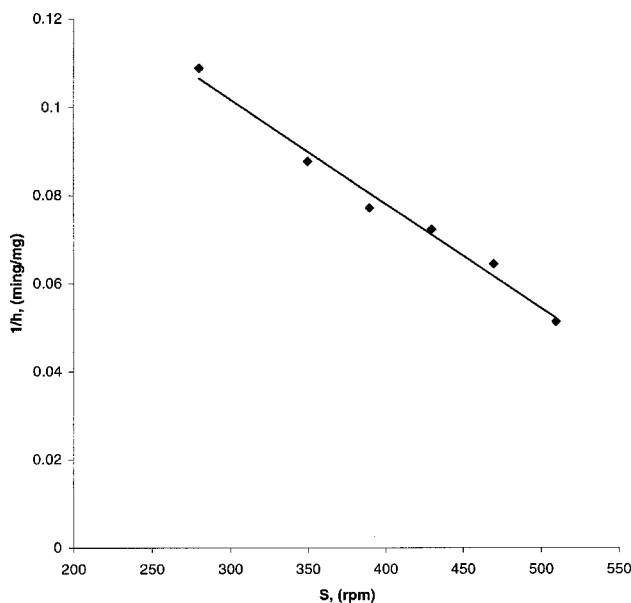


Figure 5. Plot of initial sorption rate and agitation speed.

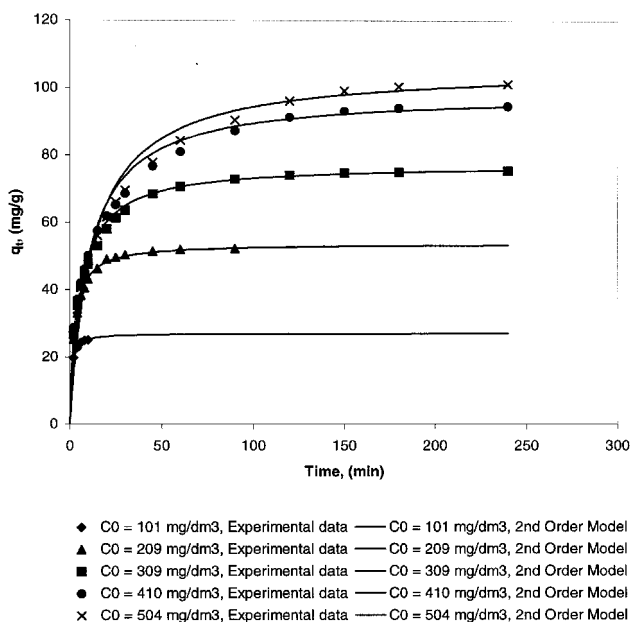


Figure 6. Plot of sorbed amount versus time for lead(II) at various initial concentrations.

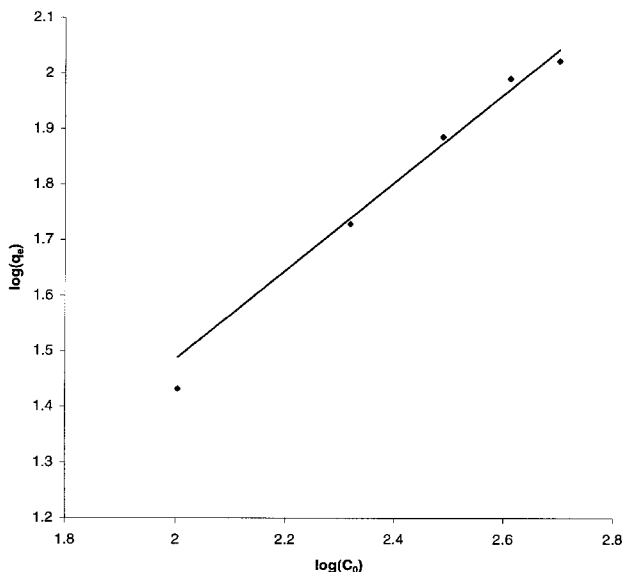


Figure 7. Plot of equilibrium sorption capacity against initial lead(II) sorption onto peat.

as follows:

$$q_t = \frac{t}{2.53 \times 10^{-4} C_0 - 6.68 \times 10^{-3} + \frac{t}{0.776 C_0^{0.798}}} \quad (16)$$

Equation (16) represents a generalized predictive model for lead ions sorbed onto peat at any contact time and initial lead(II) concentration within the given range at a temperature of 24°C.

The pH values have been measured during the sorption reaction. Figure 9 shows the trend in pH over the reaction period. For the same sorbent dosage and temperature the pH drifts are similar but the values are changed by the effect of initial lead(II) concentration. There are two sources

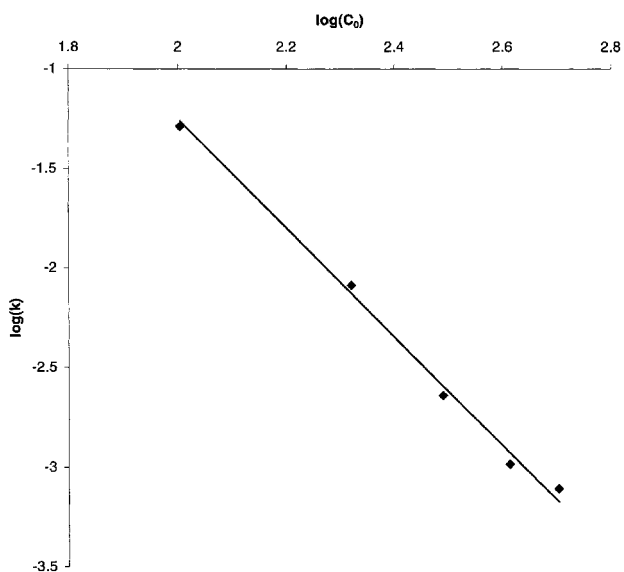


Figure 8. Plot of rate constant against initial lead(II) concentration for lead(II) sorption on peat.

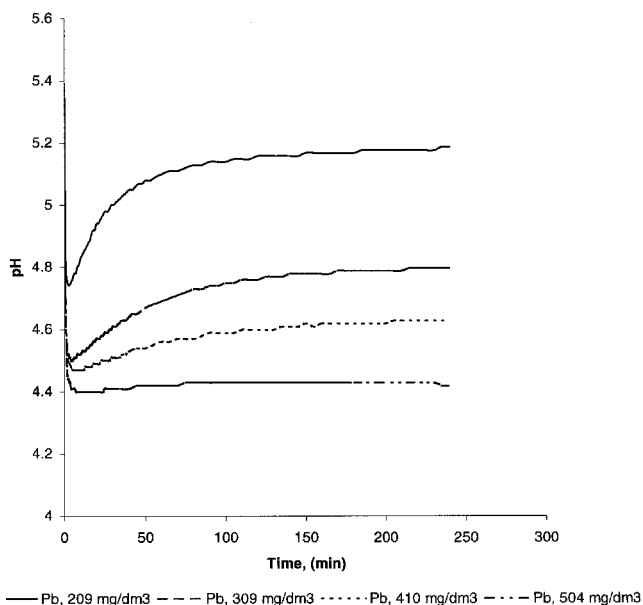


Figure 9. Plot of pH of solution against time for lead(II) sorption onto peat.

which may contribute to an increase in the hydrogen ion concentration during the sorption process. Peat specimens possess acidic groups such as carboxylic, phenolic and enolic. Such groups are believed to be responsible for the cation exchange capacity, which generally lies between 2 and 3 milliequivalents per gram<sup>44</sup>. The intrinsic ionization constant for the carboxylic groups appears to be about  $10^{-5}$  according to Dawson and Danielson<sup>45</sup> and these are the only acidic groups thought to be ionized to an appreciable extent at a pH of 7.0 and below.

Table 4 shows that when the initial lead(II) concentration was between 209 and 504 mg dm<sup>-3</sup>, the solution hydrogen concentration change,  $\Delta H^+$ , increased with increasing initial lead ion concentration. This suggests that as more lead ions are sorbed onto the peat, more hydrogen ions are released from the peat into the solution, consequently decreasing the pH of the reaction mixture.

Clearly the resulting equilibrium pH is governed by the factor of the lead(II) present in the solution initially when temperature, the initial pH and peat dose are fixed. This phenomenon can also be represented as a functional relationship of these two parameters, given by:

$$\Delta H^+ = 8.05 \times 10^{-11} C_0^{2.88} \quad (17)$$

There are a number of possible explanations for the pH variations which occur when peat is mixed with metal cation solutions. The pH variation could be from the acidic group's properties: there are carboxylic and phenolic functional groups present in humic substances<sup>46,47</sup> or ion

Table 4. Hydrogen ion milliequivalent per gram peat for different initial lead(II) concentrations.

$C_0$ , mg dm <sup>-3</sup>	pH <sub>0</sub>	pH <sub>240</sub>	$\Delta H^+$ , meq g <sup>-1</sup>
209	5.39	5.19	$3.50 \times 10^{-4}$
309	5.23	4.80	$1.46 \times 10^{-3}$
410	5.24	4.63	$2.60 \times 10^{-3}$
504	5.18	4.42	$4.62 \times 10^{-3}$

exchange reactions, such as proton release when metal cations bind to peat<sup>47-49</sup>.

### Effect of temperature

Figure 10 shows that the rate of lead(II) uptake increases rapidly with temperature since the sorption rate terms increase with increasing temperature as the second order rate constant increases with increasing temperature. The values of the pseudo-rate constants,  $k$ , were determined at each temperature using equation (3) and the theoretical values of  $q_t$  from equation (5) are plotted as the solid curves in Figure 10. Good agreement is obtained with experimental data points. The values of the pseudo-second order rate constants and the correlation coefficients are presented in Table 3.

The activation energy for the sorption of lead(II) on peat has been determined to be  $29.8 \text{ kJ mol}^{-1}$  from the slope of the linear Arrhenius plot of log rate constant versus reciprocal absolute temperature in Figure 11. Thus increasing the temperature increases the pseudo-second order rate constant and the initial rate of lead(II) sorption onto peat. The increase in the initial sorption rate,  $h$ , with increasing temperature,  $T$ , is described by the equation:

$$h = \frac{T}{2.79 \times 10^2 - 0.851T} \quad (18)$$

The Arrhenius equation for Figure 11 is:

$$k = 356 \exp\left(\frac{-29800}{RT}\right) \quad (19)$$

A series of equilibrium isotherms at different temperatures was not performed. Only contact time experiments were carried out at 6, 15, 25 and 35°C using an initial lead ion concentration at this temperature as shown in Table 5.

The equilibrium capacities show every little variation with temperature. In sorption processes the monolayer saturation equilibrium capacities,  $X_m$ , usually decrease with increasing temperature. This is not inferred from Table 5.

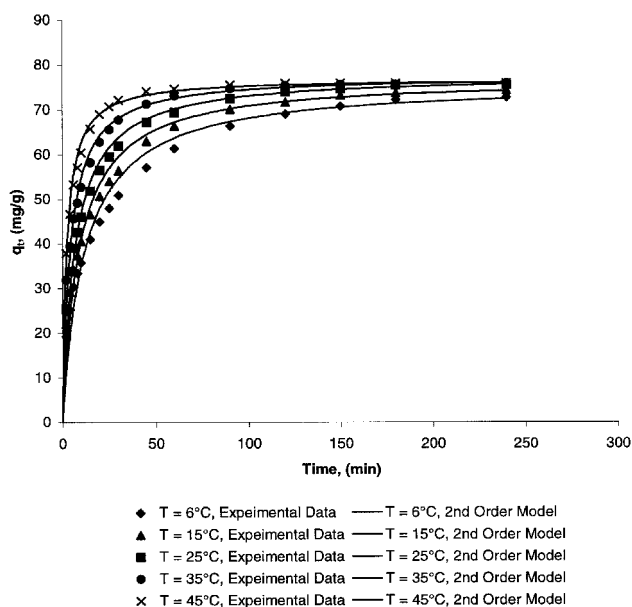


Figure 10. Plot of sorbed amount versus time for lead(II) at various temperatures.

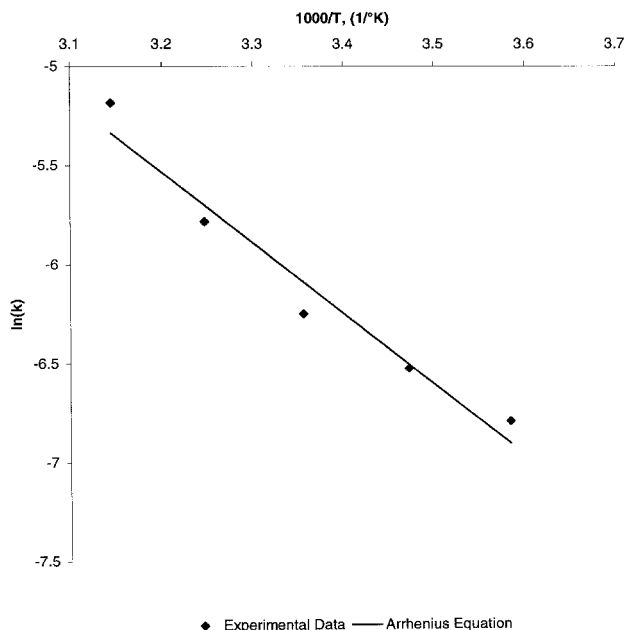


Figure 11. Plot of  $\ln(k)$  against reciprocal temperature for lead(II) sorption onto peat.

Table 5. Equilibrium capacities at various temperatures.

$T, ^\circ\text{C}$	6	15	25	35
$C_0, \text{mg dm}^{-3}$	310	310	309	311
$Q_0, \text{mg g}^{-1}$	76.3	77.3	78.0	77.7

However, by inspection of Figure 2 it can be seen that the operating line, corresponding to  $C_0 = 310 \text{ mg dm}^{-3}$ , is very close to the vertical axis. This corresponds to solution concentrations of around  $10 \text{ mg dm}^{-3}$ . Since errors due to experimental procedures and equipment measurement errors are around 1% for high concentrations and around 2% for low concentrations, the error in  $[C_0 - C_t]$  values makes the error in  $q_t$  values approximately  $\pm 3 \text{ mg g}^{-1}$ . Therefore, it is not possible to identify a temperature trend in equilibrium sorption capacities with temperature on the steep initial slope of the adsorption isotherm.

## CONCLUSIONS

The equilibrium sorption isotherm of lead(II) onto peat has been analysed by the Redlich-Peterson, the Langmuir and the Freundlich isotherm equations. The Redlich-Peterson and the Langmuir isotherms have the highest correlation coefficients of 1.000 and 0.999 respectively. The kinetics of the sorption of lead(II) have been analysed using a pseudo-second order kinetic model. The results were able to correlate the process variables—initial lead ion concentration, agitation speed and temperature. Correlations have been developed which will facilitate the design of batch adsorbers using peat to remove lead(II) from wastewaters.

Peat has a significant sorption capacity for lead ions of  $122 \text{ mg Pb g}^{-1}$  peat. The low cost and easy accessibility for recovery of sphagnum moss peat make potential industrial application a strong possibility. Particulate peat can be used in batch or fixed bed sorption systems.

## NOMENCLATURE

$a_r$	Redlich-Peterson constant, $\text{dm}^3 \text{gm}^{-1}$
$b_R$	Redlich-Peterson exponent
$a_L$	equilibrium constant, $\text{dm}^3 \text{mg}^{-1}$
$C_e$	equilibrium liquid phase lead concentration, $\text{mg dm}^{-3}$
$C_0$	initial liquid phase lead concentration, $\text{mg dm}^{-3}$
$d_p$	mean particle diameter, micron
$E$	activation energy of sorption, $\text{kJ mol}^{-1}$
$h$	initial sorption rate, $\text{mg lead g}^{-1} \text{peat min}^{-1}$
$\Delta H^\ddagger$	change in hydrogen ion concentration, $\text{meq g}^{-1}$
$k$	rate constant for pseudo-second order sorption, $\text{g peat mg}^{-1} \text{lead min}^{-1}$
$k_1$	rate constant for pseudo-second order sorption, $\text{g peat mg}^{-1} \text{lead min}^{-1}$
$k_i$	intraparticle diffusion rate parameter, $\text{mg lead g}^{-1} \text{peat min}^{-1}$
$k_o$	temperature independent factor, $\text{g lead mg}^{-1} \text{lead min}^{-1}$
$K$	Langmuir equilibrium constant, $\text{dm}^3 \text{mg}^{-1}$
$K_F$	Freundlich equilibrium constant, $\text{mg g}^{-1} \text{dm}^3 \text{mg}^{-1}$
$K_R$	Redlich-Peterson isotherm constant, $\text{dm}^{-3} \text{g}^{-1}$
$m_s$	mass of peat per unit volume, $\text{g peat dm}^{-3}$
$n$	reciprocal Freundlich exponent
$q_1$	amount of lead adsorbed at equilibrium in the pseudo-first model, $\text{mg lead g}^{-1} \text{peat}$
$q_2$	amount of lead adsorbed at equilibrium in the pseudo-second order model, $\text{mg lead g}^{-1} \text{peat}$
$q_e$	amount of lead adsorbed at equilibrium in the pseudo-first model, $\text{mg lead g}^{-1} \text{peat}$
$q_m$	amount of lead adsorbed based on Langmuir model, $\text{mg lead g}^{-1} \text{peat}$
$q_t$	amount of lead adsorbed at time, $t$ , $\text{mg lead g}^{-1} \text{peat}$
$R$	universal gas constant, $8.314 \text{ Jmol}^{-1} \text{K}^{-1}$
$r^2$	linear correlation coefficient
$S$	agitation speed, revolutions per minute
$T$	solution temperature, K
$t$	sorption contact time, min
$X_m$	monolayer equilibrium saturation capacity, $\text{mg lead g}^{-1} \text{peat}$

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*The manuscript was received 12 November 1998 and accepted for publication after revision 8 March 1999.*