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THE KINETICS OF SORPTION OF DIVALENT METAL IONS ONTO SPHAGNUM MOSS PEAT

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Abstract—A pseudo-second order rate equation describing the kinetics of sorption of divalent metal ions onto sphagnum moss peat at different initial metal ion concentrations and peat doses has been developed. The kinetics of sorption were followed based on the amounts of metal sorbed at various time intervals. Results show that sorption (chemical bonding) might be rate-limiting in the sorption of divalent metal ions onto peat during agitated batch contact time experiments. The rate constant, the equilibrium sorption capacity and the initial sorption rate were calculated. From these parameters, an empirical model for predicting the sorption capacity of metal ions sorbed was derived. © 2000 Elsevier Science Ltd. All rights reserved

Key words—peat, lead, copper, nickel, kinetics and sorption

INTRODUCTION

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. However, although the sorption kinetics of individual metal ions onto this type of material have been examined, the processes which occur are not completely understood, for instance, the rate limiting step and the bonding mechanism. Batch metal removal by sphagnum moss peat has been studied by workers such as Rock *et al.* (1985), Sharma and Forster (1993) and Ho *et al.* (1994). Column studies using moss peat for the removal of heavy metals from industrial and municipal lea-chates (McLellan and Rock, 1988) as well as from waste waters (Chaney and Hundermenn, 1979) 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 (1898). However, Gosset *et al.* (1986), Sharma and Forster (1993) as well as Ho *et al.* (1995) have used a second-order equation to des-cribe metal–peat sorption and Tien and Huang (1991) have presented a second-order expression for metal sorption onto sludge solids.

In this present work, a simple kinetic approach

to the sorption of copper, lead and nickel ions from aqueous solution onto sphagnum moss peat has been studied. Using batch studies, the equilibrium sorption, the extent of metal ion removal, the rate constants and the initial sorption rates have been calculated for these systems. The development of a simple kinetic model from these data is also reported.

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):

$$2P^- + Cu^{2+} \Leftrightarrow CuP_2 \qquad (1)$$

and

$$2HP + Cu^{2+} \Leftrightarrow CuP_2 + 2H^+ \qquad (2)$$
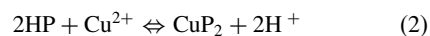
where P^- and HP are polar sites on the peat surface.

In an attempt to present the equation representing sorption of divalent metals onto sphagnum moss peat 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

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between sorbent and sorbate as covalent forces. In developing any mathematical description of the sorption process, certain assumptions must be made. Initially, it must be assumed that the sorption follows the Langmuir equation and this has been confirmed previously (Ho *et al.*, 1994). This means that:

- there is a monolayer of metal ion on the surface of peat;
- the energy of sorption for each ion is the same and independent of surface coverage;
- the sorption occurs only on localised sites and involves no interactions between sorbed ions;
- the rate of sorption is almost negligible in comparison with the initial rate of sorption.

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

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

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

or

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

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

The kinetic rate equations can be rewritten as follows:

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

where k is the rate constant of sorption, (g/mg min), 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 Eq. (3) gives:

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

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

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

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

Eq. (4) can be rearranged to obtain:

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

which has a linear form of

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

If the initial sorption rate is:

$$h = kq_e^2, \qquad (7)$$

then Eqs (5) and (6) become:

$$q_t = \frac{t}{1/h + t/q_e}, \qquad (8)$$

and

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

The constants can be determined experimentally by plotting of t/q_t against t.

Although there are many factors which will influence sorption, contact time, pH, temperature, sorbent concentration, nature of the solute and its concentration, a kinetic model is concerned only with the effect of observable parameters on the overall rate. These include initial metal ion concentration, temperature, peat dose and nature of solute.

MATERIALS AND METHODS

Materials

The sphagnum moss peat used in this study, which was from Northern Ireland, was obtained from a local garden centre. It was dried at 105°C for 24 h and then screened though a 14 mesh sieve (B.S. 410/43) before being used.

Stock solutions of lead nitrate and copper sulphate (analytical grade) (1 g/l) were prepared in distilled water. All solutions used in this study were diluted with distilled water as required.

Methods

The sorption of metal ions to peat was studied by batch experiments. The factors which were examined were;

- the initial metal ion concentration,
- the type of metal and
- the peat dose.

All the tests (Table 1) were done in capped conical flasks (500 ml), by suspending the peat in the metal ion solution, adjusting the pH to a value of 5 with either sulphuric acid or sodium hydroxide solution and mixing on a shaker with a constant speed of 100 rpm. Samples were withdrawn at suitable time intervals, filtered through a 0.45-μm membrane filter and then analysed with an atomic absorption spectrophotometer.

Table 1. Sorption studies

Study	Metal	Mass of peat (g)	Test solution volume (ml)	Metal concentration (mg/l)
C_0	Pb	2	250	35–210
C_0	Cu	1	250	25–200
C_0	Ni	1	250	10–100
Peat dose	Pb	1–8	250	100

RESULTS AND DISCUSSION

The first-order reaction model was used to check all the results but the correlation coefficient is not high. However, the rate law for a pseudo-second order could be fixed with very high correlation coefficient. The sorption of metal ion onto peat could be a pseudo-second order process rather than first-order.

Effect of initial metal ions concentration and nature of solute

The sorption data obtained when the type of metal ion and its initial concentration was varied are shown in Figs 1 and 2 and in Table 2. Fig. 1 shows typical data for the copper, the nickel and the lead series plotted so that the constants in Eq. (9) can be derived. These constants are given in Table 2, and Fig. 2 shows three typical sets of data in relation to the curves calculated from the constants. The experimental points are shown together with the theoretically generated curves. The agreement between the sets of data reflect the extremely high correlation coefficients obtained and shown in Table 2. Fig. 3 shows typical sorption curves for effect of initial metal ion concentration on the sorption kinetics of metal ion onto sphagnum moss peat. In other words, the data showed good compliance with the proposed pseudo-second order equation. Indeed, the regression coefficients for the linear plots were better than 0.996. The data also showed that the initial metal ion concentrations influenced the contact time necessary to reach equilibrium and that the sorption capacity increased for the higher initial metal ion concentrations (Table 2).

The value of the initial sorption rates, h, were determined by using the values of the intercept of the straight lines plotted in Fig. 1. The initial sorption rate increases with a decrease in the initial metal concentrations. While h varies from 10.9 to

Fig. 1. Plot of sorbed capacity versus time for effect of metal ions on the sorption kinetics of metal ions onto sphagnum moss peat at temperature of 25°C, pH = 5 and peat dose 4 g/l.
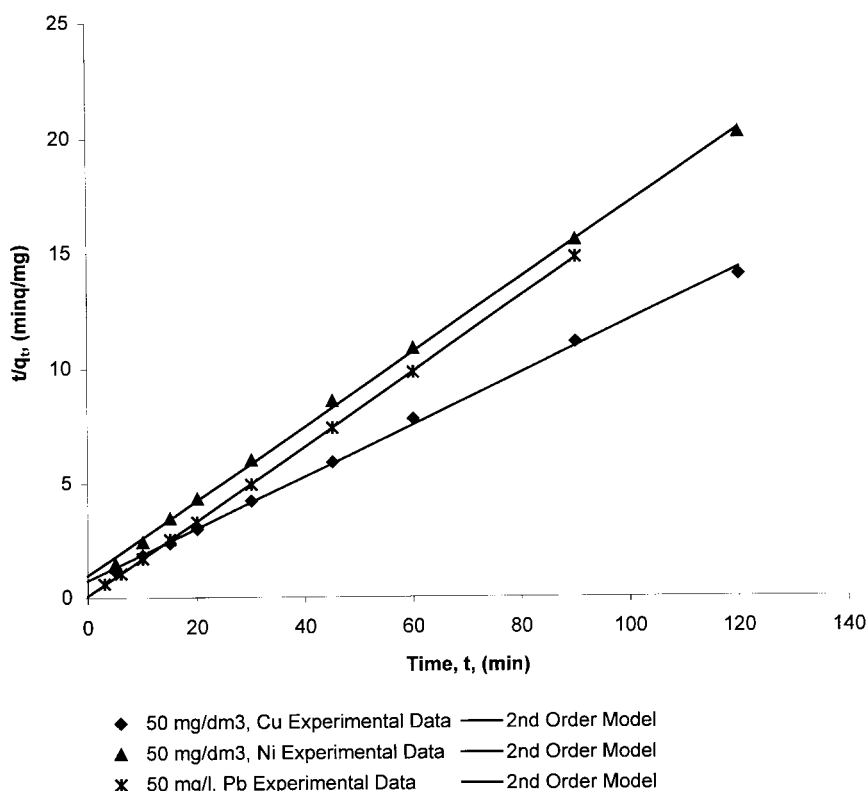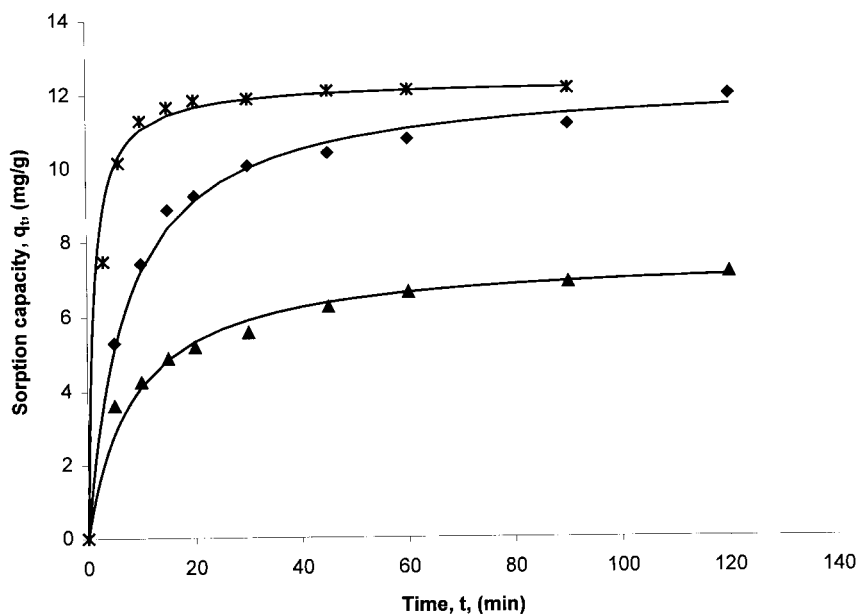
Fig. 2. Plot of sorbed capacity versus time for effect of metal ions on the sorption kinetics of metal ions onto sphagnum moss peat at temperature of 25°C, pH = 5 and peat dose 4 g/l.

17.3 mg/g min, the C_0 varies from 210 to 35 mg/l for lead; from 1.81 to 3.19 mg/g min, the C_0 varies from 200 to 25 mg/l for copper and from 0.905 to 0.804 mg/g min, the C_0 varies from 100 to 10 mg/l for nickel, respectively.

The values of rate constant, k, were found to increase from 1.79×10^{-2} to 0.919 g/mg min, for a decrease in the initial lead concentration from 210 to 35 mg/l; from 8.91×10^{-3} to 9.64×10^{-2} g/mg min, for a decrease in the initial copper concentration from 200 to 25 mg/l and from 1.59×10^{-2} to 0.175 g/mg min, for a decrease in the initial nickel concentration from 100 to 10 mg/l, respectively.

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 metal ion concentration with high correlation coefficients (Table 3). Therefore it is further considered

that q_e, k and h can be expressed as a function of C_0 for copper, nickel and lead as follows:

$$q_e = \frac{C_0}{A_q C_0 + B_q} \qquad (10)$$

$$k = \frac{C_0}{A_k C_0 + B_k} \qquad (11)$$

$$h = \frac{C_0}{A_h C_0 + B_h} \qquad (12)$$

Substituting the values of q_e and h from Table 3 into Eqs (10) and (12) and then into Eq. (8), the rate law for a pseudo-second order and the relationship of q_t, C_0 and t can be represented as follows: for copper:

Table 2. The effect of initial metal ion concentration on metal ions sorption data[a]

M^{2+}	C_0 (mg/l)	r^2	q_e (mg/g)	k (g/mg min)	h (mg/g min)
Cu	25	1.00	5.75	9.64×10^{-2}	3.19
	50	0.999	8.87	1.68×10^{-2}	1.32
	100	0.998	12.4	1.13×10^{-2}	1.73
	200	0.996	14.3	8.91×10^{-3}	1.81
Ni	10	1.00	2.14	0.175	0.804
	25	0.999	3.88	4.27×10^{-2}	0.643
	50	0.999	6.19	2.64×10^{-2}	1.01
	100	0.999	7.54	1.59×10^{-2}	0.905
Pb	35	1.00	4.34	0.919	17.3
	50	1.00	6.15	0.335	12.7
	100	1.00	12.3	6.98×10^{-2}	10.6
	210	1.00	24.6	1.79×10^{-2}	10.9

[a]C_0: initial metal ion concentration; r^2: correlation coefficient; q_e: metal ion removal capacity at equilibrium; k: rate constant; h: initial sorption rate.
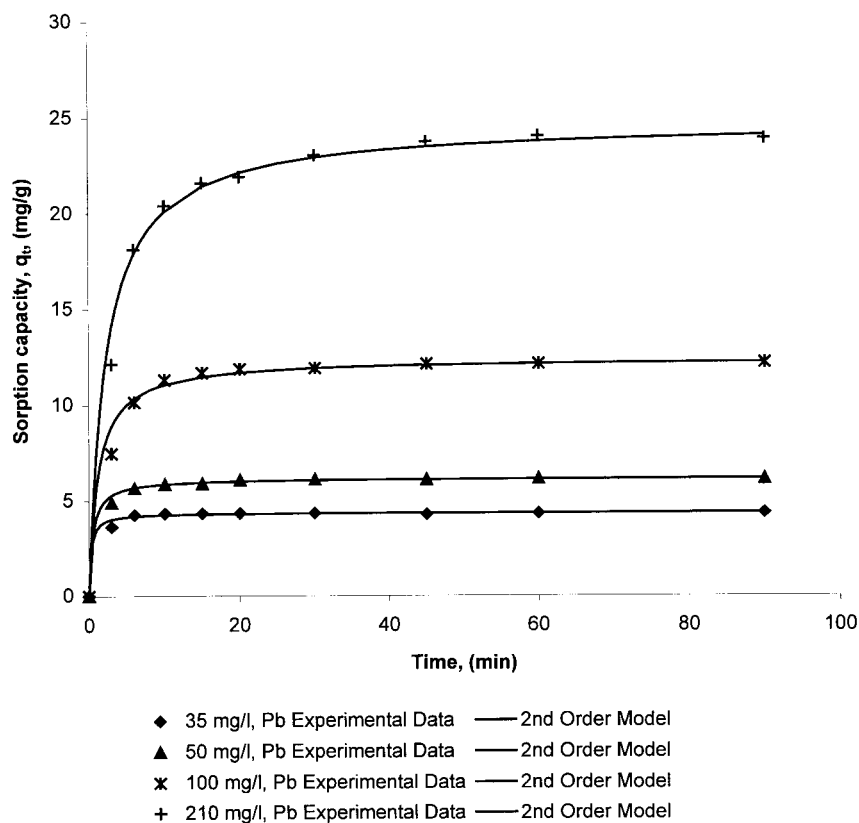
Fig. 3. Plot of sorbed amount versus time for lead at various initial concentrations.

$$q_t = \frac{C_0 t}{0.551C_0 + 1.83 + \left(5.54 \times 10^{-2}C_0 + 2.83\right)t} \quad (13)$$

for nickel:

$$q_t = \frac{C_0 t}{1.04C_0 + 4.79 + \left(9.36 \times 10^{-2}C_0 + 3.78\right)t} \quad (14)$$

for lead:

$$q_t = \frac{C_0 t}{9.97 \times 10^{-2}C_0 - 9.74 + \left(2.56 \times 10^{-3}C_0 + 7.95\right)t} \quad (15)$$

Eqs (13–15) represent generalised predictive models for the copper, nickel and lead ion sorbed at any contact time and initial metal ion concentration within the given ranged. It indicated that the metal ion sorbed at any contact time is higher for a greater initial metal ion concentration. This is obvious for higher C_0 values, as a more efficient utilisation of the sorptive capacities of the sorbent is expected due to greater driving force (by a higher concentration gradient pressure) (Bhargava and Sheldarkar, 1993).

These equations can then be used to derive the amount of metal sorbed at any given ion concentration and the reaction time. The three-dimensional plot of Eq. (13) is shown in Fig. 4 for copper.

Effect of peat dose

The results of the effect of peat dose on experiments carried out using the same initial ion concentration 100 mg/l, temperature of 25°C and pH = 5 are shown in Fig. 5. Data from a series of kinetics experiments at five different peat doses between 4 and 32 g/l are shown in Table 4. Fig. 5 shows typical sorption curves for effect of peat dose on the sorption kinetics of lead ion onto sphagnum moss peat. The data also showed a good compliance with the pseudo-second order equation and the re-

Table 3. Empirical parameters for predicted q_e, k and h from C_0

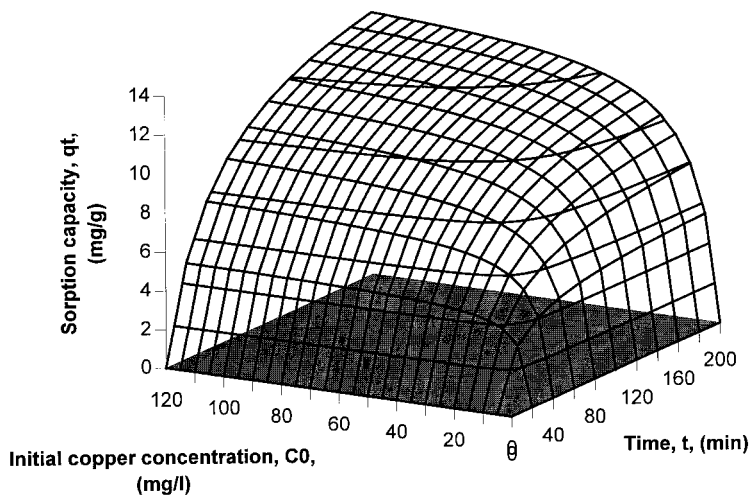|	A_q (g/mg)	B_q (g/l)	r^2	A_k (mg min/g)	B_k (mg^2 min/g l)	r^2	A_h (g min/mg)	B_h (g min/l)	r^2
Cu	5.54×10^{-2}	2.83	0.998	1.28×10^2	-3.33×10^3	0.998	5.51×10^{-1}	1.83	0.976
Ni	9.36×10^{-2}	3.78	0.993	70.8	-1.07×10^3	0.975	1.04	4.79	0.975
Pb	2.56×10^{-3}	7.95	0.895	68.9	-3.46×10^3	0.940	9.77×10^{-2}	-9.74	0.997

Fig. 4. Effect of initial concentration on copper sorption at various reaction times.

gression coefficients for the linear plots were 1.00. These plots show that for all peat doses, the amount of lead ion sorbed increases rapidly with time in the beginning and very slowly towards the end of the reaction. Furthermore, a large fraction on the total amount of metal was removed within a short time. The plots also manifest that the sorption increased for lower peat dosages at any specific time. There is an effect on the contact time required to reach saturation due to the variation in peat

dose. It was found that the equilibrium sorption of lead ion is a function of peat dose. The rate constant, k, the equilibrium sorption, q_e and the initial sorption rate, h, of sorption at different peat doses were calculated from the intercept and slope of the straight line plots of t/q_t versus t in Eq. (6). The initial sorption rate increased with an increase in the peat dose.

The corresponding linear plots of the values of q_e, k and h against m_s were regressed to obtain ex-

- ◆ 4 g/l, Pb Experimental Data ——2nd Order Model
- ▲ 8 g/l, Pb Experimental Data ——2nd Order Model
- ✱ 16 g/l, Pb Experimental Data ——2nd Order Model
- + 24 g/l, Pb Experimental Data ——2nd Order Model
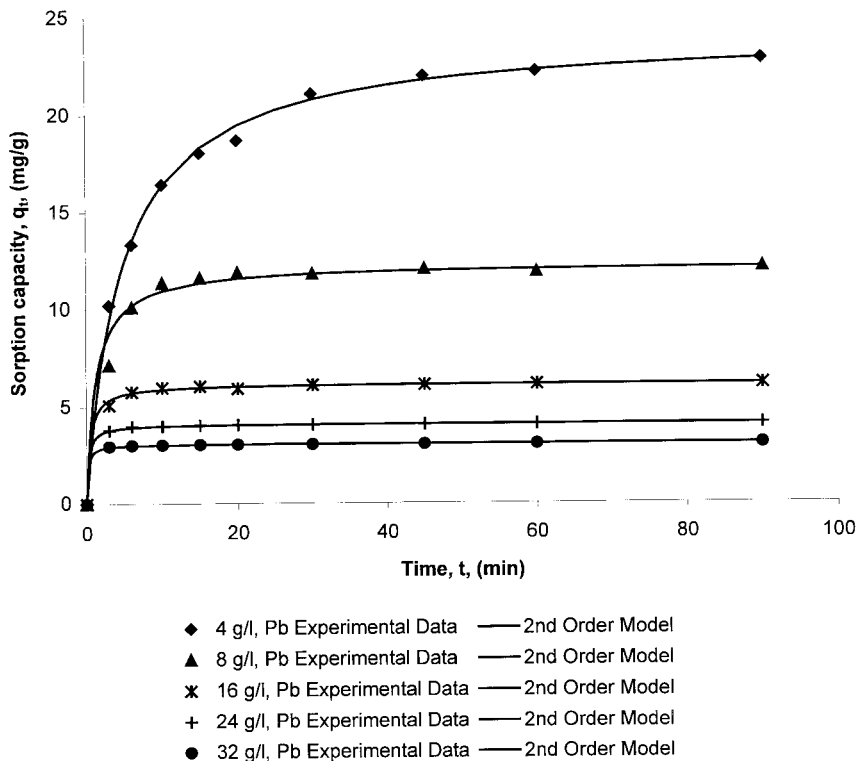- ● 32 g/l, Pb Experimental Data ——2nd Order Model

Fig. 5. Plot of sorbed capacity versus time for effect of peat does on the sorption kinetics of lead ion onto sphagnum moss peat at temperature of 25°C and pH = 5.
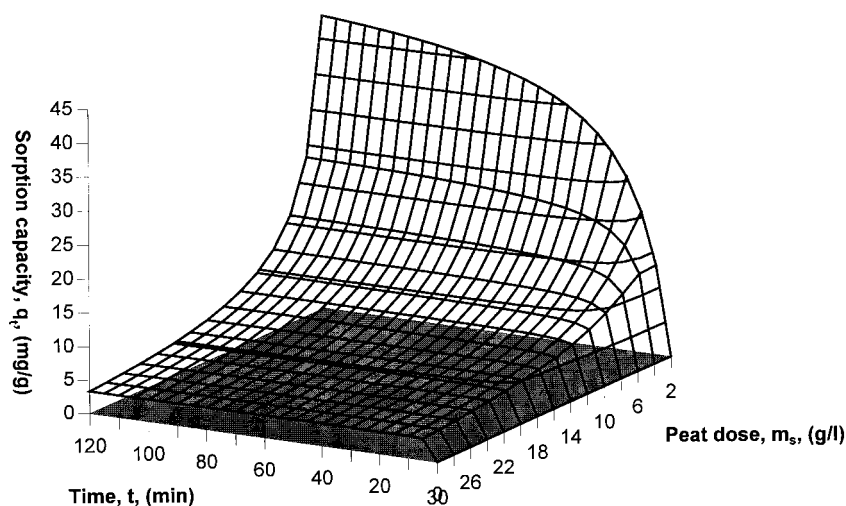
Fig. 6. Effect of peat dose on lead sorption at various reaction times.

pressions for these values in terms of the m_s parameters with correlation coefficients of 1.00, 0.999 and 0.971, respectively, as follows:

$$q_e = 9.53 \times 10m_s^{-0.990}$$

$$k = 2.59 \times 10^{-4}m_s^{2.61}$$

$$h = 2.35m_s^{0.633}$$

Substituting the values of q_e and k from the equations above in Eq. (8), the rate law for a pseudo-second order reaction and the relationship between q_t, m_s and t can be represented as:

$$q_t = \frac{t}{1/2.59 \times 10^{-4}m_s^{2.61}\left(95.3m_s^{-0.990}\right)^2 + t/95.3m_s^{-0.990}}$$

These equations can then be used to derive the sorption amount of lead at any given initial lead ion concentration and the reaction time. The three-dimensional plot of the equation is shown in Fig. 6.

This equation represents a generalised predictive model for the amount of lead ion sorbed at any contact time and involved peat dose. It indicates that the lead sorbed at any contact time is higher as the peat dose is decreased. This is due to the fact that increasing the peat dose increases the surface area for sorption and hence the rate of lead sorption is increased when the initial lead ion concentration is constant.

A kinetics model has been developed and fitted for the sorption of the three divalent metal ions onto sphagnum moss peat. The parameter which has the greatest influence on the kinetics of the sorption reaction was sorption equilibrium, q_e is a function of initial metal ion concentration, peat dose and nature of solute.

CONCLUSION

A kinetic model has been developed and fitted for the sorption of the divalent metal ions onto sphagnum moss peat. The result show sorption of three divalent metals onto sphagnum moss peat during agitation by suspended shaking; the process can be described by a pseudo-second order model based on the assumption that the rate limiting step may be chemical sorption or chemisorption involving valency forces through sharing or exchange of electrons between sorbent and sorbate. The parameter which has the influence on the kinetics of the sorption reaction was the sorption equilibrium capacity, q_e, which is a function of initial metal ion concentration, peat dose and the nature of solute ion.

Table 4. The effect of peat dose on lead ion sorption data[a]

m_s (g/l)	r^2	q_e (mg/g)	k (g/mg min)	h (mg/g min)
4	1.00	24.0	8.88×10^{-3}	5.13
8	1.00	12.2	6.82×10^{-2}	10.2
16	1.00	6.15	0.359	13.6
24	1.00	4.09	1.03	17.2
32	1.00	3.07	2.17	20.4

[a]m_s: peat dose; r^2: correlation coefficient; q_e: metal ion removal capacity at equilibrium; k: rate constant; h: initial sorption rate.

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