# Application of Kinetic Models to the Sorption of Copper(II) on to Peat

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**ABSTRACT:** A comparison of the kinetics of the sorption of copper(II) on to peat from aqueous solution at various initial copper(II) concentrations and peat doses was made. The Elovich model and the pseudo-second order model both provided a high degree of correlation with the experimental data for most of the sorption process. There was a small discrepancy at the initial stages of sorption which suggested that film diffusion or wetting of the peat may be involved in the early part of the sorption process. Models evaluated included the fractional power equation, the Elovich equation, the pseudo-first order equation and the pseudo-second order equation. The kinetics of sorption were followed based on the sorption capacity of copper(II) on peat at various time intervals. Results show that chemical sorption processes may be rate-limiting in the sorption of copper(II) 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

Numerous kinetic models have been investigated for the sorption of contaminants from wastewater by biosorbents. The mechanism of sorption often involves chemical reaction between functional groups on the biosorbent and the metal ions, thus forming metal–organic complexes, or a cation-exchange reaction due to the high cation-exchange capacity of the biosorbent. 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 becomes slower as equilibrium is approached. Such kinetics are often described by a first-order kinetic reaction (Panday *et al.* 1985; Periasamy and Namasivayam 1996; Namasivayam and Kadirvelu 1997) and are sometimes interpreted as a combination of two or three different mechanisms (Sarkar and Chattoraj 1993; Taylor *et al.* 1995; Varshney *et al.* 1996; Singh *et al.* 1996a,b; Atun and Sismanoglu 1996; Comber *et al.* 1996).

The sorption of dyes on to peat has been studied extensively (Poots *et al.* 1976; McKay and Allen 1980, 1983) and diffusional mass-transport models have been developed and used successfully to predict the dye concentration versus time decay curves (McKay and Allen 1984; McKay *et al.* 1984). However, these systems exhibit traditional diffusional characteristics in taking several days to reach equilibrium (Allen and McKay 1987; Allen *et al.* 1988).

The sorption of metal ions on to peat is complete within 3–4 h and therefore analysis of contact

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time data requires a different approach from the method used for diffusional-controlled processes. The uptake of metal ions on to peat has been studied for the initial 30-min period of the sorption process (Allen *et al.* 1992; Bencheikh-Lehocine 1989; Chen *et al.* 1990). Gosset *et al.* (1986) developed a kinetic model for the sorption of copper, zinc, cadmium and nickel on to peat but a very restricted range of parameters was used. In particular, extensive studies by Bunzl (1974) and Bunzl *et al.* (1976) on the adsorption and desorption of metal ions on to peat suggested that the cations participate in ion exchange with the protons from the humic acids.

Bunzl and co-workers (1974, 1976) demonstrated by the use of interruption tests that the rate-controlling step for the sorption of copper on to peat was film diffusion. However, there were differences between that work and that described here. Bunzl *et al.* (1976) added the peat as a wet slurry with a particle size ratio of 2.5:1; in the present study, the peat was added as dry peat with a particle size ratio of 1.42:1. A key difference between the present work and that of Bunzl was that the vessel used by Bunzl was not baffled and hence the particles were able to move around in a vortexing motion but with only limited shear force on the particle boundary layer film. In the present work, the use of a baffled vessel produced complete mixing and extensive shear on the surface of the particles, thus minimizing the boundary layer thickness and reducing the film-diffusion effect. Finally, examination of Bunzl's experimental results demonstrates that 90% copper uptake had occurred within the first 2 min. The data depicted in the figures below indicate that film resistance was effective for the first 15 min of the sorption process, and that other factors became rate-controlling as the concentration driving force from the bulk solution to the particle surface across the boundary layer became much smaller with time.

This present study compares the suitability of several different kinetic models for describing copper(II) sorption on to peat in a controlled system. The rate parameters have been determined and the effectiveness of each model assessed.

## MATERIALS AND METHODS

The experiments were conducted using peat obtained from New Zealand as supplied by the Moutere River Co. Ltd. It was dried for 8 h at $105 \pm 5°C$ and then screened to obtain a particle size range of 500–710 µm peat.

The peat was a sphagnum moss peat and elemental analysis gave the following results on a dry basis: carbon, 57.2%; hydrogen, 5.7%; oxygen, 36.0%; nitrogen, 0.7%; and sulphur, 0.4%. The BET surface area was determined as 26.5 $m^2/g$ and the pore volume as $0.73 \times 10^{-6}$ $m^3/g$. The absolute density was measured in paraffin oil and was found to be 1.220 $kg/m^3$.

The copper sulphate used in the experiments was supplied by Aldrich Chemicals. Stock solutions of copper(II) sulphate (analytical grade $CuSO_4 \cdot 5H_2O$) (1 $g/dm^3$) were prepared in distilled water. All solutions used in this study were diluted with distilled water as required. Before addition of peat, all initial solutions were adjusted to pH 4.5 using sulphuric acid and the final pH of all solutions was $4.1 \pm 0.2$ pH units.

A range of copper(II) concentrations was used with agitation employed until equilibrium was achieved. All contact investigations were carried out using a baffled agitated sorber vessel and a constant agitation speed of 400 rpm (see Figure 1). The adsorber vessel was a 2-$dm^3$ plastic beaker with an internal diameter of 0.13 m. It was capable of holding a volume of 1.7 $dm^3$ solution. A six-bladed, flat plastic impeller was used to achieve complete mixing. The diameter of the impeller and the blade height were 0.065 m and 0.013 m, respectively. A Heidolph motor (type RZR 1) was used to drive the impeller using a 0.005-m diameter plastic shaft. Six plastic baffles were evenly spaced around the circumference of the vessel, positioned at 60° intervals and held
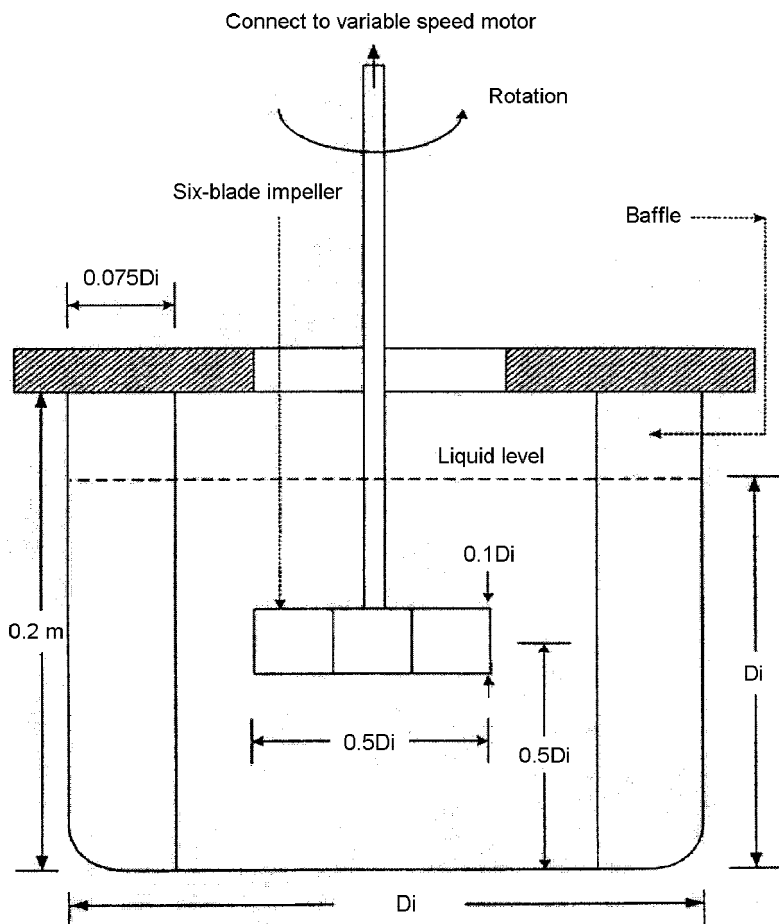
**Figure 1.** Schematic representation of sorber vessel. Construction data: height of baffles = 0.2 m; baffle width = 0.075Di; height of liquid in vessel = Di; distance between impeller blade and vessel bottom = 0.5Di; width of blade of impeller = 0.1Di; impeller diameter = 0.5Di.

securely in place on top of the vessel. The polystyrene baffles were 0.2 m long and 0.01 m wide. They were used to prevent the formation of a vortex, to reduce the relative motion between liquid and solid particles and, consequentially, to reduce power losses due to air entrainment at the impeller. They were secured in a position slightly away from the vessel wall and tank bottom in order to prevent particle accumulation. The use of a thick polystyrene sheet on top of the vessel prevented the evaporation of liquid.

Samples were withdrawn at suitable time intervals, filtered through a 0.45-$\mu$m membrane filter and then analysed by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Perkin-

**TABLE 1.** Experimental Conditions Employed

| Experiment No. | Initial copper(II) conc., $C_0$ (mg/dm³) | Equilibrium copper(II) conc., $C_e$ (mg/dm³) | Mass of peat employed, $m_s$ (g/dm³) | Reaction volume, V (dm³) | Particle diameter, $D_p$ (µm) | Stirring speed, S (rpm) |
|---|---|---|---|---|---|---|
| 1 | 0.643 | 0.142 | 4.00 | 1.7 | 605 | 400 |
| 2 | 1.33 | 0.186 | 4.00 | 1.7 | 605 | 400 |
| 3 | 1.56 | 0.190 | 4.00 | 1.7 | 605 | 400 |
| 4 | 1.83 | 0.191 | 4.00 | 1.7 | 605 | 400 |
| 5 | 1.33 | 0.188 | 3.00 | 1.7 | 605 | 400 |
| 6 | 1.33 | 0.186 | 4.00 | 1.7 | 605 | 400 |
| 7 | 1.33 | 0.179 | 5.00 | 1.7 | 605 | 400 |
| 8 | 1.33 | 0.170 | 6.00 | 1.7 | 605 | 400 |

Elmer, Optima 3000XL). The vessel contained 1.7 dm³ copper(II) solution and was designed to conform to specified standards to achieve complete and uniform mixing of particles at a constant power number (Furusawa and Smith 1973, 1974; McKay and Allen 1980). Several experiments were performed in duplicate and identical concentration versus time decay curves were obtained.

Table 1 provides a list of the experiments undertaken and the experimental conditions used to study the effect of the initial copper(II) concentration and the effect of peat mass.

## MODEL DEVELOPMENT

Sorption in a copper/peat system results in the transfer of copper(II) to the surface of the peat, where it increases in concentration until a dynamic equilibrium is reached between the peat and copper(II) remaining in the liquid phase. Most biosorbent sorption processes take place by a multistep mechanism comprising of transport processes such as diffusion in the bulk of the liquid phase, diffusion across the liquid film surrounding the solid particles, diffusion in liquid-filled micropores and macropores as well as chemical reactions. In order to investigate the mechanism of sorption and potential rate-controlling steps such as mass transport and chemical reaction processes, several kinetic models were tested including the fractional power equation, the Elovich equation, a pseudo-first order equation and a pseudo-second order equation.

### Fractional power model

The fractional power function model is a modified form of the Freundlich equation and may be expressed by equation (1) (Dalal 1974) or its linear form as given in equation (2):

$$q_t = at^b \tag{1}$$

$$\ln q_t = \ln a + b \ln t \tag{2}$$

where $q_t$ is the amount of copper(II) sorbed by peat at a time t, while a and b are constants with b < 1. The function ab is also a constant, being the specific sorption rate at unit time, i.e. when t = 1.

## Elovich model

The Elovich or Roginsky–Zeldovich equation is generally expressed as follows (Low 1960):

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \tag{3}$$

where $q_t$ is the amount of copper(II) sorbed by peat at a time t, $\alpha$ is the initial copper(II) sorption rate [mmol/(g min)] and $\beta$ is the desorption constant (g/mmol) during any one experiment.

To simplify the Elovich equation, Chien and Clayton (1980) assumed $\alpha\beta t \gg 1$, and on applying the boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, equation (3) then becomes (Sparks 1986):

$$q_t = \beta \ln(\alpha\beta) + \beta \ln t \tag{4}$$

Thus the constants can be obtained from the slope and intercept of the linear plot of $q_t$ versus ln t. Equation (4) will be used to test the applicability of the Elovich equation to the kinetics of copper(II) sorption on to peat.

## Pseudo-first order model

For a batch contact time process where the rate of sorption of copper(II) on to the peat surface is proportional to the amount of copper(II) sorbed from the solution phase, the first-order kinetic equation may be expressed as:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{5}$$

where $q_e$ and $q_t$ are the sorption capacity (mmol/g) of the copper(II) ion at equilibrium and at a time t, respectively, and $k_1$ is the rate constant for pseudo-first order sorption (l/min). After integration and applying boundary conditions, viz. that the initial conditions are $(q_e - q_t) = 0$ at $t = 0$, equation (5) becomes:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{6}$$

The equation, applicable to experimental results, generally differs from a true first-order equation in two ways (Aharoni and Sparks 1991): (i) the parameter $k_1(q_e - q_t)$ does not represent the number of available sites; and (ii) the parameter ln $q_e$ is an adjustable parameter which is often not equal to the intercept of a plot of $\ln(q_e - q_t)$ versus t, whereas for a true first-order process ln $q_e$ should be equal to the intercept of a plot of $\ln(q_e - q_t)$ versus t.

## Pseudo-second order model

To describe copper(II) sorption, the modified pseudo-second order equation can be written as:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \tag{7}$$

where $q_e$ and $q_t$ are the sorption capacity (mmol/g) of copper(II) ions at equilibrium and at a time t, respectively, and k is the rate constant for pseudo-second order sorption [g/(mmol min)]. For the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, the integrated form of equation (7) becomes:
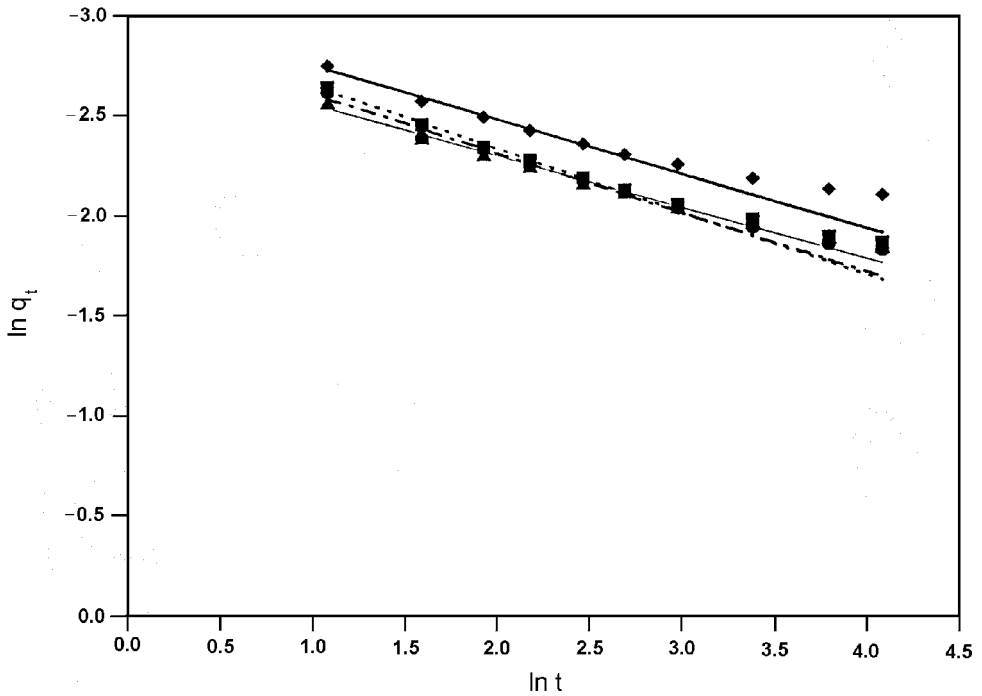
**Figure 2.** Plot of fractional power function equation for sorption of copper(II) ions on to peat at various initial concentrations: ◆, 0.643 mmol/dm³ experimental data; ——, power function model; ■, 1.33 mmol/dm³ experimental data, ..... , power function model; ▲, 1.56 mmol/dm³ experimental data; ——, power function model; ●, 1.83 mmol/dm³ experimental data, –·––, power function model.

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + kt \tag{8}$$

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

which is the integrated rate law for a pseudo-second order reaction. This has a linear form:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t \tag{10}$$

In the limit $q_t/t \to 0$, the initial sorption rate, h, is given by $kq_e^2$. Thus, a plot of $t/q_t$ against t of equation (10) should give a linear relationship with a slope of $1/q_e$ and an intercept of $1/kq_e^2$, i.e. l/h.
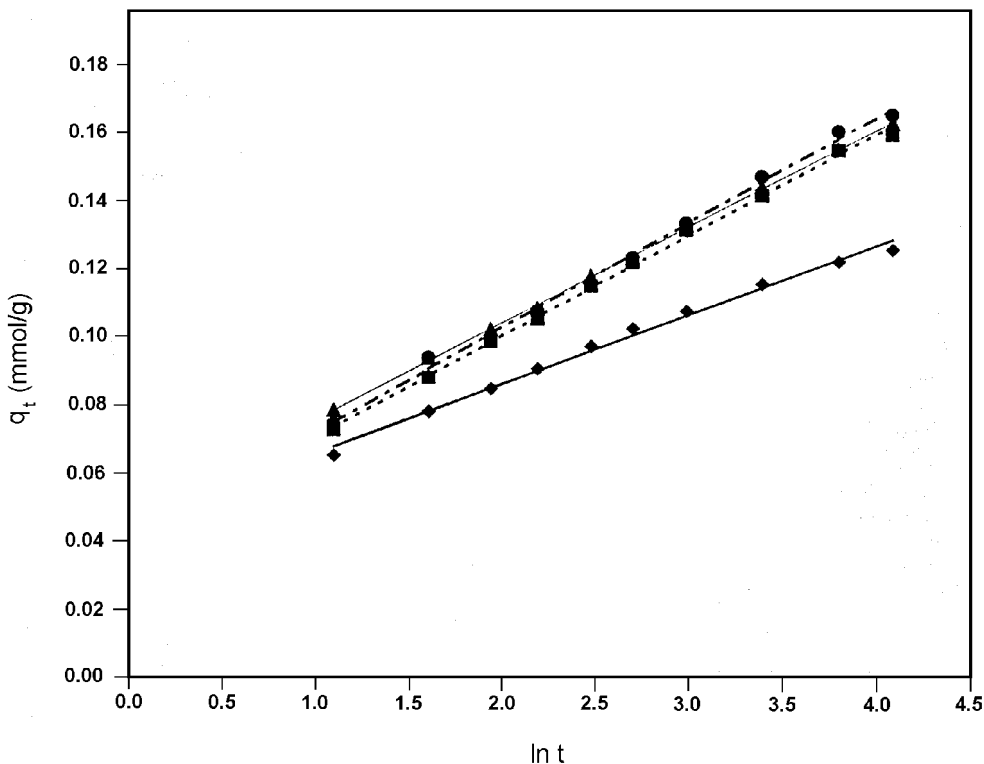
**Figure 3.** Plot of Elovich equation for sorption of copper(II) ions on to peat at various initial concentrations: ◆, 0.643 mmol/dm³ experimental data; ——, Elovich model; ■, 1.33 mmol/dm³ experimental data, ....., Elovich model; ▲, 1.56 mmol/dm³ experimental data; ——, Elovich model; ●, 1.83 mmol/dm³ experimental data, –·–·–, Elovich model.

## RESULTS AND DISCUSSION

### Fractional power model

Figure 2 shows a plot of ln $q_t$ against ln t of the fractional power function equation for the results of the sorption of copper(II) on to peat at various initial ion concentrations. The figure shows that, although a linear relationship existed over the initial 15-min period of the sorption process, the overall line was not straight.

### Elovich analysis

Figure 3 shows a plot of the Elovich equation for the same data. In this case, a linear relationship was obtained between copper(II) sorbed, $q_t$, and ln t over the whole sorption period, with high correlation coefficients (> 0.993) for all the lines (Table 2). The same type of plot for the sorption

**TABLE 2.** Calculated Values of $\alpha$ and $\beta$ in the Elovich Equation for the Sorption of Copper(II) on to Peat[a]

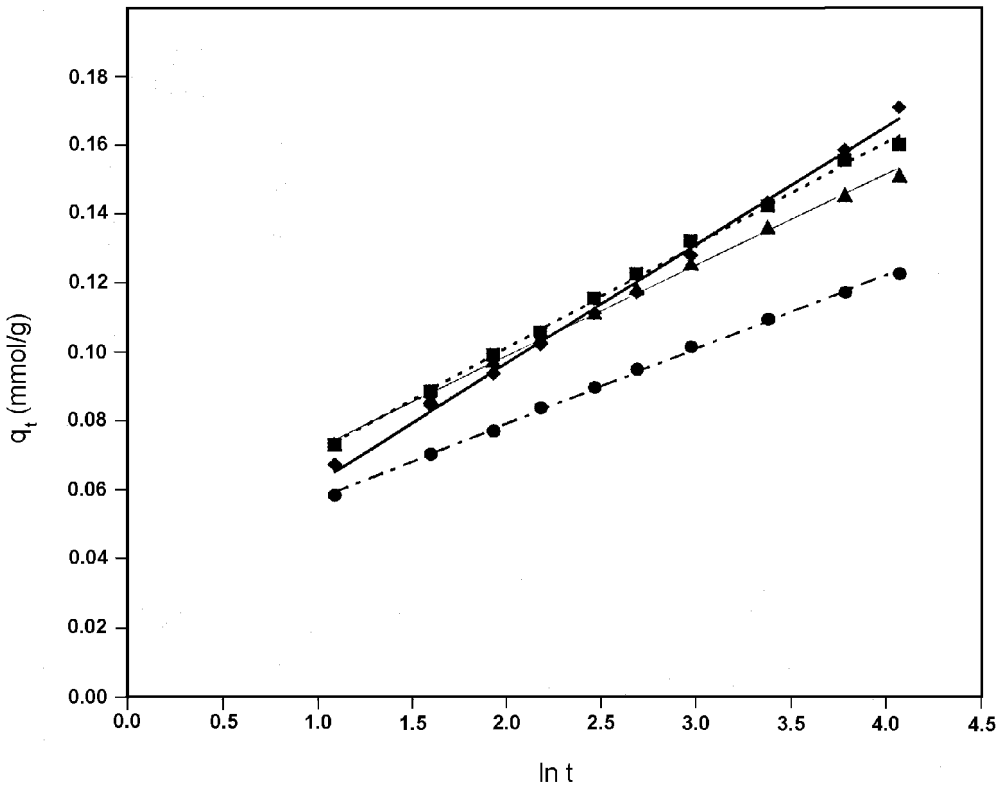| $C_0$ (mmol/ dm$^3$) | $r^2$ | $\alpha$ [mmol/ (g min)] | SE | $\beta$ (g/mmol) | $m_s$ (g/dm$^3$) | $r^2$ | SE | $\alpha$ [mmol/ (g min)] | $\beta$ (g/mmol) |
|---|---|---|---|---|---|---|---|---|---|
| 0.643 | 0.993 | 461 | $1.73 \times 10^{-3}$ | $2.02 \times 10^{-2}$ | 3.00 | 0.996 | $2.10 \times 10^{-3}$ | 65.4 | $3.39 \times 10^{-2}$ |
| 1.33 | 0.998 | 134 | $1.36 \times 10^{-3}$ | $2.95 \times 10^{-2}$ | 4.00 | 0.998 | $1.36 \times 10^{-3}$ | 134 | $2.95 \times 10^{-2}$ |
| 1.56 | 0.999 | 189 | $6.52 \times 10^{-4}$ | $2.81 \times 10^{-2}$ | 5.00 | 0.997 | $1.36 \times 10^{-3}$ | 217 | $2.60 \times 10^{-2}$ |
| 1.83 | 0.996 | 123 | $1.87 \times 10^{-3}$ | $3.07 \times 10^{-2}$ | 6.00 | 0.999 | $8.36 \times 10^{-4}$ | 247 | $2.12 \times 10^{-2}$ |

[a] $r^2$ = correlation coefficient; SE = standard error.



**Figure 4.** Plot of Elovich equation for sorption of copper(II) ions on to peat at various peat doses: ◆, 3 g/dm$^3$ experimental data; ——, Elovich model; ■, 4 g/dm$^3$ experimental data, ..... , Elovich model; ▲, 5 g/dm$^3$ experimental data; ——, Elovich model; ●, 6 g/dm$^3$ experimental data, – – –, Elovich model.

of copper(II) on to peat at various peat doses is shown in Figure 4. Again, in this case, the linear correlation coefficients were highly significant (> 0.996) and once more demonstrated a high degree of correlation between the experimental data and the theoretical data predicted by the Elovich model as defined by equation (4). It is clear that a simple Elovich equation may be used to describe the kinetics of sorption of copper(II) on to peat while an expression for a fractional power function kinetic reaction failed.

Table 2 lists the kinetic constants obtained from the Elovich equation. It will be seen from the data that the values of $\alpha$ and $\beta$ varied as a function of the initial copper(II) concentration, $C_0$, and peat dose, $m_s$. Thus, on increasing the initial copper(II) concentration from 0.643 to 1.83 mmol/dm³, the value of $\alpha$ decreased from 461 to 123 mmol/(g min) and the value of $\beta$ increased from $2.02 \times 10^{-2}$ to $3.07 \times 10^{-2}$ g/mmol. On increasing the peat dose from 3 to 6 g/dm³, the value of $\alpha$ increased from 65.4 to 247 mmol/(g min) and the value of $\beta$ decreased from $3.39 \times 10^{-2}$ to $2.12 \times 10^{-2}$ g/mmol. The quantity $\alpha$ in the Elovich equation is equivalent to the initial gradient which varied different $C_0$ values and different peat masses.

Although the Elovich equation does not provide any mechanistic evidence, it has proved suitable for highly heterogeneous systems of which the adsorption of copper(II) on to peat is undoubtedly such a case.

## Pseudo-first order model

The results of the sorption of copper(II) on to peat have been represented in the form of the first-order equation in Figures 5 and 6 at various initial ion concentrations as well as at various peat doses, respectively. From these plots, a linear relationship between $\ln(q_e - q_t)$ and t was established for the later portion (15–60 min) with high correlation coefficients (> 0.987). These plots showed different distinct linear regions within individual sets of data. In these cases, it was thus necessary to perform multiple regressions on different ranges of the data. The kinetics could be approximated by two basic equations, each valid over a limited range of time: the fractional power equation at the beginning of the experiment (15 min) and the first-order equation when saturation was approached (15–60 min). However, the Elovich equation provides an excellent description of the sorption of copper(II) on to peat (Figures 2 and 3) with high correlation coefficients. If the sorption process is chemisorption, the experimental results may be described by the Elovich model (Aharoni and Ungarish 1976).

## Pseudo-second order model

It should be noted that an improvement in the experimental procedure used to obtain the rate data presented in this paper was believed to have been made relative to previous experimental methodologies (McKay 1982). The same data are shown as pseudo-second order equations in Figures 7 and 8. These plots show the data-fits had extremely high correlation coefficients (> 0.994) when the pseudo-second order equation was employed; it was possible to ascertain from them whether the rate-determining process is a chemical reaction. The results in Tables 3 and 4 show the sorption rate constant, k, initial sorption rate, h, and equilibrium sorption capacity, $q_e$, as a function of the initial copper(II) concentration, $C_0$ and peat dose, $m_s$. Thus, on increasing the initial copper(II) concentration from 0.643 to 1.83 mmol/dm³, the copper(II) equilibrium sorption capacity, $q_e$, increased from 0.132 to 0.178 mmol/g. However, on increasing the peat dose from 3 to 6 g/dm³, the copper(II) equilibrium sorption capacity, $q_e$, decreased from 0.185 to 0.129 mmol/g. The experimental equilibrium values, $q_{exp}$, can be determined by plotting the operating lines for the
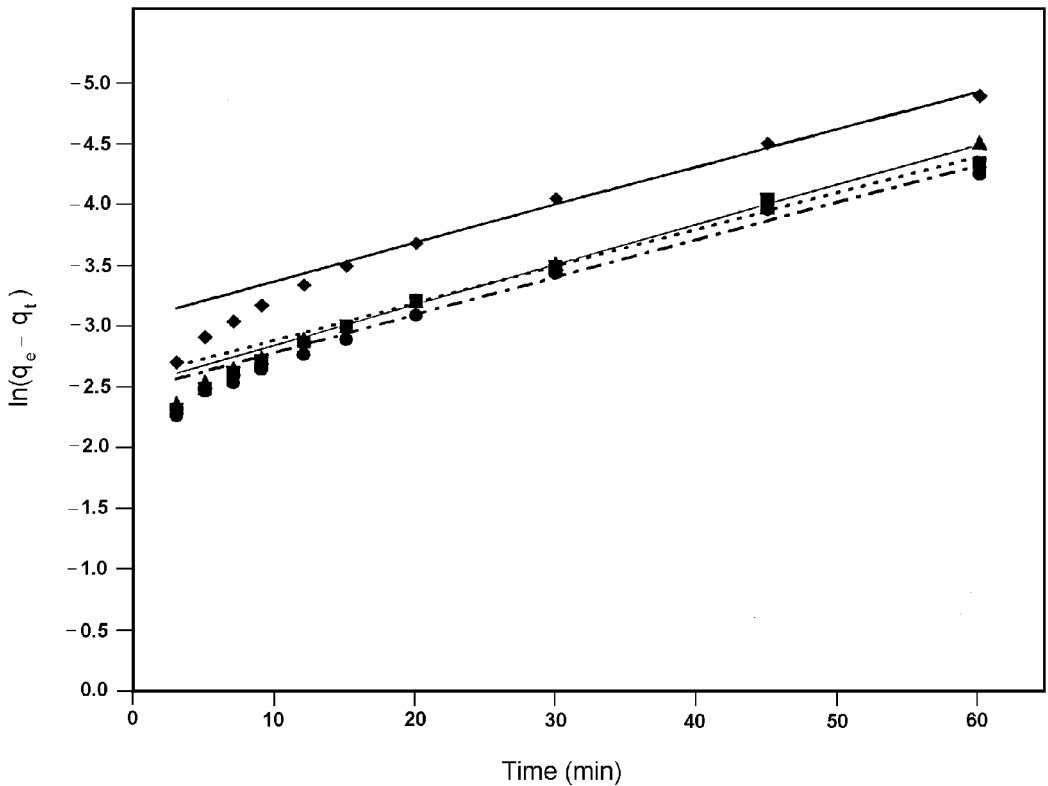
**Figure 5.** Plot of first-order equation for sorption of copper ions on to peat at various initial concentrations: ◆, 0.643 mmol/dm³ experimental data; ——, first-order model; ■, 1.33 mmol/dm³ experimental data, ....., first-order model; ▲, 1.56 mmol/dm³ experimental data; ——, first-order model; ●, 1.83 mmol/dm³ experimental data, –·–·–, first-order model.

**TABLE 3.** Parameters for the Effect of Initial Copper(II) Concentration[a]

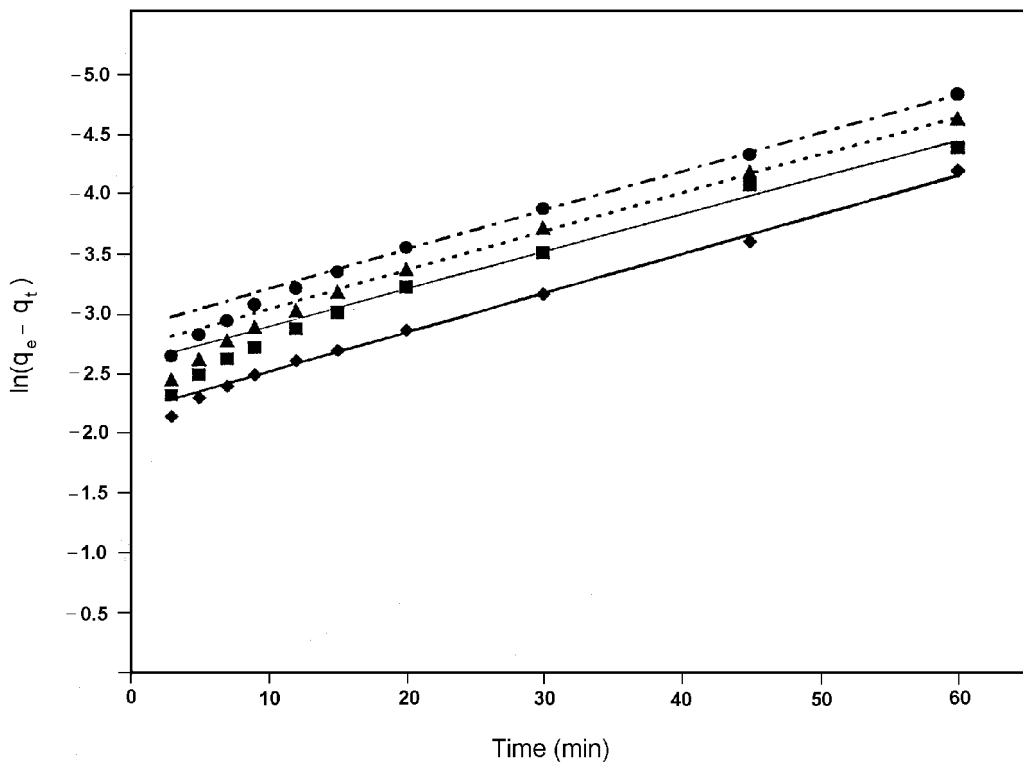| Initial copper(II) conc., $C_0$ (mg/dm³) | $r^2$ | SE | Equilibrium sorption capacity, $q_e$ (mmol/g) | k [g/(mmol min)] | h [mmol/(g min)] |
|---|---|---|---|---|---|
| 0.643 | 0.999 | 4.22 | 0.132 | 1.87 | $3.26 \times 10^{-2}$ |
| 1.33 | 0.998 | 4.77 | 0.171 | 1.07 | $3.13 \times 10^{-2}$ |
| 1.56 | 0.997 | 5.81 | 0.173 | 1.12 | $3.33 \times 10^{-2}$ |
| 1.83 | 0.997 | 5.66 | 0.178 | 0.973 | $3.10 \times 10^{-2}$ |

[a]$r^2$ = correlation coefficient; SE = standard deviation.

**Figure 6.** Plot of first-order equation for sorption of copper(II) ions on to peat at various peat doses: ◆, 3 g/dm³ experimental data; ——, first-order model; ■, 4 g/dm³ experimental data, ....., first-order model; ▲, 5 g/dm³ experimental data; ——, first-order model; ●, 6 g/dm³ experimental data, –·–·–, first-order model.

**TABLE 4.** Parameters for the Effect of Peat Dose[a]

| Peat dose, $m_s$ (g/dm³) | $r^2$ | SE | Equilibrium sorption capacity, $q_e$ (mmol/g) | k [g/(mmol min)] | h [mmol/(g min)] |
|---|---|---|---|---|---|
| 3.00 | 0.994 | 8.34 | 0.185 | 0.725 | $2.48 \times 10^{-2}$ |
| 4.00 | 0.998 | 4.77 | 0.171 | 1.07 | $3.13 \times 10^{-2}$ |
| 5.00 | 0.999 | 4.60 | 0.159 | 1.30 | $3.30 \times 10^{-2}$ |
| 6.00 | 0.998 | 6.34 | 0.129 | 1.55 | $2.57 \times 10^{-2}$ |

[a]$r^2$ = correlation coefficient; SE = standard deviation.

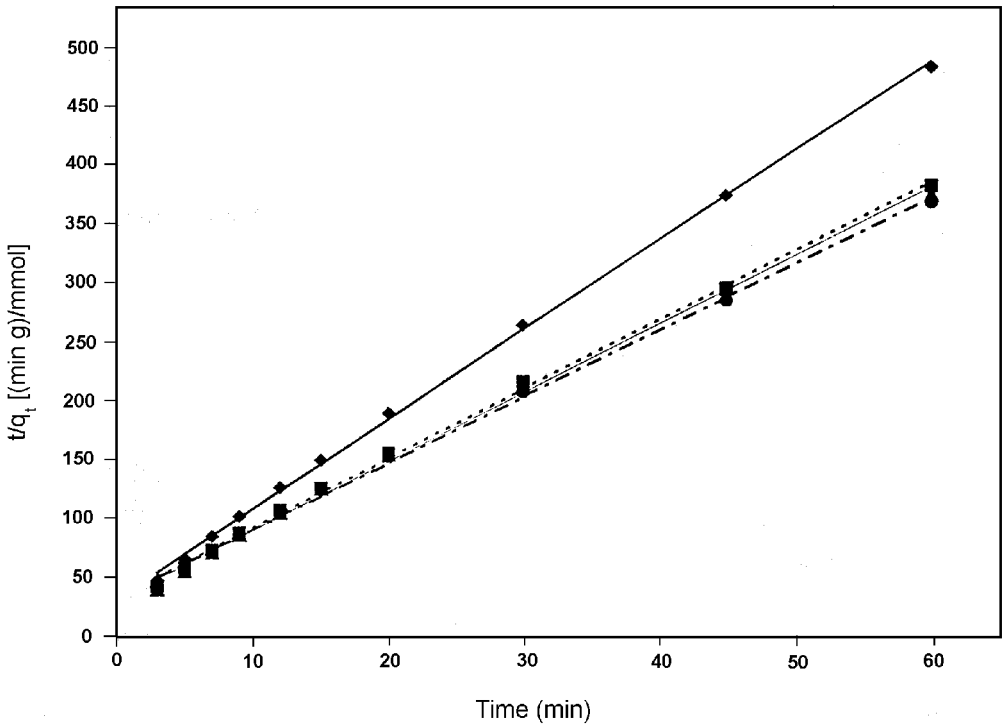**Figure 7.** Plot of pseudo-second equation for sorption of copper(II) ions on to peat at various initial concentrations: ◆, 0.643 mmol/dm³ experimental data; ——, second-order model; ■, 1.33 mmol/dm³ experimental data, ....., second-order model; ▲, 1.56 mmol/dm³ experimental data; ——, second-order model; ●, 1.83 mmol/dm³ experimental data, —·—·, second-order model.

batch contact time experiments on to the equilibrium isotherm as shown in Figure 9. All the $q_e$ and $q_{exp}$ values were within 10% of each other, except for the high mass experiment.

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 copper(II) concentration, $C_0$, with high correlation coefficients (> 0.990). Hence, it was further considered that $q_e$, k and h could be expressed as functions of $C_0$ as follows:

$$q_e = \frac{C_0}{4.55C_0 + 1.89} \tag{11}$$

$$k = \frac{C_0}{1.26C_0 - 0.468} \tag{12}$$

$$h = \frac{C_0}{32.2C_0 - 1.18} \tag{13}$$

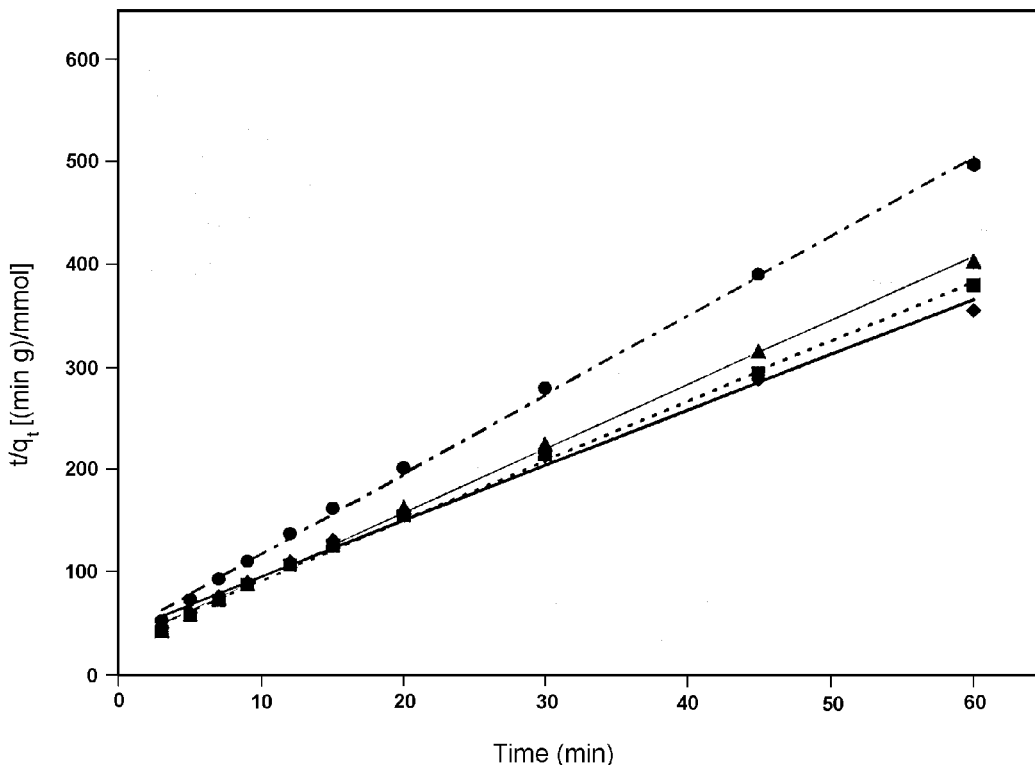**Figure 8.** Plot of pseudo-second order equation for sorption of copper(II) ions on to peat at various peat doses: ◆, 3 g/dm³ experimental data; ——, second-order model; ■, 4 g/dm³ experimental data, ....., second-order model; ▲, 5 g/dm³ experimental data; ——, second-order model; ●, 6 g/dm³ experimental data, –·–·–, second-order model.

Substituting the values of $q_e$ and h from equations (11) and (13) into equations (9) and (10), the rate law for a pseudo-second order reaction and the relationship of $q_t$, $C_0$ and t can then be represented as:

$$q_t = \frac{C_0 t}{32.2C_0 - 1.18 + (4.55C_0 + 1.89)t} \tag{14}$$

Equation (14) represents the generalised predictive model for copper(II) sorbed at any contact time and initial copper(II) concentration within the specified concentration range. It indicates that the amount of copper(II) sorbed at any contact time increased with increasing initial copper(II) concentration. This is obvious for higher $C_0$ values, as a more efficient utilisation of the sorptive capacities of the sorbent would be expected due to the greater sorption driving force. This equation can then be used to derive the amount of copper(II) sorbed at any given copper(II) concentration and reaction time. The three-dimensional plot of the equation (14) is shown in Figure 10.
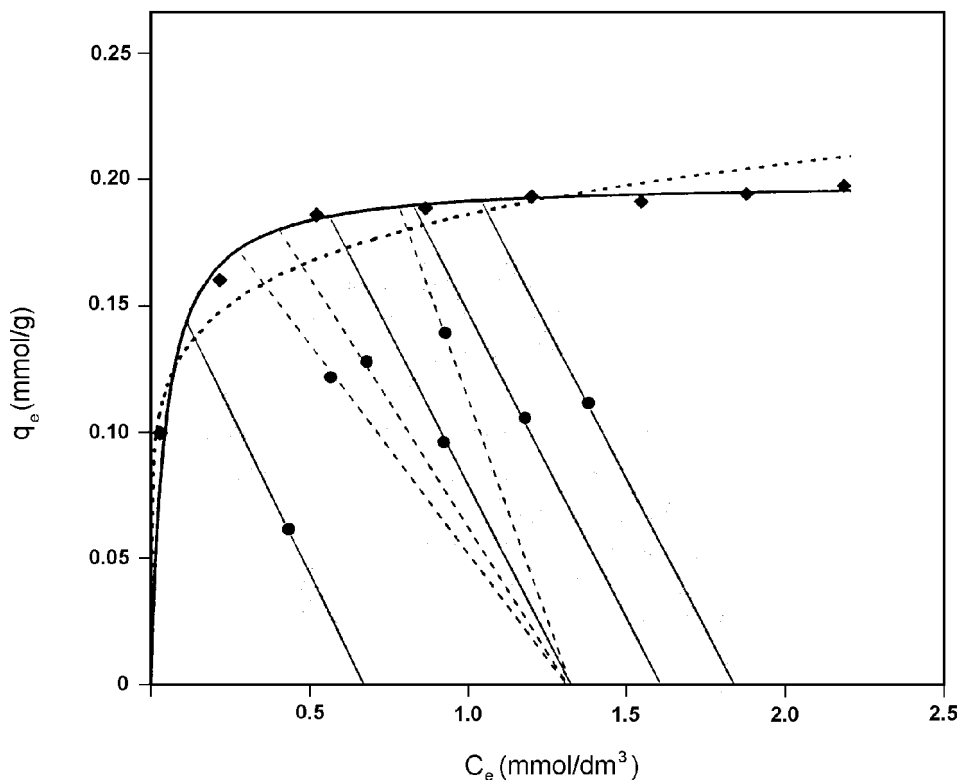
**Figure 9.** Isotherms of copper(II) ions sorbed on to peat: ◆, copper(II) experimental data; ———, Langmuir isotherm, ....., Freundich isotherm; —•—, concentration operating lines; ·····•·····, mass operating lines.

Figures 11 and 12 show plots of the empirical Elovich model [equation (4)] and the pseudo-second order model [equation (9)] employing the experimental data. The models show excellent fits to the data over a 1-h time range for the experimental curves. In addition, the fractional power function model [equation (1)] provides a good fit with experimental data for the initial 15 min and the first-order model [equation (6)] fits the experimental data over the period 15–60 min.

The statistical data for all four kinetics models are presented in Tables 1–4 and the results based on the linear correlation coefficient, $r^2$, and the standard error, SE, show that the Elovich equation and the pseudo-second order models provided a far better fit to the experimental data than the other models.

## Mechanism for sorption of copper(II) on to peat

Because of the high correlation coefficients obtained using the Elovich and pseudo-second order kinetic models, it was impossible to conclude which sorption mechanism actually occurred and
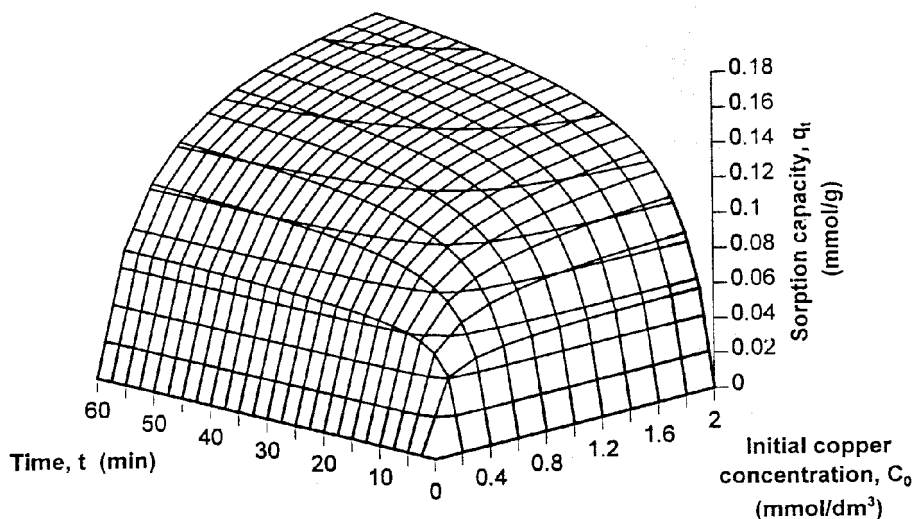
**Figure 10.** Effect of initial copper(II) concentration on its sorption at various reaction times.

was responsible for the ability of peat to sorb copper ions. It was therefore necessary to review other sources of information in an attempt to identify the specific sorption mechanism. Most authors (Lalancette 1974; Coupal and Lalancette 1976; Zhipei *et al.* 1984; Gosset *et al.* 1986) agree that peat is a material rich with chemical functional groups such as alcohols, aldehydes, ketones, carboxylic acids, phenolic hydroxides and ethers, and that metal sorption may readily take place via chelation, exchange sorption, polar organic bonding and polar inorganic bonding.

Furthermore, many researchers have implicated carboxylic acid (COOH) groups in the reaction of divalent metals with humic acids (Schnitzer 1978; Schnitzer and Khan 1972; Vinkler and Meisel 1976; Boyd *et al.* 1981; da Silva *et al.* 2002). 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. The mechanism of reaction between ionic metal and peat is the subject of some debate and has often been attributed to the type of peat used. Some authors such as Aho and Tummavouri (1984), Bunzl *et al.* (1976) and Kadlec and Keoleian (1986) have developed models based only on ion exchange and single copper(II) ion interaction with peat according to the scheme:

$$2Peat-H \quad + \quad Cu^{2+} \quad \Leftrightarrow \quad R_2Cu \quad + \quad 2H^+ \tag{15}$$
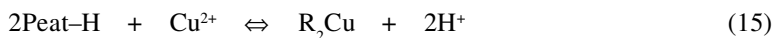
However, Gangiotti *et al.* (1986) provided evidence for copper fixing by complexation in addition to ion exchange. This gives rise to a mechanism supported by Coleman *et al.* (1956), Gossett *et al.* (1986) and Ringqvist and Oborn (2002) which may be represented by a global scheme incorporating two copper(II) ions interacting with peat as:

$$2Peat-H \quad + \quad 2Peat^{-1} \quad + \quad 2Cu^{2+} \quad \Leftrightarrow \quad 2(Peat)_2Cu \quad + \quad 2H^+ \tag{16}$$
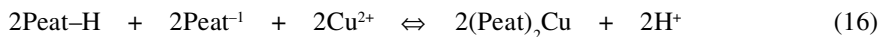
where $Peat^{-1}$ is a complexing site. Another factor that could influence the sorption mechanism is the presence of soluble components in solutions containing peat particles (Leenheer *et al.* 1998).
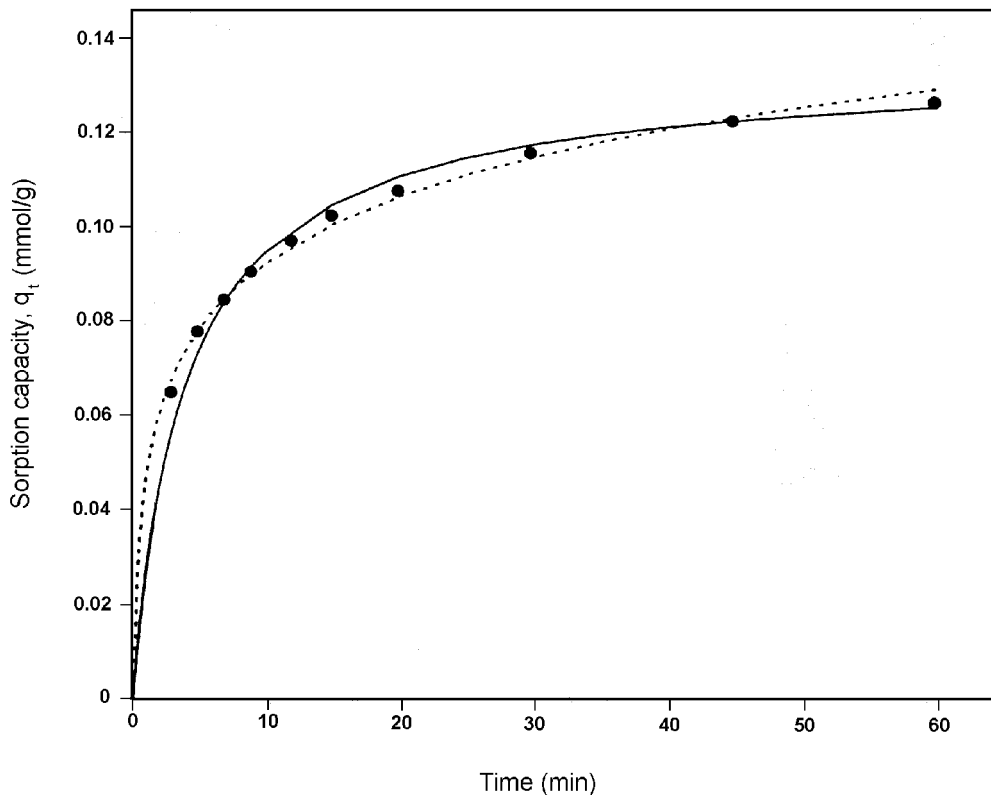
**Figure 11.** Plots of Elovich and second-order models for the sorption of copper(II) on to peat: ●, $C_0 = 0.643$ mmol/dm$^3$; ....., Elovich model; ——, power function model.

Thus, it is possible that the presence of dissolved organic carbon could influence the equilibrium concentrations of copper(II) ions.

In more recent work, Stevenson and Chen (1991) determined the stability constants for copper(II)–humate complexes based on binding at two sites. These authors proposed that the binding of copper(II) ions may occur through the formation of a coordinate link with a single carboxylate (COO$^-$), a link between two carboxylates on the same molecule, a chelate-ring structure with a COOH phenolic OH$^-$ site, or 2:1 complexes with copper(II) serving as a bridge between two macromolecules. Spark *et al.* (1997) proposed that copper(II) has a tendency to form crosslinked sphero colloids involving the carboxylate functional groups on the humic acid macromolecules.

A more recent study by Francioso *et al.* (1996), using IR, Raman and NMR spectroscopic evidence, again supported a metal-ion complex involving the carboxylic acid group. The authors concluded that the presence of a greater number of carboxylate and phenolic groups could explain the high affinity of peat for metal ions.

Other recent work, involving NMR and FT-IR structural studies was performed by Averett *et al.* (1994) and Leenheer *et al.* (1998) on copper(II) binding with carboxylate groups on humic and fulvic acid. These authors concluded that an inner-sphere complex of the metal-binding fraction occurred based on chemisorption in which the copper(II) ions were not bound irreversibly, with an
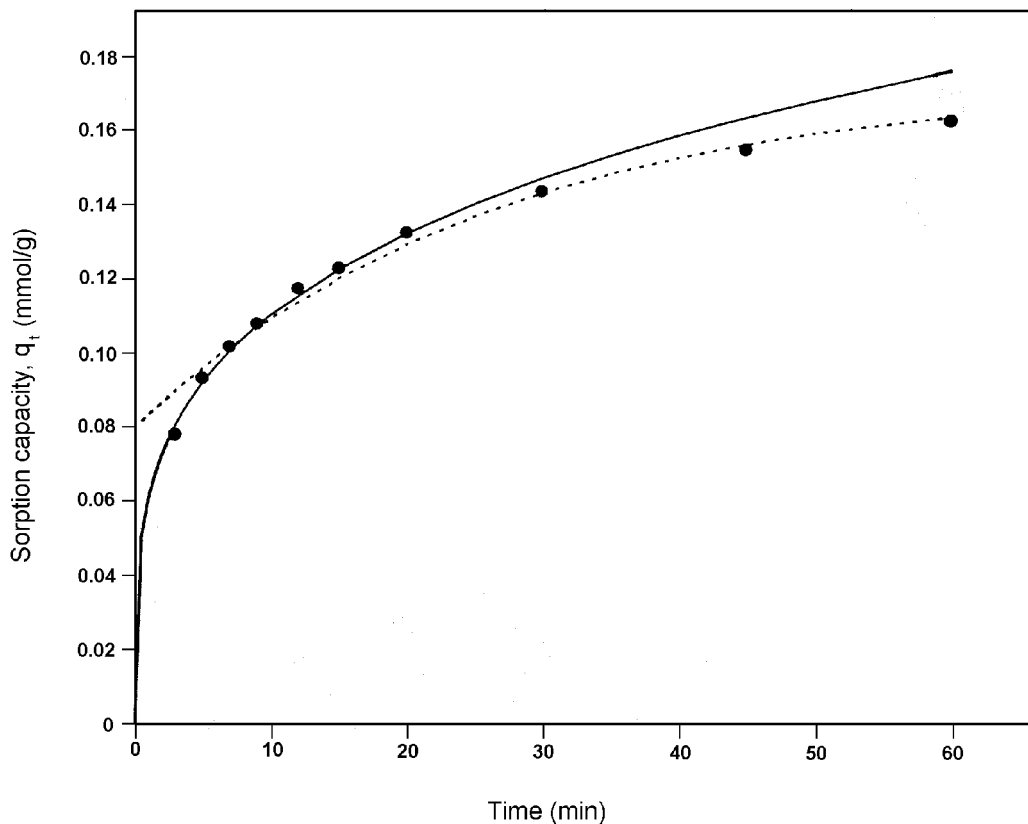
**Figure 12.** Plots of fractional power function and first-order models for the sorption of copper(II) on to peat: ●, $C_0$ = 1.56 mmol/dm³; **.....**, first-order model; ——, power function model.

outer-sphere binding complex also being formed. Obviously, the best kinetic models must be based on binding mechanisms and coordination numbers, and this would involve complex kinetic modelling for the various substrates. However, the objective of the present work was to identify a best-fit kinetic model based on four approaches used to analyse the sorption of copper(II) on to peat in which several complex reactions occurred. The values listed in Table 5 show that the pseudo-second order reaction and the Elovich equation exhibited almost identical $r^2$ values. In terms of standard error values, the Elovich equation had a significantly lower SE value and provided the best correlation of the experimental data overall.

**TABLE 5.** Mean Error Coefficients for Models Studied[a]

| Model | $r^2$ | SE |
|---|---|---|
| Fractional power | 0.9806 | 0.03515 |
| Elovich | 0.9970 | 0.001471 |
| Pseudo-first order | 0.9827 | 0.09298 |
| Pseudo-second order | 0.9975 | 5.5637 |

[a]$r^2$ = correlation coefficient; SE = standard deviation.

## CONCLUSIONS

The Elovich and pseudo-second order kinetic equations provided a best-fit description for the sorption of copper(II) on to peat. Both the Elovich and pseudo-second order models were considered the most appropriate due to their high correlation coefficients relative to other kinetic models. The experimental results could also be represented approximately by two other simple equations, with the fractional power equation applying at the beginning of the experiment (first 15 min) and the first-order equation being satisfactory when saturation was approached (15–60 min).

Both the Elovich and pseudo-second order models provided excellent data-fitting based on the statistical correlation coefficients, but the Elovich correlation coefficient had the lowest SE value. However, the plots depicted in Figures 3 and 7 did not pass through the origin. Similarly, for the first-order plots depicted in Figures 5 and 6, the data for short contact times led to curved plots. A rate-limiting film or surface effect may possibly control the sorption at short time intervals. This effect may be a film diffusion-controlled process, wetting of the adsorbent or an initial enhanced surface sorption due to highly energetic heterogeneous sites on the peat surface. Further work is necessary to define this phenomenon.

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