

Study of the Sorption of Divalent Metal Ions on to Peat

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ABSTRACT: A pseudo-second order rate equation describing the kinetics of sorption of divalent metal ions on to sphagnum moss peat at various initial metal ion concentrations and peat doses has been developed. The sorption kinetics were followed based on the concentrations of metal sorbed at various time intervals. Results show that chemical sorption processes might be rate-limiting for the sorption of divalent metal ions on to 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 concentrations of metal ions sorbed was derived.

INTRODUCTION

Peat has been recognised as a suitable material for the treatment of wastewater for over 40 years. Surakka and Kamppi (1971) described the use of a ditched peatland area for wastewater treatment in use in a village in Finland since 1957. As early as 1930, Ottemeyer (1930) described a peat/sand filter to treat textile effluents. The specific application of peat to remove dyestuffs from aqueous effluents has been described (Dufort and Ruel 1972; Poots *et al.* 1976; Allen and McKay 1987). Detailed modelling based on diffusion-controlled processes (McKay and Allen 1983) has been carried out due to the long contact times required to reach equilibrium.

In more recent years, the ability of peat to sorb metal ions has attracted much attention. In batch and column studies, Lalancette and Coupal (1972) found peat to be an efficient means of removing Hg from water. Coupal and Lalancette (1976) found that Hg, Cd, Zn, Cu, Fe, Ni, Cr^{VI}, Cr^{III}, Ag, Pb and Sb can be treated efficiently by contacting wastewater with peat moss. They found sorption to be quite high due to the polar character of peat. In a later study, Zhipei *et al.* (1984) investigated the removal of Pb, Cd, Zn, Ni and Cr from wastewater and concluded that, in treating water containing heavy metal ions with peat, the best results were obtained when the ion concentrations in wastewater were low. Parkash and Brown (1976), in their investigation of the sorption of zirconium and titanium from aqueous solutions by peat, found that peat accommodated almost four times more zirconium than titanium. Gosset *et al.* (1986) revealed that the maximum binding capacities in 10 mmol/dm³ metal cation solutions were very similar regardless of metal or type of peat used: all values fall in the range 180–200 mmol/dm³ dry weight.

Ong and Swanson (1966) studied the sorption of copper on to peat and, using IR spectroscopy, concluded that humic acids could complex with copper in solution, but they also confirmed that

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this was not the sole mechanism for copper removal. Furthermore, many workers have implicated carboxylic acid (COOH) groups in the reaction of divalent metals with humic acids (Gamble *et al.* 1970; Schnitzer 1978; Schnitzer and Kahn 1972; Stevenson and Ardakani 1972; Van Dijk 1971; Vinkler *et al.* 1976; Boyd *et al.* 1981). They support the general view that the reaction of metal ions, such as Cu and Fe, with humic acids is one of chelate ring formation involving adjacent aromatic carboxylate COOH and phenolic OH groups or, less predominantly, two adjacent COOH groups which participate in ion-exchange reactions by binding metal ions with the release of H⁺ ions. Others believe that there is no direct evidence for chelation: NMR studies (Gamble *et al.* 1976; Deczky and Langford 1978) and an ESR study (Alberts *et al.* 1976) have shown that the Mn²⁺ ion does not form an inner sphere and is bound electrostatically. This was supported by Bloom and McBride (1979) who, after extensive investigations with acid-washed peat, concluded the following: peat and humic acids are likely to bind most divalent metal ions, with the exception of Cu²⁺, largely as hydrated ions. The binding of copper appears to involve the exchange of one or two aquo ligands by carboxylate oxygens. Thus, neither chelation by adjacent functional groups nor heterogeneity with respect to acidity constants can be postulated solely to explain the binding of metal ions by peat and humic acids.

Sharma and Forster (1993) have studied the sorption of hexavalent chromium on to peat and Ho *et al.* (1995) have studied nickel sorption on to peat. Several other papers during the past 10 years reported the sorption capacity of various metal ions on peat. However, there is very limited information on sorption kinetics. Gosset *et al.* (1986), Chen *et al.* (1990) and Ho *et al.* (1994) have developed and successfully used an expression for modelling the effect of pH on equilibrium data. However, the major omission in the area of application is the lack of detailed, fundamental design data on the sorption of multicomponent metal ions on to peat.

THEORETICAL

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



and



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

In an attempt to present the equation representing the sorption of divalent metals on to sphagnum moss peat during agitation, the assumption has been made that the process may be pseudo-second order and the rate-limiting step may be chemical sorption or chemisorption (generally termed sorption throughout this paper) involving valency forces through sharing or the exchange of electrons between sorbent and sorbate. 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: (i) there is a monolayer of metal ion on the surface of the peat; (ii) the energy of sorption for each ion is the same and independent of surface coverage, the sorption occurring only on localised sites and involving no interactions between the sorbed ions; and (iii) the rate of sorption is almost negligible in comparison with the initial rate of sorption. The rate of the pseudo-second order reaction may be dependent on the sorbed metal ion concentration. The equilibrium sorption

capacity, q_e , is a function of, for example, the temperature, the initial metal ion concentration, the peat dose and the nature of the solute–sorbent interaction.

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

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

or

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

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 be rewritten as follows:

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

where k is the rate constant for sorption [$\text{dm}^3/(\text{mg min})$], q_t is the amount of divalent metal ion sorbed at equilibrium (mg/g) and q_t is the amount of divalent metal ion sorbed at time, t (mg/g). Separating the variables in equation (5) gives

$$\frac{dq_t}{(q_e - q_t)^2} = k dt \quad (6)$$

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

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + kt \quad (7)$$

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

Equation (7) can be rearranged to obtain

$$q_t = \frac{t}{1/kq_e^2 + t/q_e} \quad (8)$$

which has the linear form of

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e} t \quad (9)$$

If the initial sorption rate, h [$\text{mg}/(\text{g min})$], is

$$h = kq_e^2 \quad (10)$$

then equations (8) and (9) become

$$q_t = \frac{t}{1/h + t/q_e} \quad (11)$$

and

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \quad (12)$$

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

Although there are many factors which will influence sorption, e.g. contact time, pH, temperature, sorbent concentration, the 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 the nature of the 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 through a 14 mesh sieve (B.S. 410/43) before being used.

Stock solutions of lead nitrate and copper sulphate (analytical grade) (1 g/dm³) were prepared in distilled water. All solutions used in this study were diluted with distilled water as required.

Methods

The sorption of metal ions on to peat has been studied by batch experiments. The factors examined were the initial metal ion concentration, the type of metal and the peat dose.

All the tests (see Table 1) were undertaken 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 at 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. Conditions Employed for Sorption Studies Undertaken

Nature of investigation	Metal ion studied	Mass of peat employed (g)	Volume of test solution employed (ml)	Metal ion concentration employed (mg/dm ³)
Initial ion conc. effect	Pb	2.0	250	35–210
Initial ion conc. effect	Cu	1.0	250	25–200
Initial ion conc. effect	Ni	1.0	250	10–100
Peat dose effect	Pb	1.0–8.0	250	100

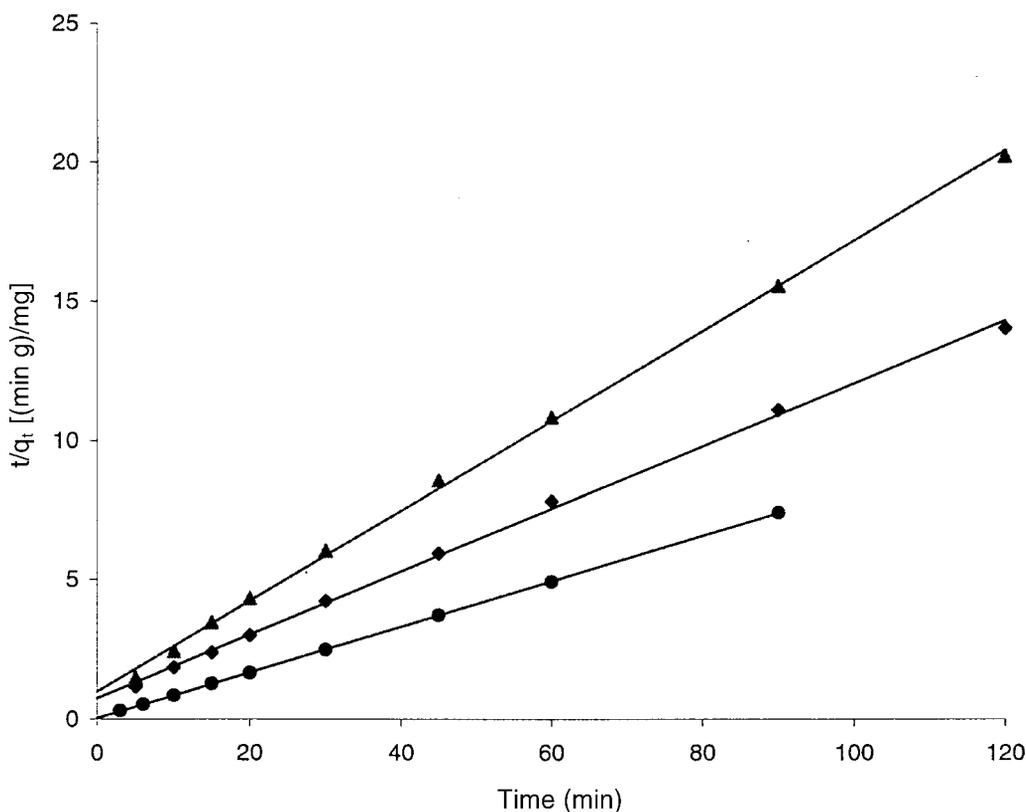


Figure 1. Second-order sorption kinetics of divalent ions on to sphagnum moss peat. Experimental conditions: temp., 25°C; pH, 5; peat dose, 4 g/dm³; ◆, 50 mg/dm³ Cu; ▲, 50 mg/dm³ Ni; ●, 50 mg/dm³ Pb. Full lines depict the application of the second-order model in each case.

RESULTS AND DISCUSSION

Effect of initial metal ion concentration and nature of solute

Pseudo-second order model

The sorption data obtained for the effect of metal ion type and initial concentration are shown in Figures 1 and 2 and listed in Table 2. Figure 1 shows typical plots of equation (9) for the copper system as t/q_t against t . The nickel and the lead series were also plotted so that the constants in equation (12) could be derived. These constants are listed in Table 2 and Figure 2 shows three typical sets of data in relation to the curves calculated from the derived 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 (r^2) obtained as shown in Table 2. Figure 3 shows typical sorption curves for the effect of initial metal ion concentration on the sorption kinetics of metal ion on to sphagnum moss peat. In other words, the data show good compliance with the proposed pseudo-second order equation. Indeed, the regression coefficients

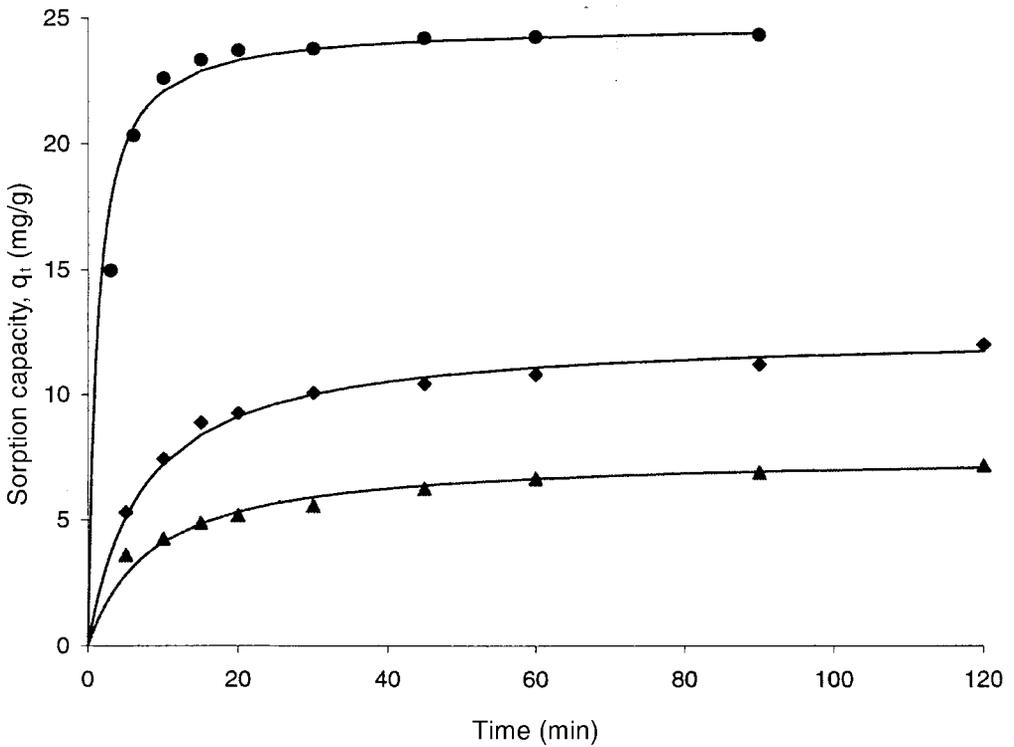


Figure 2. Plot of concentration of metal ions sorbed on to sphagnum moss peat versus time. Experimental conditions: temp., 25°C; pH, 5; peat dose, 4 g/dm³; ◆, 100 mg/dm³ Cu; ▲, 100 mg/dm³ Ni; ●, 100 mg/dm³ Pb. Full lines depict the application of the second-order model in each case.

TABLE 2. Effect of Initial Metal Ion Concentration on Sorption Data on Sphagnum Moss Peat

Divalent metal ion	Initial metal ion concentration, C_0 (mg/dm ³)	Correlation coefficient, r^2	Equilibrium sorption capacity, q_e (mg/g)	Rate constant, k [g/(mg min)]	Initial sorption rate [mg/(g min)]
Pb ²⁺	35	1.000	8.68	0.459	34.7
	50	1.000	12.3	0.167	25.3
	100	1.000	24.7	3.49×10^{-2}	21.2
	210	1.000	49.3	8.69×10^{-3}	21.7
Cu ²⁺	25	1.000	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	8.97×10^{-3}	1.81
Ni ²⁺	10	1.000	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

for the linear plots were better than 0.996. The data also show 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. Thus, on increasing the initial lead concentration from 35 to 210 mg/dm³, the equilibrium sorption capacity, q_e , increased from 8.68 to 49.3 mg/g, whilst for copper the sorption increased from 5.75 to 14.3 mg/g as the initial concentration increased from 25 to 200 mg/dm³ and for nickel the sorption increased from 2.14 to 7.54 mg/g as the initial concentration increased from 10 to 100 mg/dm³.

The values of the initial sorption rates, h , were determined by using the values of the intercept of the straight lines plotted in Figure 1. The values of the rate constant, k , were found to increase from 8.69×10^{-3} to $0.459 \text{ dm}^3/(\text{mg min})$ for a decrease in the initial lead concentration from 210 to 35 mg/dm³, from 8.97×10^{-3} to $9.64 \times 10^{-2} \text{ g}/(\text{mg min})$ for a decrease in the initial copper concentration from 200 to 25 mg/dm³ and from 1.59×10^{-2} to $0.175 \text{ g}/(\text{mg min})$ for a decrease in the initial nickel concentration from 100 to 10 mg/dm³, respectively.

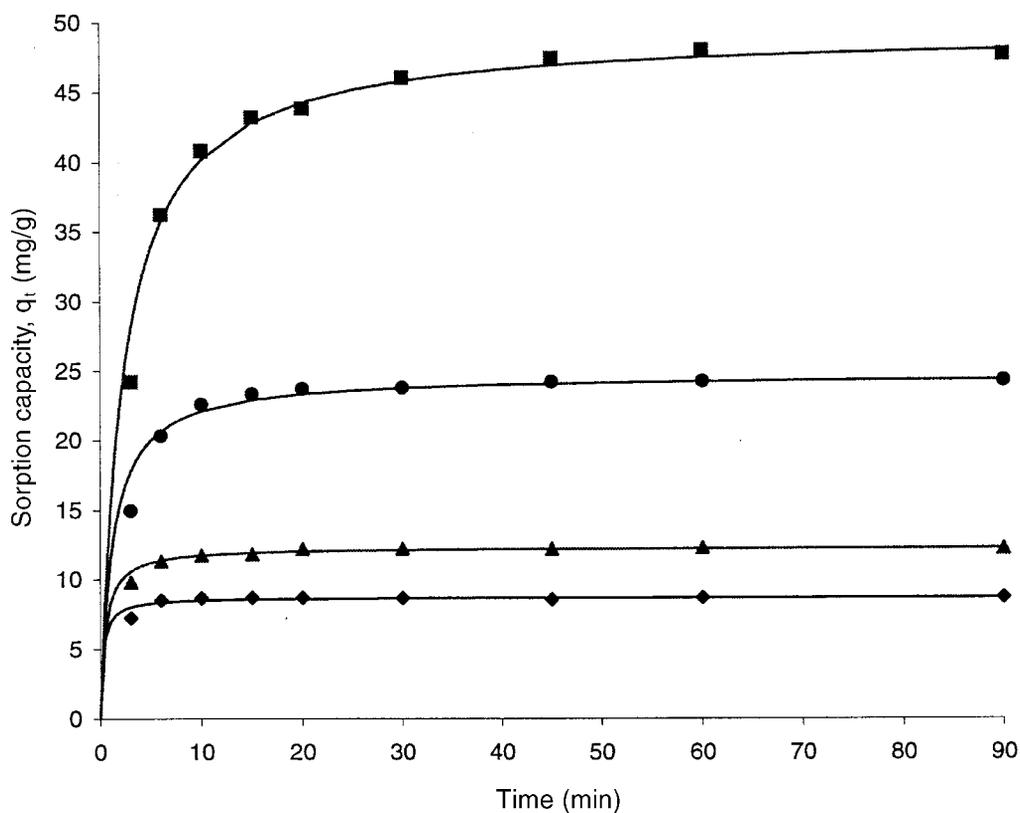


Figure 3. Effect of initial ion concentration on the sorption of Pb ions on to sphagnum moss peat. Experimental conditions: temp., 25°C; pH, 5; peat dose, 4 g/dm³; ♦, 35 mg/dm³ Pb; ▲, 50 mg/dm³ Pb; ●, 100 mg/dm³ Pb; ■, 210 mg/dm³ Pb. Full lines depict the application of the second-order model in each case.

Pseudo-first order model

The pseudo-first order rate expression may be written as:

$$\frac{dq_t}{dt} = k_1(q_1 - q_t) \quad (13)$$

This can be linearised for plotting purposes, to obtain the constants, k_1 and q_1 , as shown in equation (14):

$$\log(q_1 - q_t) = \log(q_1) - \frac{k_1}{2.303} t \quad (14)$$

where k_1 is the rate constant of pseudo-first order sorption (1/min), q_1 is the amount of metal ion sorbed at equilibrium (mg/g) and q_t is the amount of metal ion sorbed on the surface of the sorbent at any time t (mg/g).

The linear plots are shown in Figure 4 as $\log(q_1 - q_t)$ versus time t for the sorption of copper ions on to peat at various times. The gradients, k_1 , have been determined and are listed in Table 3. The correlation coefficients, r_1^2 , are also listed and are significantly lower than the equivalent pseudo-second order correlation coefficients. This strongly suggests that the sorption of divalent metal ions on to peat is most appropriately represented by a pseudo-second order rate process.

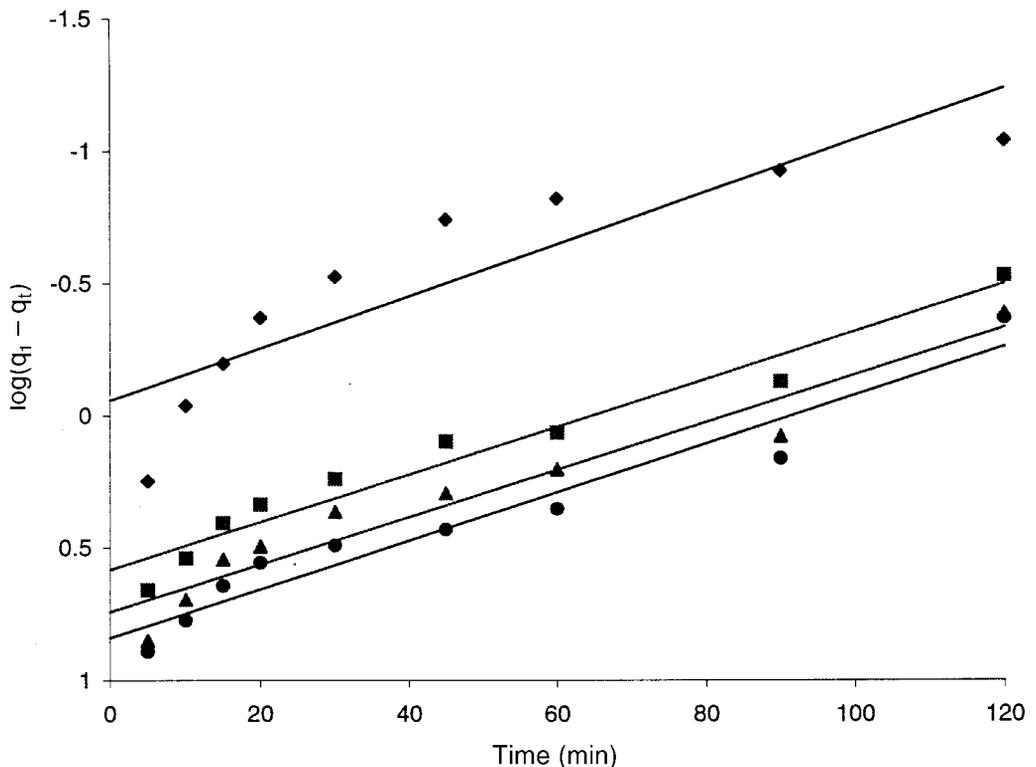
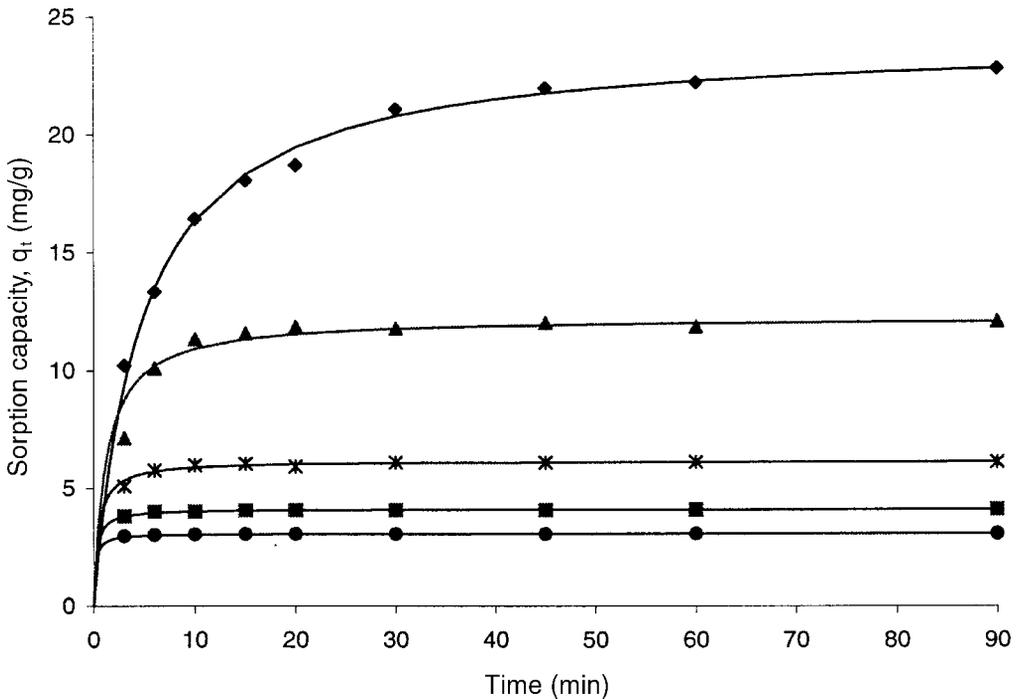


Figure 4. First-order sorption kinetics of copper ions on to sphagnum moss peat. Experimental conditions: temp., 25°C; pH, 5; peat dose, 4 g/dm³; ♦, 25 mg/dm³ Cu; ■, 50 mg/dm³ Cu; ▲, 100 mg/dm³ Cu; ●, 200 mg/dm³ Cu. Full lines depict the application of the first-order model in each case.

TABLE 3. Effect of Initial Copper Metal Ion Concentration on Sorption Data on Sphagnum Moss Peat

Initial Cu ion concentration, C_0 (mg/dm ³)	Correlation coefficient, r_1^2 (mg/dm ³)	Equilibrium concentration of Cu ion sorbed, q_1	Rate constant, k_1 (1/min)
25	0.794	0.875	2.25×10^{-2}
50	0.956	3.82	2.07×10^{-2}
100	0.933	5.52	2.06×10^{-2}
200	0.940	6.92	2.11×10^{-2}

**Figure 5.** Plot of concentration of lead ions sorbed on to sphagnum moss peat versus time. Experimental conditions: temp., 25°C; pH, 5; peat dose, 4 g/dm³; ◆, 4 g/dm³ Pb; ▲, 8 g/dm³ Pb; *, 16 g/dm³ Pb; ■, 24 g/dm³ Pb; ●, 32 g/dm³ Pb. Full lines depict the application of the second-order model in each case.

Effect of peat dose

The results of the effect of peat dose on experiments carried out using the same initial ion concentration of 100 mg/dm³, temperature of 25°C and pH = 5 are shown in Figure 5. Data from a series of kinetics experiments at five different peat doses between 4 to 32 g/dm³ are listed in Table 4. Figure 5 shows typical sorption curves for the effect of peat dose on the sorption kinetics of lead ion on sphagnum moss peat. The data also show a good compliance with the pseudo-second order equation, the regression coefficients for the linear plots being 1.00. These plots show that, for all peat doses, the amount of lead ion sorbed increased rapidly with time at the beginning and very slowly towards the end of the process. Furthermore, a large fraction of the total amount of metal was removed within a short period of time. The plots also demonstrated that the sorption increased for lower peat dosages at any specific time. There was also an effect on the contact time required to reach saturation due to the variation in the peat dose.

As the peat dose, m_s , increased from 4 to 32 g/dm³, the equilibrium sorption capacity, q_e , increased from 96.1 to 98.2 mg/dm³ when sphagnum peat moss was used as a sorbent. It was found that the equilibrium sorption of lead ion is a function of the peat dose. The rate constant, k , the equilibrium sorption capacity, 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 obtained through application of equation (9). The initial sorption rate increased with an increase in the peat dose, the initial sorption rate varying from 20.5 to 654 mg/(dm³ min) as the peat dose was varied from 4 to 32 g/dm³. The values of the rate constants were found to increase from 2.22×10^{-3} to $6.78 \text{ dm}^3/(\text{mg min})$ with an increase in the peat dose from 4 to 32 g/dm³.

The corresponding linear plots of the values of q_e , k and h against m_s were regressed to obtain expressions for these values in terms of the m_s parameters with correlation coefficients of 1.00, 0.999 and 0.971, respectively, as follows:

$$q_e = 95.3m_s^{-0.990} \quad (15)$$

$$k = 2.59 \times 10^{-4}m_s^{2.61} \quad (16)$$

$$h = 2.35m_s^{0.633} \quad (17)$$

Substituting the values of q_e and k from equations (13) and (14) into equation (8) allows the rate law

TABLE 4. Effect of Peat Dose on Lead Ion Sorption Data

Peat dose, m_s (g/dm ³)	Correlation coefficient, r^2	Equilibrium sorption capacity, q_e (mg/g)	Rate constant, k [g/(mg min)]	Initial sorption rate [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	2.14	20.4

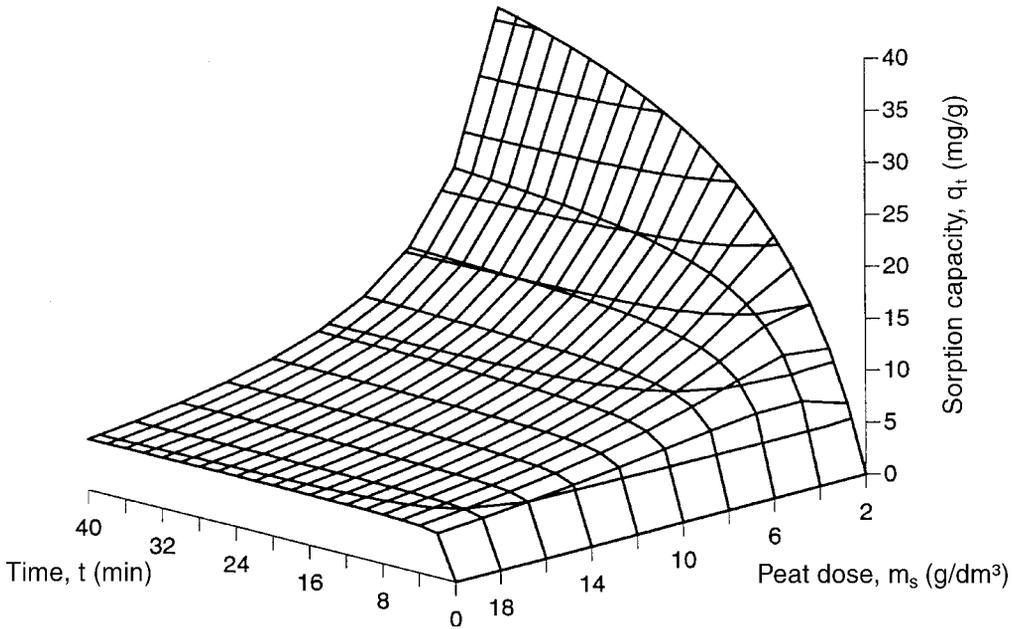


Figure 6. Effect of peat dose on the extent of lead ion sorption on to sphagnum moss peat at various reaction times.

for a pseudo-second order reaction and the relationship between q_t , m_s and t to be represented as:

$$q_t = \frac{t}{\frac{1}{(2.59 \times 10^{-4} m_s^{2.61})(95.3 m_s^{-0.990})^2} + \frac{t}{(95.3 m_s^{-0.990})}} \tag{18}$$

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

This equation represents a generalised predictive model for the concentration of lead ion sorbed at any contact time and involved peat dose. It indicates that the lead sorbed at any contact time increases as the peat dose decreases. 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.

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

CONCLUSIONS

A kinetic model has been developed and fitted for the sorption of divalent metal ions on to sphagnum peat moss. The results show that the sorption of three divalent metals (Cu, Pb and Ni) on to

sphagnum moss peat using an agitated sorber can be described by a pseudo-second order model, based on the assumption that the rate-limiting step may be chemical sorption involving valency forces through sharing or exchange of electrons between the sorbent and sorbate. The parameter which has a major influence on the kinetics of the sorption reaction is the equilibrium sorption capacity, q_e , which is a function of the initial metal ion concentration, peat dose and the nature of the solute ion.

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