

# SORPTION OF COPPER(II) FROM AQUEOUS SOLUTION BY PEAT

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**Abstract.** The use of peat for removal of copper(II) from aqueous solution has been investigated at various initial copper ion concentrations and masses of peat. The equilibrium sorption study can be described by the Langmuir equation and defined in terms of the operating lines for each batch contacting system. The mechanisms of the rate of sorption of copper(II) were analysed using the Elovich equation and a pseudo-second-order model. Both rate mechanisms provided a very high degree of correlation of the experimental sorption rate data suggesting either model could be used in design applications.

**Keywords:** copper, kinetics, peat, sorption

## 1. Introduction

Since copper is an essential metal in a number of enzymes for all forms of life, problems arise when it is deficient or in excess. However, the carcinogenic character of copper is accepted and epidemiological evidence, such as the higher incidence of cancer among coppersmiths, suggests a primary carcinogenic role for copper (Luckey and Venugopal, 1977). In addition, copper is phytotoxic and, indeed, has been used as an algicide to control algal blooms. It can, therefore, cause plant damage if, for example, it is present at too high a concentration in sewage sludge that is applied to agricultural land. There are many routes by which metals can enter the air, water and soil as a result of man's activities. A principal source of copper in industrial waste streams is metal cleaning and plating baths, and rinses, as brass, boiler pipe, cooking utensils, fertilizers, and from copper metal working, which requires periodic oxide removal by immersing the metal in strong acid baths. Solution adhering to the cleaned metal surface is rinsed from the metal and contaminates the waste rinse water. Similarly, plated metal parts are also rinsed and produce wastewater.

For humans, copper is an essential element and the body can regulate its level haemostatically, although large, acute doses can have harmful, even fatal, effects. There is evidence to suggest that copper may be carcinogenic. In addition, copper can cause damage to a variety of aquatic fauna (fish and invertebrates).

During the past 20 years, most research work on peat has been focused on metal and organic removal from industrial waste streams. Indeed, even earlier,



Ong and Swanson (1966) reported on the ability of peat to adsorb copper from solution. Still earlier, Coleman *et al.* (1956) reported formation constants for Cu(II)-peat complexes. Many types of peat and potential processes to remove copper ions have been proposed (Ho *et al.*, 1994). The sorption capacity of peat varies with the type of material being sorbed but because of its relatively low cost compared to other sorbents, it is believed that it will be able to compete successfully for particular applications (McKay *et al.*, 1978). However, the search for new commercial uses of peat has been gaining extensive attention in the area of pollution control. Several biosorbents have been used as materials to adsorb copper from wastes including coconut coir husk (Low *et al.*, 1995a,b), coir pith carbon (Namasivayam and Kadirvelu, 1997), agricultural byproducts (Marshall *et al.*, 1993) and chitosan (Findon *et al.*, 1993; Ngah *et al.*, 2002). Equilibrium studies on the use of peat to remove cadmium, copper, chromium, lead, mercury, nickel and zinc from a wide range of metal bearing wastewaters (Gosset *et al.*, 1986; Viraraghavan and Dronamraju, 1993; Allen *et al.*, 1992; Sharma and Forster, 1993; Ho *et al.*, 1995; Ho and McKay, 2000; Ho *et al.*, 2002).

In the present study the sorption of copper ions onto peat has been studied and a kinetic analysis has been developed and presented to establish the kinetic mechanism. The Elovich equation and pseudo-second-order equation have been compared and used to predict sorption rates.

## 2. Materials and Methods

The experiments were conducted with peat obtained from New Zealand. The peat as supplied, was dried at a temperature of  $105 \pm 5$  °C for 8 h and then screened using sieves to obtain a particle size 500–710  $\mu\text{m}$  peat.

The copper sulphate used in the experiments was supplied by Aldrich Chemicals. Stock solutions of copper(II) sulphate (analytical grade  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) ( $1 \text{ g/dm}^3$ ) were prepared in distilled water. All solutions used in this study were diluted with distilled water as required.

The pH of the initial solutions were buffered to 5.0 using sulphuric acid in order not to change the anion species. The effect of pH was not studied in the present work because peat is a natural buffer and the pH of all final solutions was  $4.2 \pm 0.2$  pH units.

Equilibrium isotherms were determined by shaking a fixed mass of peat (0.5 g) with 125 mL copper(II) solution in screw cap plastic bottle. A range of copper(II) concentrations were used. Shaking was carried out until equilibrium had been achieved. All contact investigations were carried out using a baffled agitated  $2 \text{ dm}^3$  sorber vessel (Figure 1). Samples 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 spectroscopy (ICP-AES).

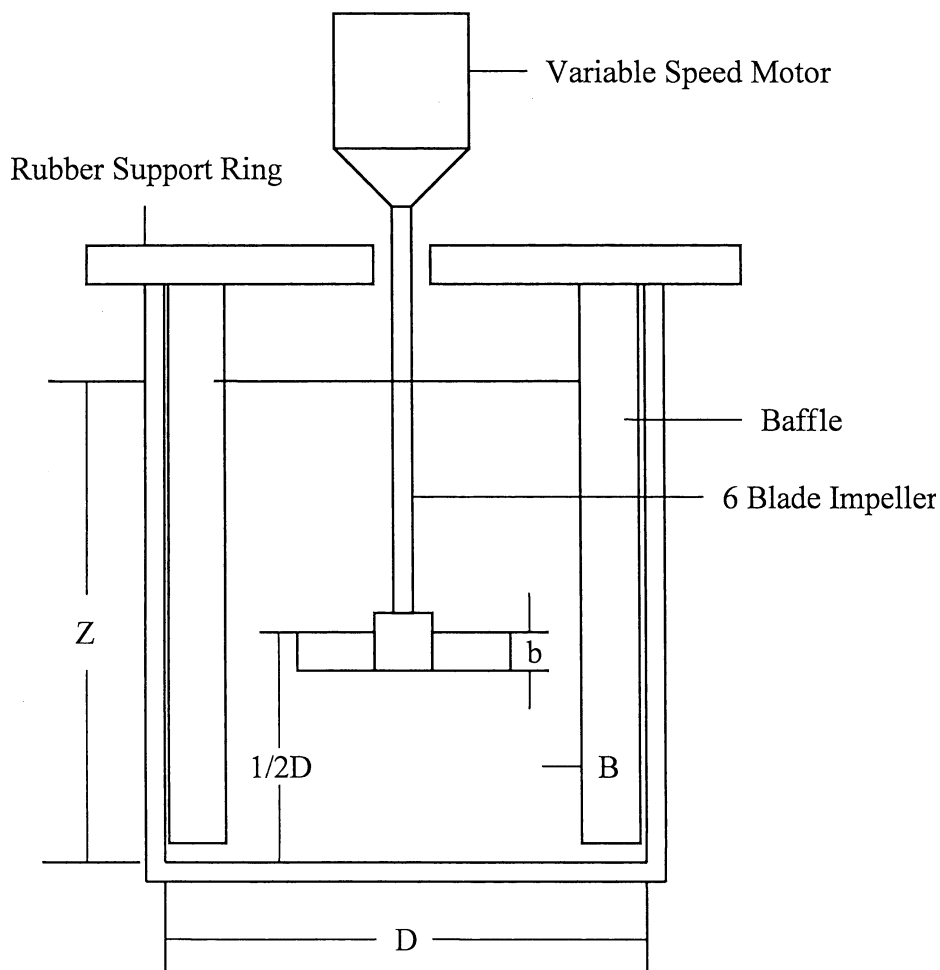


Figure 1. Schematic representation of sorber vessel.

The vessel contained  $1.7 \text{ dm}^3$  copper(II) solution and was designed to conform to specified standards (Furusawa and Smith, 1973, 1974) for agitated mixing vessels.

## 2.1. SORPTION DYNAMICS

### 2.1.1. Effect of Initial Concentration

A 6.8 g sample of peat ( $500\text{--}710 \mu\text{m}$ ) was added to each  $1.7 \text{ dm}^3$  volume of copper(II) solution. The initial concentrations of copper(II) solution tested were 0.643, 1.33, 1.56 and  $1.83 \text{ mmol/dm}^3$ .

### 2.1.2. *Effect of Different Peat Masses*

1.7 dm<sup>3</sup> volume of copper(II) solution (1.33 mmol/dm<sup>3</sup>) was used with masses of peat (500–710 μm) to be tested, namely, 3, 4, 5 and 6 g/dm<sup>3</sup>.

## 2.2. EQUILIBRIUM ISOTHERMS

Isotherm experiments were carried out at room temperature (20 ± 2 °C). The sorption isotherm was obtained by shaking various weights of the peat with particle size 500–710 μm with 125 dm<sup>3</sup> of copper(II) solution of known initial concentration in individual plastic bottles. The time to reach equilibrium was 3 h, and after this time the solution was filtered and analysed for concentrations.

## 3. Results and Discussion

Several steps can be used to express the mechanism of solute sorption onto a sorbent. To investigate the mechanism of copper sorption and the potential rate controlling steps, such as diffusion mass transport and chemical reaction processes, it is necessary to characterize the main sorption mechanisms. Diffusion processes can be controlled by film/external boundary layer diffusion, diffusion in the liquid-filled pores of adsorbents or surface diffusion of sorbed-soluble molecules that migrate along the surface of the adsorbent. The rate controlling mechanism may be one diffusional mass transfer resistance or a combination of two or three of these processes. However, peat is composed of several thousand different chemical species that could be involved in a wide range of mechanisms such as physical adsorption, ion exchange with several organic acids, chelation, lone pair electron sharing, chemical reaction with phenolic hydroxyls or other similar species. Due to this wide range of possible copper removal processes on peat we have used the general term 'sorption' throughout the paper. Diffusion-controlled physical sorption takes a long time, often several days or weeks. On the basis of the experimental results over 75% of the copper removal occurs within the first hour of contact with peat. On this basis, we have decided to analyse the data using kinetic models.

The Elovich equation was developed to describe the kinetics of chemisorption of a gas onto solids (Low, 1960), and its differential form is represented in Equation (1). The parameter  $\alpha$  represents the rate of chemisorption at zero coverage and the parameter  $\beta$  is related to the extent of surface coverage and the activation energy of chemisorption. The application of the Elovich equation is rapidly gaining popularity (Aharoni and Ungarish, 1976; Sparks, 1986). Taylor *et al.* (1995) successfully used the Elovich equation for the sorption of zinc ions onto soils and Juang and Chen (1997) studied the sorption kinetics of metal ions from sulphate solutions onto solvent impregnated resins. Other applications include work on radioisotopes (Mishra and Singh, 1995; Mishra *et al.*, 1996; Raouf and Daifullah, 1997).

The Elovich equation is generally expressed as:

$$dq_t/dt = \alpha \exp(-\beta q_t) \quad (1)$$

where  $q_t$  is the amount sorbed at time  $t$ , and  $\alpha$  and  $\beta$  are constants during any one experiment. The constant  $\alpha$  can be regarded as initial rate since  $dq_t/dt \rightarrow \alpha$  as  $q_t \rightarrow 0$ . Integration of Equation (1) assuming the initial boundary condition  $q_t = 0$  at  $t = 0$  gives

$$q_t = (1/\beta) \ln(1 + \alpha\beta t) \quad (2)$$

To simplify the Elovich equation, Chien and Clayton (1980) assumed  $\alpha\beta t \gg 1$  and applying the boundary conditions  $q_t = 0$  at  $t = 0$  and  $q_t = q_t$  at  $t = t$  then Equation (2) becomes (Sparks, 1986):

$$q_t = (1/\beta) \ln(\alpha\beta) + (1/\beta) \ln(t) \quad (3)$$

Thus, the constants can be obtained from the slope and intercept of the linearised plots of  $q_t$  against  $\ln(t)$ . Equation (3) will be used to test the applicability of the Elovich equation to the kinetics of copper(II) sorption in peat.

For the rate constant of the pseudo-second-order chemical sorption process:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \quad (4)$$

The concentrations are expressed in terms of copper sorbed on sorbent peat,  $q$ , and for a second-order process, the rate of copper sorption is expressed to the power of the sorbed copper loading difference to the power of two.

where  $q_e$  is the amount of copper(II) sorbed at equilibrium, (mmol/g);  $q_t$  is the amount of copper(II) sorbed at time  $t$ , (mmol/g) and  $k$  is the equilibrium rate constant of pseudo-second-order sorption, (g/mmol min). Assuming that  $q_t = 0$  at  $t = 0$ , the integrated form of Equation (4) becomes:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + kt \quad (5)$$

Equation (5) can be rearranged to obtain:

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

Equation (6) can be rearranged to obtain a linear form:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e} t \quad (7)$$

or

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

$h$  can be regarded as initial sorption rate since  $t \rightarrow 0$ , therefore:

$$h = kq_e^2 \quad (9)$$

then Equations (6) and (7) become:

$$q_t = \frac{t}{\frac{1}{h} + \frac{t}{q_e}} \quad (8)$$

and

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

Thus, a plot of  $t/q_t$  against  $t$  should give a linear relationship with the slope of  $1/q_e$  and intercept of  $1/h$  or  $1/kq_e^2$ .

### 3.1. EFFECT OF INITIAL CONCENTRATION

The experimental results of sorption of copper ions on peat at various concentrations are shown in Figure 2. It is apparent from Figure 2 that the amount of copper ions sorbed at equilibrium increases with an increase in initial sorbate concentration. The removal of copper increases by 34.8% from 0.132 to 0.178 mmol/dm<sup>3</sup> (Table I) by increasing the initial copper ions concentration from 0.643 to 1.83 mmol/dm<sup>3</sup> at 20 °C and pH 5. However, the percentage sorption decreases from 82.2 to 39.0% with an increase in the initial copper ions concentration from 0.643 to 1.83 mmol/dm<sup>3</sup>.

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 with high correlation coefficients (>0.990). Therefore it is further considered that  $q_e$ ,  $k$  and  $h$  can be expressed as a function of  $C_0$  as follows:

$$q_e = \frac{C_0}{4.55C_0 + 1.89} \quad (10)$$

$$k = \frac{C_0}{1.26C_0 - 0.468} \quad (11)$$

$$h = \frac{C_0}{32.2C_0 - 1.18} \quad (12)$$

TABLE I  
Parameters for effect of initial concentration

$C_0$	Pseudo-second-order equation					Elovich equation		
	$r^2$	$q_e$	$R_e$	$k$	$h$	$r^2$	$\alpha$	$\beta$
0.643	0.999	0.132	82.2	1.87	$3.26 \times 10^{-2}$	0.993	0.188	49.5
1.33	0.998	0.171	51.4	1.07	$3.13 \times 10^{-2}$	0.998	0.117	33.9
1.56	0.997	0.172	44.3	1.12	$3.33 \times 10^{-2}$	0.999	0.150	35.6
1.83	0.997	0.178	39.0	0.973	$3.10 \times 10^{-2}$	0.996	0.115	32.6

$C_0$ : mmol/dm<sup>3</sup>;  $q_e$ : mmol/g;  $k$ : g/mmol min;  $h$ : mmol/g min;  $R_e$ : %.

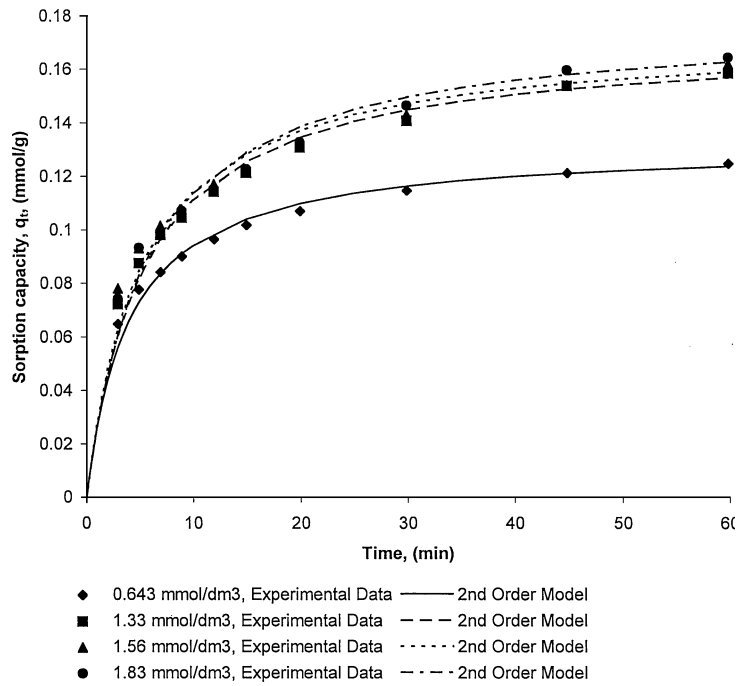


Figure 2. Effect of initial concentration on the sorption of copper ions onto peat.

Substituting the values of  $q_e$  and  $h$  from Equations (10) and (12) into Equation (8), the rate law for a pseudo-second-order reaction and the relationship of  $q_t$ ,  $C_0$  and  $t$  can be represented as:

$$q_t = \frac{C_0 t}{32.2C_0 - 1.18 + (4.55C_0 + 1.89)t} \quad (13)$$

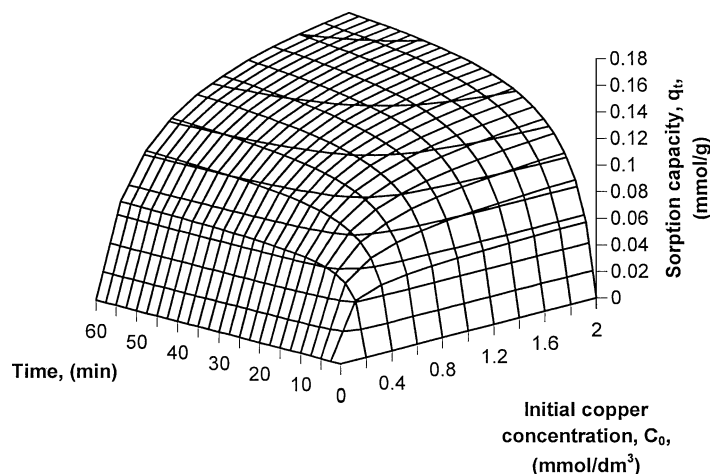


Figure 3. Effect of initial concentration on copper sorption at various reaction times.

Equation (13) represents the generalised predictive model for copper(II) sorbed at any contact time and initial copper(II) concentration within the given range of parameters. It indicates that the copper(II) sorbed at any contact time increases for greater initial copper(II) concentrations. This is obvious, since at for higher  $C_0$  values, a more efficient utilisation of the sorptive capacity of the sorbent is expected due to greater driving force.

This equation can then be used to derive the amount of copper(II) sorbed at any given copper(II) concentration and the reaction time. The three-dimensional plot of the Equation (13) is shown in Figure 3.

A simple kinetic analysis of sorption on peat has been tested according to the Elovich equation. Figure 4 shows a plot of Equation (3) for the sorption of copper ions with peat. The results demonstrate a highly significant linear relationship between copper(II) sorbed,  $q_t$ , and  $\ln(t)$  in these studies with high correlation coefficients ( $>0.993$ ). The linear correlation coefficients are highly significant. Chien and Clayton (1980) suggest that a simple Elovich equation may be used to describe the kinetics of sorption while a simple first-order kinetic reaction fails. Whereas a plot of Equation (7) for the same data is shown in Figure 5. The agreement between the sets of data reflect the extremely high correlation coefficients obtained and shown in Table I. In other words, the data also show good compliance with the proposed pseudo-second-order equation. Indeed, the regression coefficients for the linear plots were better than 0.997.

### 3.2. EFFECT OF PEAT DOSE

The effect of varying the peat dose,  $m_s$ , using an initial copper(II) concentration of  $1.33 \text{ mmol/dm}^3$  at  $20^\circ\text{C}$  and pH 5 is summarized in Figure 6. Table II shows that



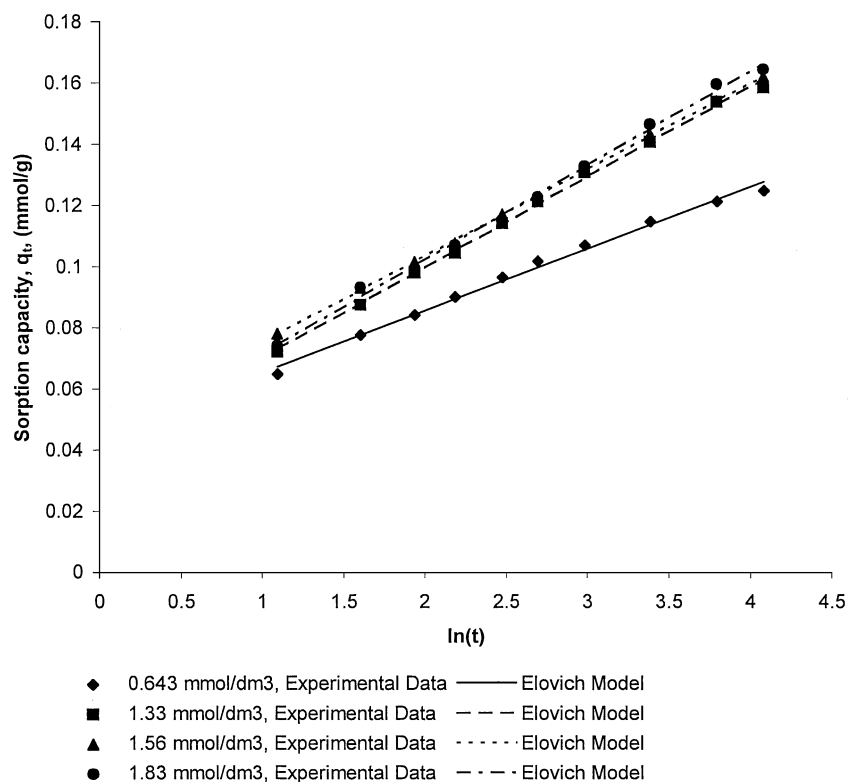


Figure 4. Plot of Elovich equation for sorption of copper ions onto peat at various initial concentrations.

the removal increased from 41.2 to 59.0% with the peat dose from 3 to 6 g/dm<sup>3</sup>. This is to be expected because, for a fixed initial solute concentration, increasing total sorbent doses provides a greater surface area (or sorption sites), although the specific sorption capacity decreased from 0.185 to 0.129 mmol/g of peat when the doses were increased from 3 to 6 g/dm<sup>3</sup>, as shown in Figure 6.

TABLE II  
Parameters for effect of peat dose

$m_s$	Pseudo-second-order equation					Elovich equation		
	$r^2$	$q_e$	$R_e$	$k$	$H$	$r^2$	$\alpha$	$\beta$
3	0.994	0.185	41.2	0.725	$2.48 \times 10^{-2}$	0.996	0.0753	29.5
4	0.998	0.171	51.4	1.07	$3.13 \times 10^{-2}$	0.998	0.117	33.9
5	0.999	0.159	57.2	1.30	$3.30 \times 10^{-2}$	0.997	0.147	38.4
6	0.998	0.129	59.0	1.55	$2.57 \times 10^{-2}$	0.999	0.112	47.1

$m_s$ : g/dm<sup>3</sup>;  $q_e$ : mmol/g;  $k$ : g/mmol min;  $h$ : mmol/g min;  $R_e$ : %.

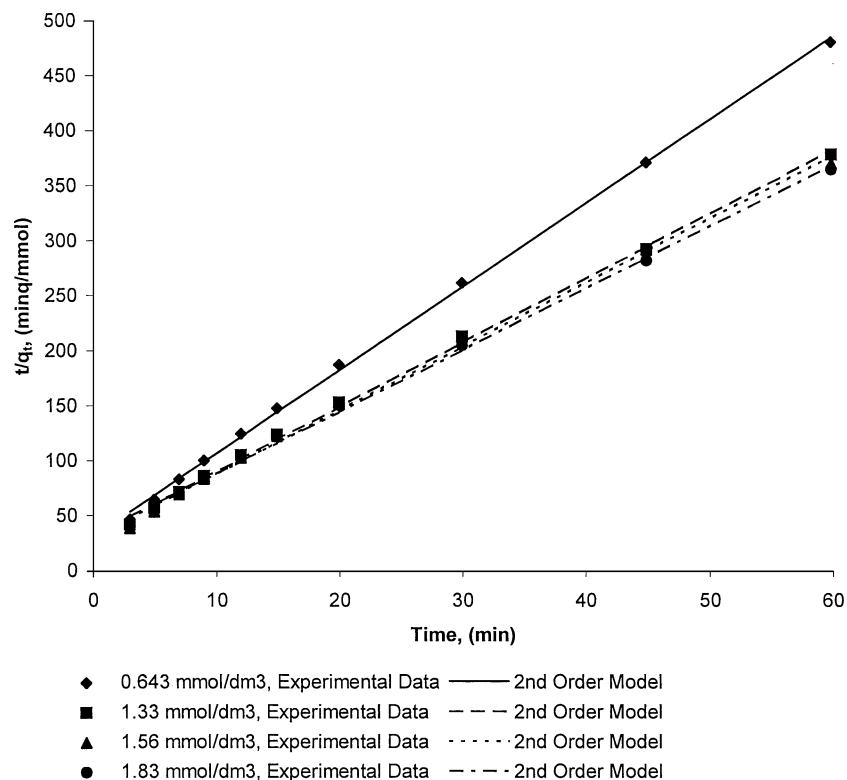


Figure 5. Pseudo-second order sorption kinetics of copper ions onto peat at various initial concentrations.

Figure 7 shows the linearised form of the pseudo-second-order model for the sorption of copper(II) onto peat. The correlation coefficients,  $r^2$ , and the pseudo-second-order rate parameters are shown in Table II. The data show a good compliance with the pseudo-second-order equation and the regression coefficients for the linear plots were higher than 0.994 for all the systems in these studies. The results are also shown in Figure 8 as a plot of  $q_t$  against  $\ln(t)$  for sorption of copper(II) for the Elovich equation. The correlation coefficients,  $r^2$ , the Elovich equation parameters  $\alpha$  and  $\beta$ , are shown in Table II. The values of  $r^2$  for both of the pseudo-second-order and the Elovich equation are all extremely high ( $>0.994$ ). For the sorption of copper(II) the results can be well represented by both the pseudo-second-order and the Elovich model. The kinetics of chemisorption have been inadequately represented in the literature by the second-order equation and the Elovich Equation (Ungarish and Aharoni, 1981).

On the basis of the excellent fits of both the pseudo-second-order and Elovich correlations, it is possible to propose some potential mechanistic steps. Due to the correlation of the experimental results with the pseudo-second-order model the main sorption mechanism is probably a chemisorption reaction with the predominant

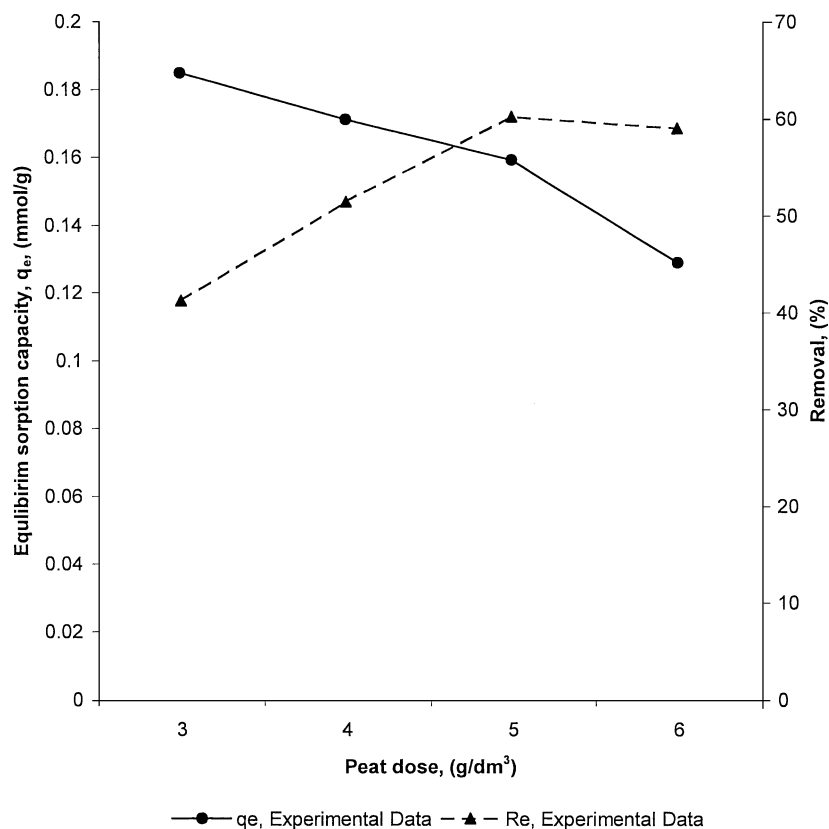


Figure 6. Variation of sorption capacity and percent copper(II) removal against peat dose.

humic acid carboxylic groups:



The Elovich correlation has proved useful for more heterogenous systems and surfaces. Peat is indeed a complex myriad of chemical systems, several of which could participate in metal ion sorption. For example, the weaker carboxylic acid group in fulvic acid:



Small amounts of amino groups and phenolic hydroxyls could provide lone pairs of electrons for chelating copper ions. Peat is a complex material containing mainly organic residues such as lignin, chelating and cork-like tissues, which are the main constituents of plants. Other compounds present include resins, waxes, proteins and

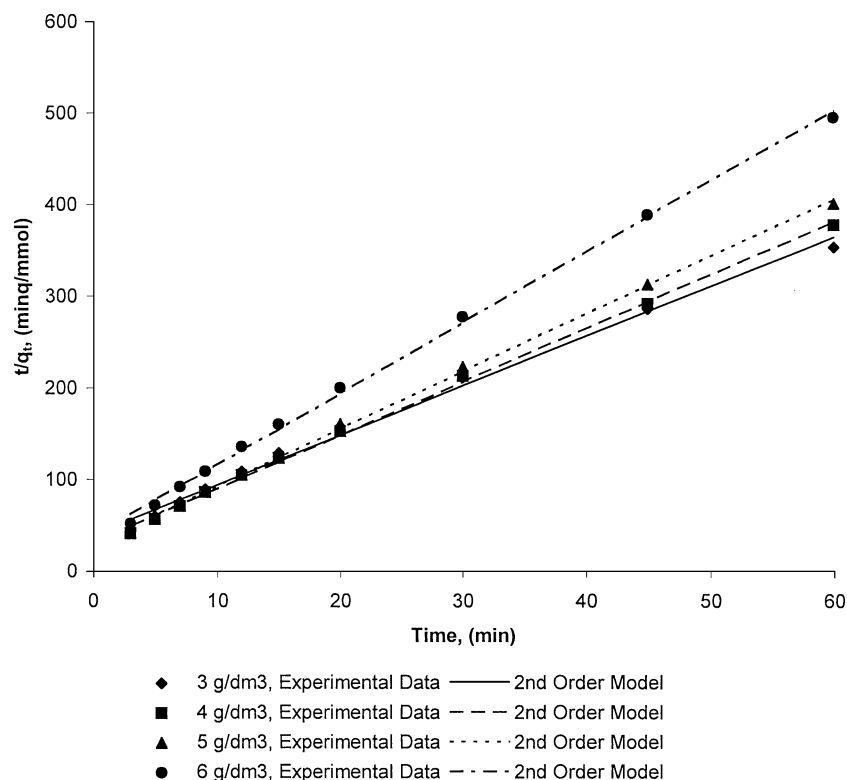


Figure 7. Pseudo-second order sorption kinetics of copper ions onto peat at various peat doses.

dyes. Chemisorption can occur by the polar functional groups of lignin, which include alcohols, aldehydes, ketones, acids, phenolic hydroxyls and ethers as potential chemical bonding agents. Because of this polar character, the adsorption/exchange capacity of peat for metal ions and polar organic molecules is potentially very high. According to Asplund *et al.* (1972) peat has an extensive surface area ( $>200 \text{ m}^2/\text{g}$ ) and is extremely porous (95%). Poots and McKay (1979) measured the specific surface of peat moss using a variety of methods and obtained values of  $27 \text{ m}^2/\text{g}$  using nitrogen BET,  $11.8 \text{ m}^2/\text{g}$  using an acid blue dye and  $100 \text{ m}^2/\text{g}$  using a basic dye. These data demonstrate the presence of negatively charged molecules associated with the polar functional groups of peat as well as the exchange sorption occurring with the hydrogen ions. Peat particles are surface active and have a high-cation exchange capacity (Trujillo *et al.*, 1991). Many characteristics influence the sorption/exchange capacity of peat materials including organic matter, particularly humic and fulvic acids (Ravichandran *et al.*, 1988) and interactions and complexation reactions between copper and the peat organic matter (Buffle, 1998).

On the basis of the very complex chemical nature of peat it is not surprising that both kinetic models show a high degree of correlation for the sorption results of copper onto peat.

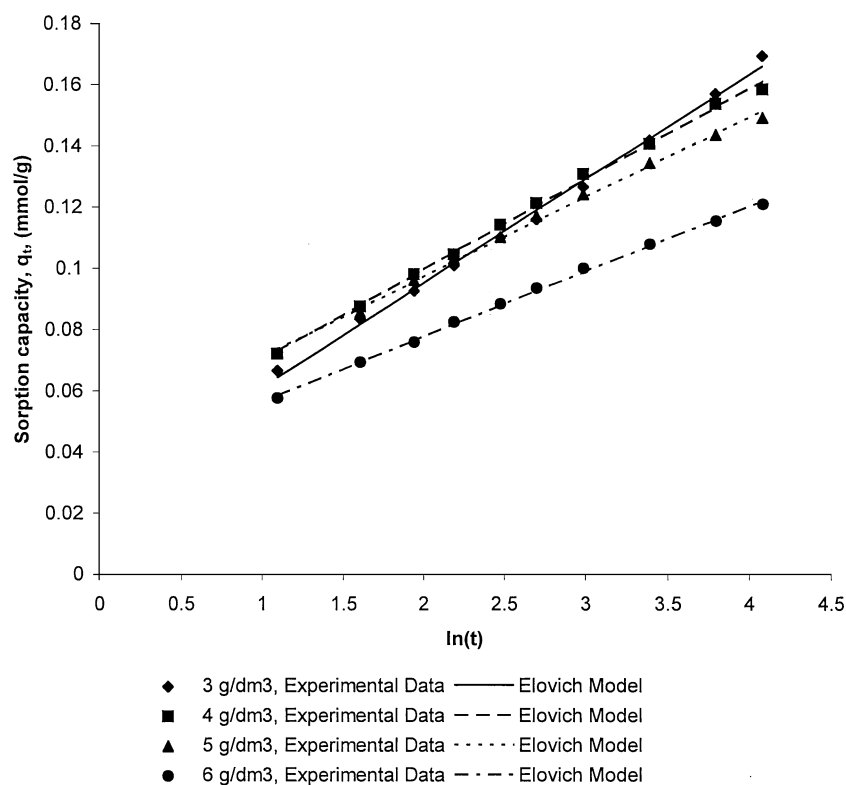


Figure 8. Plot of Elovich equation for sorption of copper ions onto peat at various peat doses.

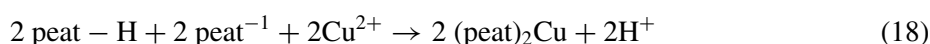
However, the diversity of peat makes its chemistry more versatile than most other adsorbents (Al-Degs *et al.*, 2000; Boehm, 2002; Strelko and Malik, 2002) containing several functional groups, such as, humic carboxylic, fulvic carboxylic and phenolic are considered to be the three major ones. The roles and exchange potentials of the humic acid group has been discussed and used in the modification of clays for adsorption (Zhou *et al.*, 1994; Vinod and Anirudhan, 2003; Huang and Yang, 1995). Active carbon surfaces usually exhibit surface basicity (Moreno-Castilla *et al.*, 1997) due to the reaction type (Abbotsi and Scaroni, 1990).



For peat, it is expected that its surface chemistry will be dominated by surface acidity dissociation reactions of the type (Strelko and Malik, 2002; Corapcioglu and Huang, 1987).



Many authors (Boyd *et al.*, 1981; da Silva *et al.*, 2002) support the concept that copper reacts with humic acid by chelate ring formation involving adjacent aromatic carboxylate COOH and phenolic OH groups, which participate in ion exchange reactions described by Equations (13), (14), (16) and (17) with the release of H<sup>+</sup>. The mechanism of the peat reaction with metal ions is the subject of extensive discussion. Aho and Tummavouri (1984), Bunzl *et al.* (1976) and Kadlec and Keolian (1986) developed models based on these ion exchange only type sorption reactions. Other authors (Gangiotti *et al.*, 1984; Gossett *et al.*, 1986; Ringqvist and Oborn, 2002) provided evidence for copper fixing by complexation in addition to ion exchange. The global scheme involved two copper ions interacting with peat as shown:



in which  $\text{peat}^{-1}$  is a complexing site.

Structural studies (Averett *et al.*, 1994; Francioso *et al.*, 1996; Spark *et al.*, 1997; Leenheer *et al.*, 1998) using a range of techniques including FT-IR, Raman and NMR, supported the evidence for a metal ion complex involving the carboxylic acid group in the humic and fulvic acids. Furthermore, the authors concluded that there was an innersphere complex of the metal binding fraction and that an outersphere binding complex was also formed.

Therefore, although the pseudo-second-order and the more heterogeneous based Elovich kinetic models both provide excellent model fits for the metal ion concentration versus time decay curve, the myriad of kinetic processes is much more complex in reality.

### 3.3. SORPTION ISOTHERMS

An isotherm is shown in Figure 9 for the sorption of copper(II) onto peat at room temperature. The graph is plotted in the form of copper(II) sorbed per unit mass of peat,  $q_e$ , against the concentration of copper(II) remaining in solution,  $C_e$ , with the Langmuir equation. The correlation coefficient was 1.00. The equilibrium sorption of copper,  $X_m$ , and constant,  $a_L$ , were determined from slope and intercept of the Langmuir equation and found to be 0.199 mmol/g and 23.4 dm<sup>3</sup>/mmol, respectively. Figure 9 also shows experimental data with the operating line which is generated with a slope of solution volume/peat mass. The final solution concentration is predicted from the point of intersection of operating line on the sorption isotherm, for the sorption of copper(II). It is therefore an operating line in general form and can be expressed as follows:

$$q_m = \frac{C_0 - C_e}{m_s} \quad (19)$$

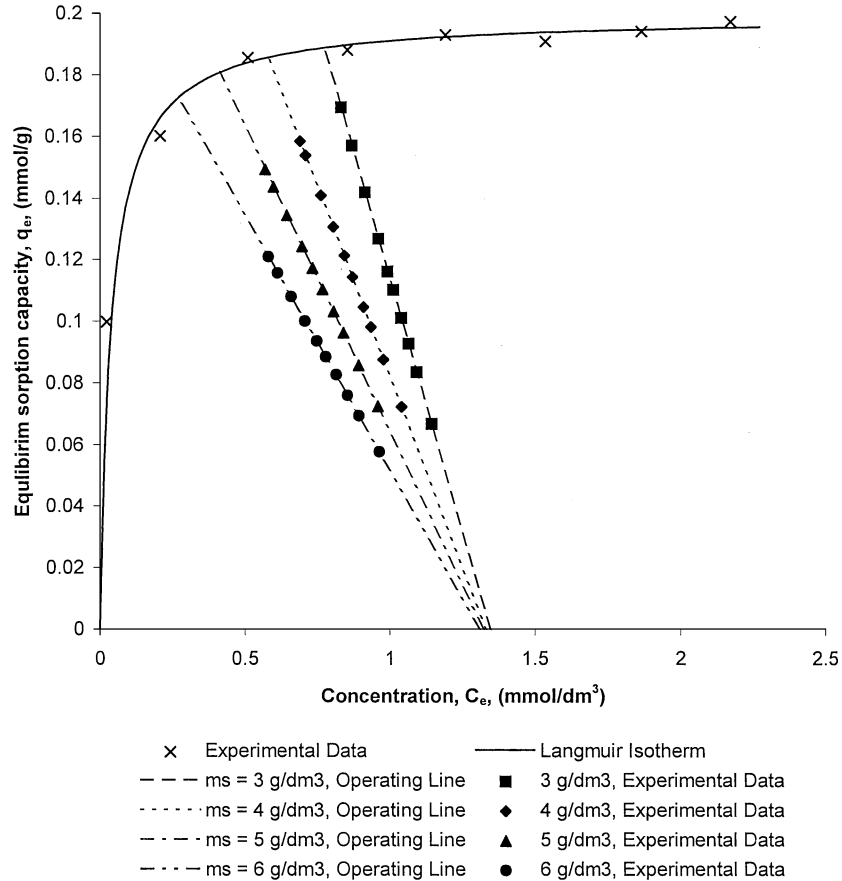


Figure 9. Langmuir isotherm for the sorption of copper of peat mass.

The equilibrium sorption capacity,  $q_m$ , can be obtained from the operating line and the Langmuir equation (Figure 9). The results are in reasonable agreement with the equilibrium sorption capacity,  $q_e$ , which is obtained from the pseudo-second-order model. A comparison is made between the equilibrium sorption capacity evaluated from Langmuir equation and the pseudo-second-order model in Table III, which shows that both equilibrium sorption capacities evaluated are reasonable in all cases except for the low  $m_s$  value of  $3 \text{ g/dm}^3$ .

A comparison was also measured at various initial concentrations. The Langmuir isotherms are shown in Figure 10 with the process operating lines. The equilibrium sorption capacity can be obtained from the operating line and the Langmuir equation. A comparison is made between the equilibrium sorption capacity evaluated from Langmuir equation and the pseudo-second-order model in Table IV, which shows both equilibrium sorption capacity evaluated are reasonable in all cases.

The sorption capacities of copper ions from aqueous systems onto various sorbents are compared in Table V for 16 studies. These are compared with the value

TABLE III  
Comparison of the equilibrium sorption capacity evaluated from Langmuir equation and the pseudo-second-order model

$m_s$ (g/dm <sup>3</sup> )	$q_m$ (mmol/g)	$q_e$ (mmol/g)
3	0.189	0.139
4	0.186	0.171
5	0.181	0.199
6	0.172	0.194

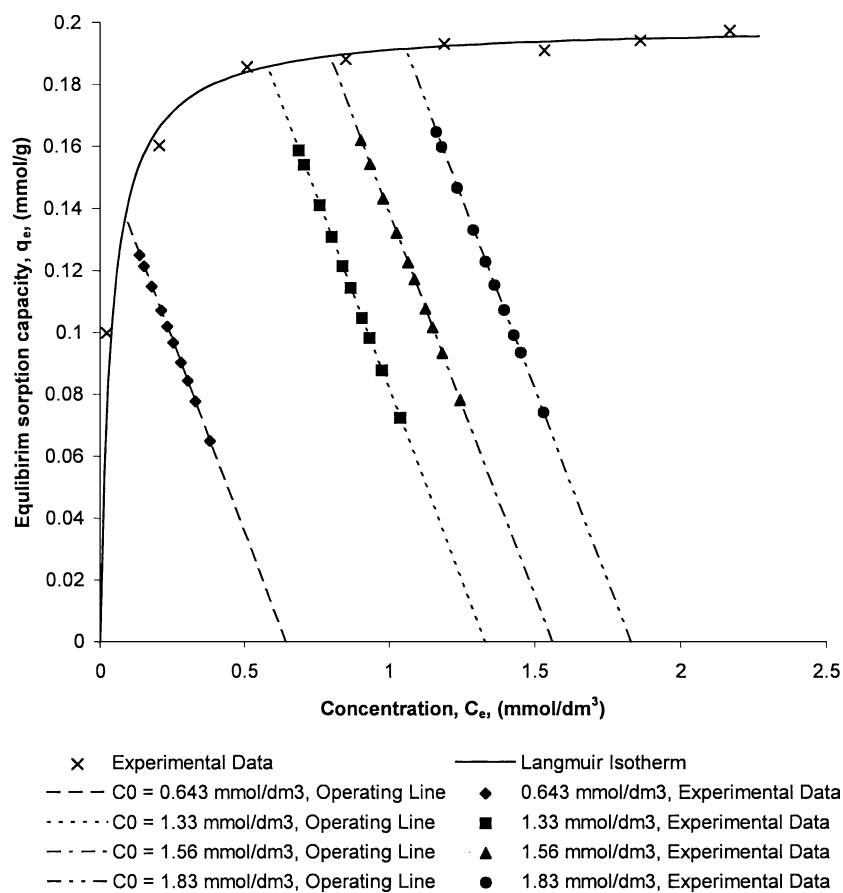


Figure 10. Langmuir isotherm for the sorption of copper of initial copper concentration.

of 12.6 mg Cu ions/g peat reported in the present study. Over 50 papers have been published in the 1990s on the specific topic of copper sorption, these can be summarized. A wide range of capacities for copper ions sorption is observed. In general for sorption capacities of greater than 30 mg Cu ions/g peat the material has been



TABLE IV

Comparison of the equilibrium sorption capacity evaluated from Langmuir equation and the pseudo-second-order model

$C_0$ (mmol/dm <sup>3</sup> )	$q_m$ (mmol/g)	$q_e$ (mmol/g)
0.643	0.137	0.132
1.33	0.186	0.171
1.56	0.189	0.173
1.83	0.191	0.178

TABLE V

Maximum sorption capacities,  $q_{max}$ , of Copper(II) onto various sorbents

$q_{max}$ (mg/g)	Material	Reference	pH	Temp (°C)
227	Coconut coir activated	Baes <i>et al.</i> , 1996	6.0	25
84.0	Chitosan	Yoshida <i>et al.</i> , 1995		25
65.6	Peanut hull carbon	Periasamy and Namasiyayam, 1996	5.0	30
52.3	Activated sludge	Sag and Kutsal, 1995	4.0	45
19.6	Eutrophic peat	Chen <i>et al.</i> , 1990	4.0	25
19.1	Cottonseed hull carbon	Marshall and Champagne, 1995	2–5	25
16.5	Acid-treated peat	Bunzl <i>et al.</i> , 1976		25
13.5	Banana pith carbon	Low <i>et al.</i> , 1995		
12.6	Sphagnum peat moss	Present work, 2004	5	25
12.1	Oligotrophic peat	Gossett <i>et al.</i> , 1986	4–5	25
9.22	Activated carbon	Ferro-Garcia <i>et al.</i> , 1998		20
5.90	Lignite carbon	Allen <i>et al.</i> , 1992	5	20
3.60	Granular active carbon	Periasamy and Namasiyayam, 1996	5	25
3.07	Coconut husk	Low <i>et al.</i> , 1995		20
2.56	Lignite	Allen <i>et al.</i> , 1997		25
2.0	Palmfibre	Low <i>et al.</i> , 1993		20
1.74	Sawdust	Vaishya and Prasad, 1991	7.3	25
1.38	Fly ash	Panday <i>et al.</i> , 1985		
0.79	<i>Aspergillus oryzae</i>	Huang and Huang, 1996		

acid treated. For the eutrophic sphagnum moss peats, the capacities are mostly in the range of 10–30 mg/g, whereas the oligotrophic peats are mostly 1–15 mg/g. Activated carbons generally show a relatively low-sorption capacity, around 10 mg/g, although a peanut hull based activated carbon has a capacity of 65.6 mg/g. Table V indicates that a number of hulls have been used directly for copper removal including soya bean, cotton seed and coconut husk with wide range of copper sorption capacities of 38.8, 19.1 and 3.1, respectively. Several natural biosorbents having a

significant cellulose structure have been tested, namely coconut coir, oil palm fibre, banana pith, lignite and sawdust and have the following coppers sorption capacities 227, 2.0, 13.5, 2.6 and 1.7, respectively. The capacity of 227 mg Cu/g using coconut coir is the highest reported literature sorption capacity for copper. A wide variety of microbial biomasses and treated biomasses have been used for copper sorption.

#### 4. Conclusion

The ability of peat to sorb copper ion has been studied. The sorption capacity at 20 °C and the value of pH 5 was 0.199 mmol/g. This capacity of 12.6 mg Cu(II)/g peat compares very well with many capacities reported in the literature. All the materials in Table V with a higher copper sorption capacity are processed sorbents requiring heat and chemicals. Consequently peat is 5–10% the cost of these materials. The Langmuir isotherm could be correlated to the experimental data over the studied concentration ranges. For the kinetic sorption studies of copper(II) in an agitated sorber vessel the results can be represented well by both the pseudo-second-order and the Elovich model. Due to the high correlation coefficients obtained by using the Elovich and the pseudo-second-order kinetic model, it is difficult to conclude which sorption mechanism is actually occurring and is responsible for the ability of peat to sorb copper ions.

Due to the large array of chemical species present in peat moss, which are capable of cation exchange with copper ions, it seems likely that copper ions can exchange with more than one species. The two most likely exchange reactions are copper ions exchanging with hydrogen ions in the humic and fulvic acids present. Consequently, a heterogeneous kinetic model, such as the Elovich equation, seems the most appropriate model for the sorption of copper ions onto sphagnum peat moss.

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