THE ADSORPTION OF DIVALENT COPPER IONS FROM AQUEOUS SOLUTION BY SPHAGNUM MOSS PEAT

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The adsorption of copper from aqueous solution was studied using Irish sphagnum moss peat. The process was found to be pH dependent, the optimum range being 4.0 to 5.0. Langmuir and Freundlich isotherms were found at different initial copper concentrations and pH values. Based on these data, an expression has been derived which enables the removal to be calculated for any initial concentration and pH value. The maximum adsorption capacity for sphagnum moss peat was found to be 16.4 mg/g of peat. This occurred (at 25°C) when the peat dose was 4 g/l and the initial adjusted pH was 5.0. The kinetics of the adsorption were also examined and, using a peat dose of 20 g/l and a pH of 5.0, were found to confirm a model which has been used previously to describe metal adsorptions by peat. An expression relating the removal efficiency to the dosage of peat, at pH 5, is also described.

Keywords: peat; copper; adsorption; Langmuir; Freundlich.

INTRODUCTION

Copper is a biological poison. For humans, acute exposure to large doses can be harmful. As such, the maximum acceptable concentration in drinking water, as specified in the Water Supply (Water Quality) Regulations 1989, is 3 µg/l. Legislation also imposes limits to protect other species—for example, 200 µg/l in fresh water being used for watering livestock and ≤112 µg/l (depending on the hardness) in waters being used for fisheries. Copper is also a phytotoxin and control must be exercised in any dissemination of copper to land to prevent plant damage. In the United Kingdom, the consumption of copper in 1991 was of the order of 270,000 tonnes[1]. There are many industrial sources of copper pollution, the main ones being electroplating, iron and steel production, agricultural operations and fertilizer manufacturing[1,2]. There are technologies which can be used to reduce aqueous copper emissions. Some of these are relatively standard processes such as lime precipitation, ion exchange and adsorption onto activated carbon[2]. However, there has been considerable interest in the use of, if not novel processes, then certainly novel materials. Fly ash, for example, has been used successfully as an adsorbent for cupric ions[3,4]. The use of natural products as adsorbents has also been examined. These include moss[5,6], agricultural wastes[7] and peat[8,9]. Most of this work has shown that natural products can be good sorbents for heavy metals and that peat, in particular, has excellent ion exchange properties[6]. Indeed, it could be argued that many of these natural adsorbents remove metals more by ion exchange than by adsorption. Nevertheless, many previous workers tend to base their analyses on adsorption theories. The previous work with peat[8,9] has used relatively high doses (> 30 g/l) and the Langmuir constants reported by these works were not totally compatible with one another. This current paper, therefore, re-examines the use of peat as an adsorbent of copper from aqueous solutions and reports not only adsorption isotherm data but also how pH changes and the dosage of peat affects the adsorption.

METHODS AND MATERIALS

Materials

Sphagnum moss peat, which is commercially available in Britain and Ireland and has an average cost for a standard pack (50 l) of £5.00, was used. The raw peat was dried in an oven for 24 hours at 105°C, and then screened through a 14 mesh sieve (B.S. 410/43) to remove any large non-peat solids. This was done to produce a uniform material for the complete set of absorption tests.

Analytical grade reagents were used in all cases. A stock copper(II) solution (1000 mg/l) was prepared in distilled water using copper sulphate. All working solutions were prepared by diluting the stock solution with distilled water. The pH adjustments were made with sulphuric acid or sodium hydroxide solutions.

Analysis and Procedures

The concentrations of copper(II) were measured by acetylene-air atomic adsorption spectrophotometry (Instrumentation Laboratory aa/ae spectrophotometer 751) with single element hollow cathode lamps.

Batch sorption experiments were conducted in a constant temperature room at 25°C on a rotary shaker at 100 rmp using capped 500 ml conical flasks. In the
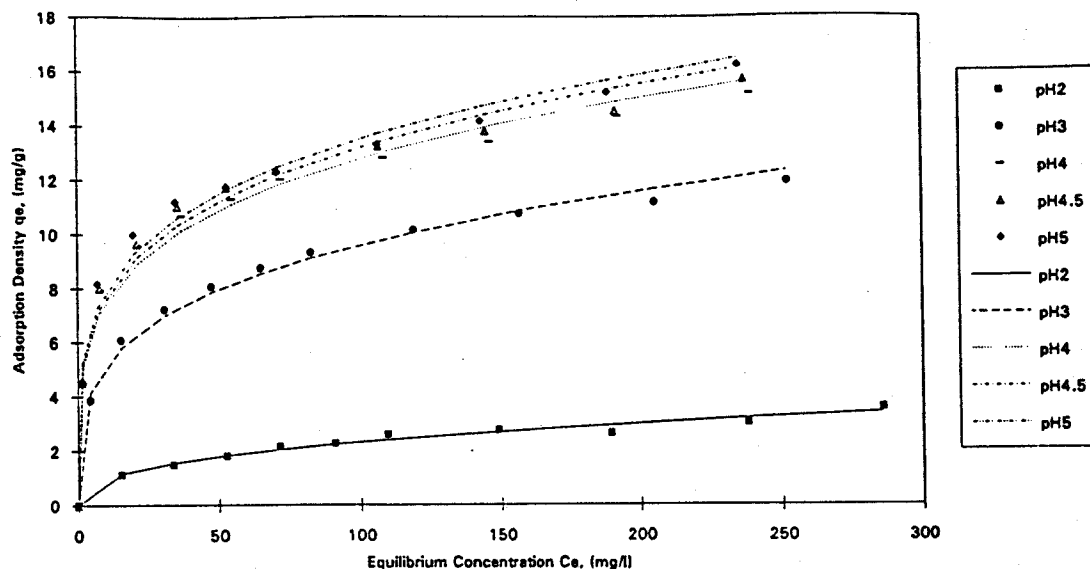
Figure 1. Typical adsorption curves at different pH_{in}.

adsorption isotherm tests, one gram of peat was thoroughly mixed with 250 ml copper(II) solution. The initial pH adjustments were carried out, either by sulphuric acid or aqueous sodium hydroxide, and recorded as pH_{in}. Five different runs at pH_{in} 2.00, 3.00, 4.00, 4.50 and 5.00 were performed, varying the initial copper(II) concentration (C_0) from 20 mg/l to 300 mg/l. The pH values were selected on the basis of results reported previously, of the requirement that no precipitation of copper should occur and of what was considered to be typical of an industrial effluent[6,10,11]. After shaking the flasks for 15 hours, the reaction mixtures were filtered (Whatman No. 1) and the filtrate was analysed for pH, recorded as pH_{fin}, and the concentration of copper(II).

In the sorption kinetic experiments, five grams of peat were thoroughly mixed with 250 ml copper(II) solution (1000 mg/l). The peat suspensions were shaken for two hours at a constant temperature of 25°C and 2 ml samples were collected and filtered through a 0.45 μm membrane filter every 3 mins for the first 15 mins, every 5 mins for the next 15 mins, every 10 mins for the next half hour and every 15 mins for the last hour. The filtrates were analysed using atomic absorption spectrophotometry. The effect of sorbent dose was carried out with an initial copper(II) concentration (C_0) of 200 mg/l at pH_{in} 5.00, while varying the peat dose (W_p) from 4.00 g/l to 40.0 g/l.

RESULTS AND DISCUSSION

Sorption Equilibria

Two important physicochemical aspects for the evaluation of the sorption process as a unit operation are the equilibria of the sorption and the kinetics. Sorption equilibrium is established when the concentration of metal in the bulk solution is in dynamic balance with that of the interface. Figure 1 shows typical isotherms for the copper-peat system. It is generally seen that the adsorption density (q_e) increases gradually

with increasing solution pH (pH_{in}). The results show that for increasing equilibrium copper concentration, the adsorption density increased very little at pH 2.00. At pH 3.00 the increase was slightly greater, but the most significant increase was found in the pH range 4.00 to 5.00. For all cases, the greatest increase occurred at the lower copper concentrations.

Adsorption Isotherms

Equilibrium relationships between adsorbent and adsorbate are described by adsorption isotherms, the most common of which are the Langmuir and Freundlich isotherms. However, they are usually unsatisfactory when applied to systems where true ion exchange is involved[10], although the Langmuir isotherm has been used to simulate some ion exchange reactions and the Freundlich isotherm for complexation reactions in saturation-type reactions[8].

Langmuir Isotherms

The adsorption data were analysed according to the linear form of the Langmuir isotherm. The isotherms were found to be linear over the whole concentration range and the correlation coefficients (r^2) were found to be between 0.963 and 0.994 (Table 1). These values for the correlation coefficients indicate that there is a strong

Table 1. Adsorption isotherm constants of copper-peat binding.

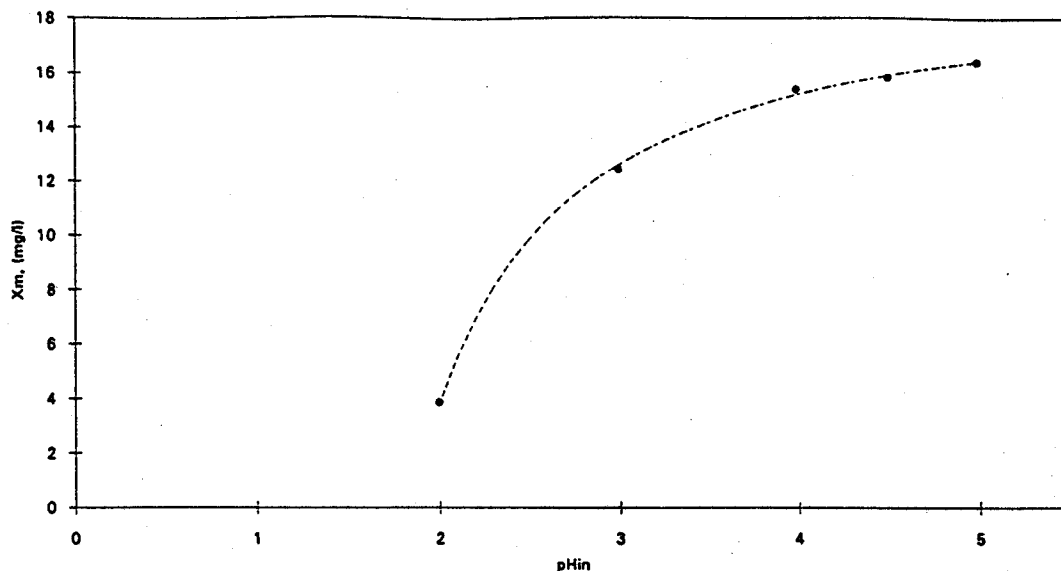|	Langmuir constants			Freundlich constants		
	Corr Coeff r^2	X_m (mg/g)	k (l/mg)	Corr Coeff r^2	K_F (mg/g)	$1/n$
2.00	0.963	3.85	0.0175	0.973	0.415	0.371
3.00	0.994	12.4	0.0455	0.987	2.74	0.271
4.00	0.993	15.4	0.0691	0.964	4.34	0.234
4.50	0.993	15.8	0.0708	0.965	4.41	0.237
5.00	0.990	16.4	0.0662	0.965	4.58	0.235

Figure 2. Variation of X_m against pH_{in}.

positive relationship for the data and that the copper-peat adsorption data follows the Langmuir model of adsorption.

The Langmuir constants are also shown in Table 1 and it can be seen that the maximum adsorption capacity (X_m) increases with increasing solution pH values. The higher values of adsorption capacity were found to be 15.4, 15.8 and 16.4 mg/g of peat. These occurred at initial adjusted pH values of 4.00, 4.50 and 5.00. When the pH was adjusted to 2.00, the adsorption capacity was reduced to a value as low as 3.85 mg/g. This could well imply that ion exchange is playing a significant role since the carboxylic acid groups in weakly acidic exchanges would effectively cease to be dissociated at this low pH. However, the high values of the correlation coefficients suggest that the process which is occurring is not true ion exchange[12]. The variations of the Langmuir constant (X_m) in relation to the adjusted pH are shown in Figure 2. Over the pH range

that was examined, the relationship had a correlation coefficient of 0.999 and can be expressed as:

$$X_m = \frac{pH_{in} - 1.84}{3.39 \times 10^{-2} + 5.02 \times 10^{-2}\,(pH_{in} - 1.84)}$$

The Langmuir constant (k), which is a measure of adsorption energy, also increased with increasing solution pH values. Again, the higher values of the Langmuir constant k were found to be at initial adjusted pH values of 4.00, 4.50 and 5.00. The variation of the Langmuir constant (k) against adjusted pH is shown in Figure 3. Thus, within the pH_{in} range of 2.0 to 5.0, the relationship had a correlation coefficient of 0.966 and can be expressed as:

$$k = \frac{pH_{in} - 1.99}{6.92 + 12.3\,(pH_{in} - 1.88)}$$

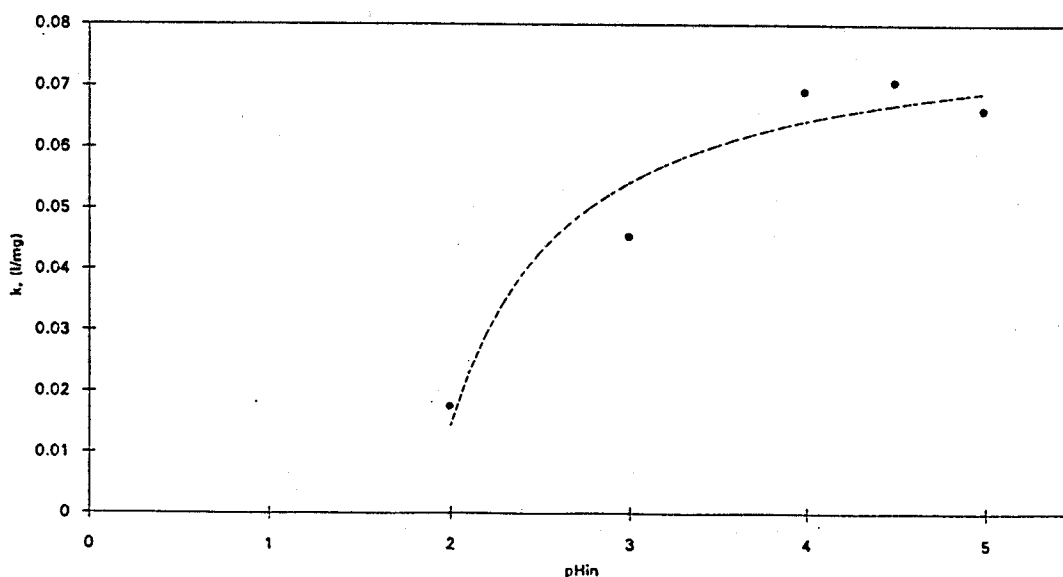These two relationships, therefore, provide a tech-

Figure 3. Variation of k against pH_{in}.

Table 2. Maximum capacities for the adsorption of copper by peat.

Maximum capacity (mg/g)	X_M (mg/g)	pH	Peat dose (g/l)	Material	Reference
22.0	—	5	—	Peat	13
10.0	—	4.5	50	Peat*	10
16.5	—	3.5–4.5	0.5	Peat*	14
> 52.4	—	4.2	(a)	Peat*	15
> 17.5	—	4.2	(a)	Peat	15
61.9	—	—	—	Peat*	16
25.4	—	—	—	Peat	16
5.1	—	3	26.6	Peat	17
6.4	—	—	(a)	Peat	17
2.6	—	—	—	Peat	18
38.7	—	4.5	40	Peat*	11
12.7	—	4.9	(a)	Moss peat[b]	19
20.0	—	4.9	(a)	Moss peat[c]	19
12.1	—	—	50	Eutrophic peat	9
12.1	—	—	50	Oligotrophic peat	9
6.8	—	—	10	Sphagnum peat	20
23.0	—	—	10	Sphagnum peat	20
—	19.6	5	30	Eutrophic peat*	8
—	6.4	3.5	30	Oligotrophic peat*	8
—	16.4	5	4	Sphagnum peat	This study

(a) Column study.
(b) Peat for energy production.
(c) Peat for agricultural use.
* Acid treated

nique for predicting the Langmuir-type adsorption for any initial pH (within the range which was examined). Whilst this is a useful tool, it is also pertinent to compare the current data with the results obtained by other workers. An examination of Table 2 shows that the value for the maximum adsorption (the Langmuir X_m) is comparable with values reported previously. This table also shows the adsorption capacities reported in earlier studies where X_m had not been derived specifically.

Freundlich Isotherms

The adsorption data have also been used to calculate the ultimate sorption capacity of peat by substituting the required equilibrium concentrations in the Freundlich equation. When the data were linearized, the correlation coefficients were found to vary between 0.964 and 0.987 (Table 1).

The Freundlich constants are also shown in Table 1. $(1/n)$, which is a measure of the adsorption intensity, decreased from 0.371 to a value of 0.234 with increasing solution pH values. Similar values of the Freundlich constant $(1/n)$ were found at initial pH values of 4.00, 4.50 and 5.00. The variation of the Freundlich constant $(1/n)$ against initial pH is shown in Figure 4. The linear relationship over the measured pH range
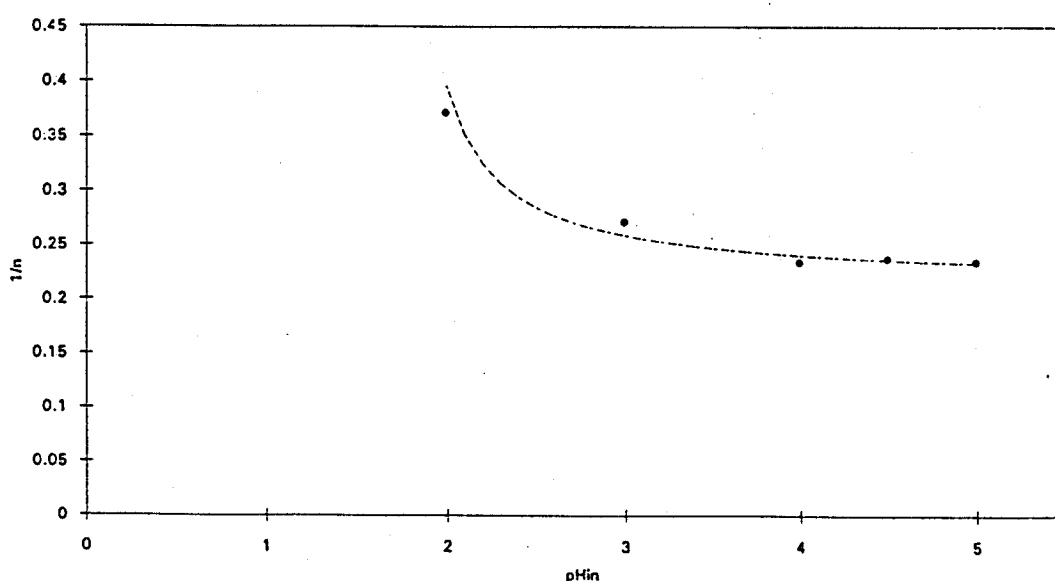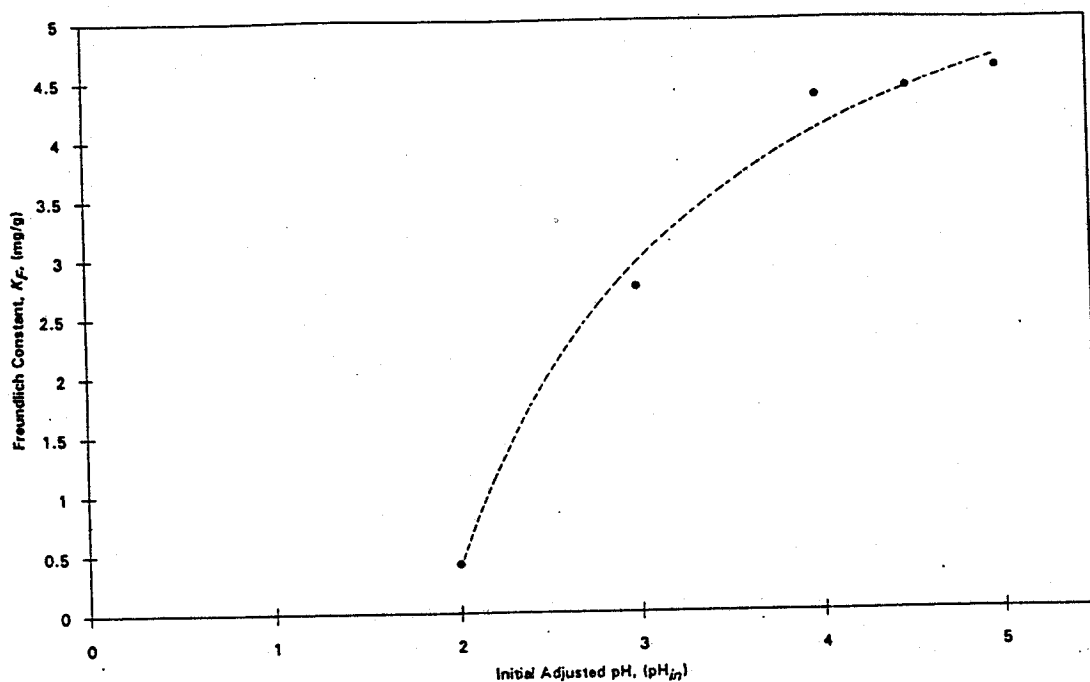

Figure 4. Variation of $1/n$ against pH_{in}.

Figure 5. Variation of K_F against pH_{in}.

had a correlation coefficient of 0.999 and can be expressed as:

$$1/n = \frac{pH_{in} - 1.45}{4.60(pH_{in} - 1.45) - 1.15}$$

The Freundlich constant (K_F), which is a measure of adsorption capacity, increased with increasing solution pH values. The highest adsorption capacity for copper was 4.58 mg/g of peat at pH 5.00. Both Langmuir and Freundlich constants showed the same increasing trend with increasing solution pH values. The variation of the Freundlich constant against adjusted pH is shown in Figure 5 and shows a linear relationship with a correlation coefficient of 0.983 which can be expressed as:

$$K_F = \frac{pH_{in} - 1.91}{2.11 \times 10^{-1} + 0.146(pH_{in} - 1.91)}$$

Effect of copper on equilibrium pH

There are several possible explanations for the pH variations which occur when peat is mixed with metal cation solutions. They could be from the acidic properties of the carboxylic and phenolic functional groups present in humic substances[21,22] or ion exchange
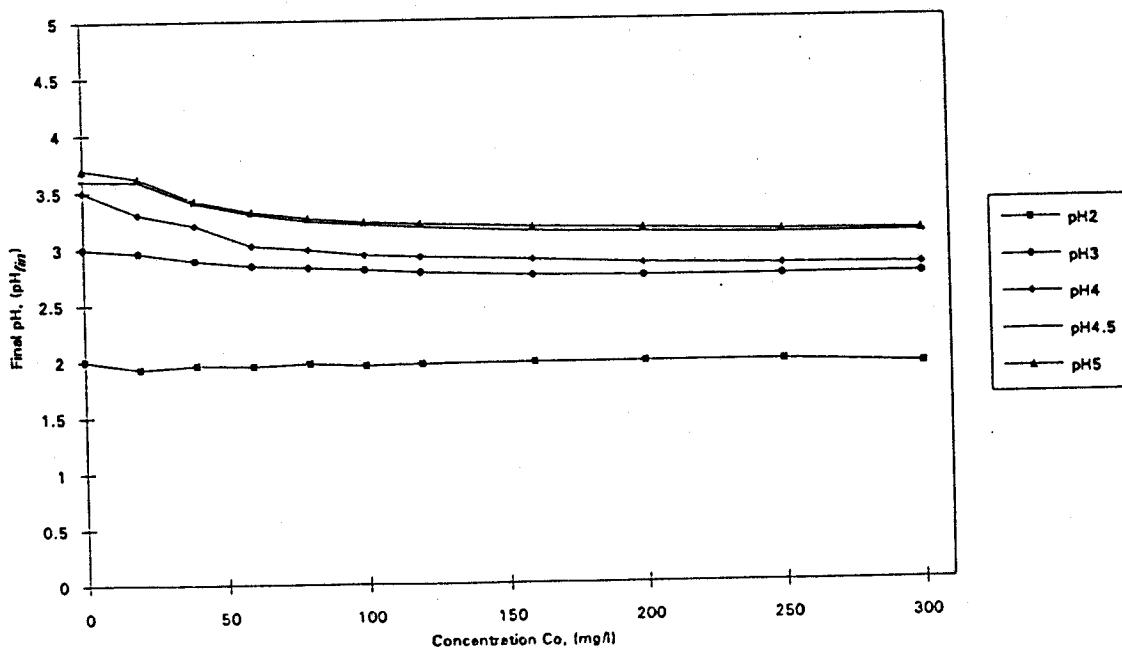

Figure 6. Equilibrium pH ($pH_{fir.}$) at different initial copper concentrations.
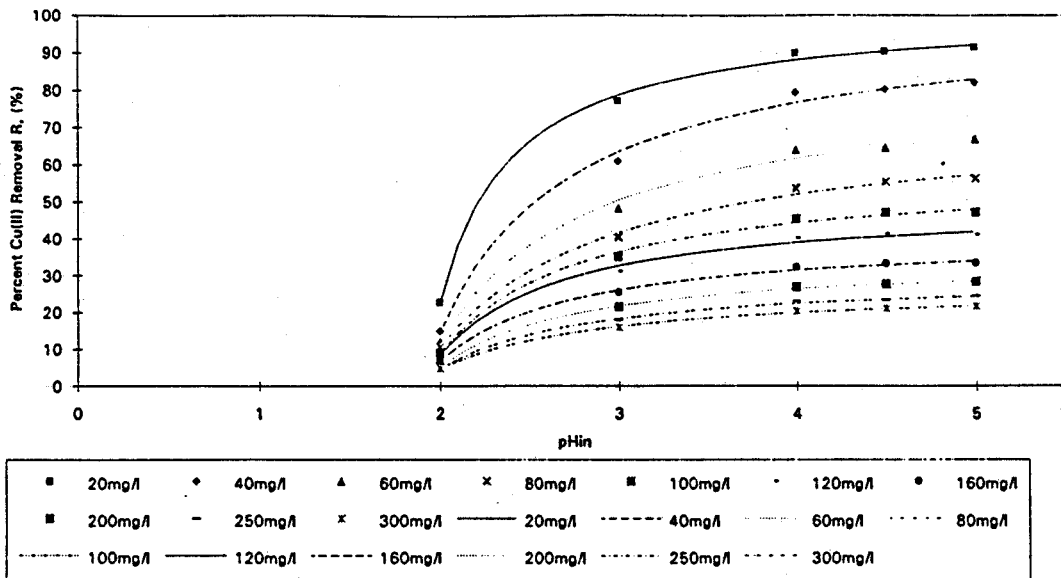
Figure 7. Effect of variations in pH_{in} on copper removal.

Table 3. Values of the non-pH parameters in the removal equation.

C_0 (mg/l)	α	β	γ	Corr Coeff r^2
20	3.12×10^{-3}	9.87×10^{-3}	1.91	0.999
40	6.47×10^{-3}	1.00×10^{-3}	1.89	0.997
60	8.83×10^{-3}	1.21×10^{-2}	1.88	0.997
80	1.20×10^{-2}	1.38×10^{-2}	1.85	0.997
100	1.16×10^{-2}	1.73×10^{-2}	1.88	0.997
120	1.19×10^{-2}	2.02×10^{-2}	1.88	0.996
160	1.59×10^{-2}	2.45×10^{-2}	1.87	0.998
200	1.95×10^{-2}	2.89×10^{-2}	1.88	0.999
250	2.49×10^{-2}	3.31×10^{-2}	1.86	0.999
300	2.99×10^{-2}	3.66×10^{-2}	1.83	0.999

reactions, such as proton release when metal cations bind to peat[14,19,21].

Figure 6 shows that, when the initial pH was between 4 and 5, as the initial copper concentration (C_0) increased, the equilibrium pH decreased. However, at lower pH values there was little or no effect. This suggests that as more copper ions are adsorbed onto the peat, more hydrogen ions are released from the peat into the solution, consequently decreasing the pH of the reaction mixture. According to Dissanayake and Weerasooriya[11], pH was found to have a marked effect on copper ions adsorption. Below pH 2.0–2.5, the adsorption of copper ions by peat was low. When the adsorption of copper ions was carried out at the initial pH 2.0 in all the concentrations on this work, the pH_{fin} were between 1.9 to 2.0 and adsorption density was much lower. It is, therefore, concluded that the adsorption of copper competes with hydrogen ions.

It is clear that the resulting equilibrium pH is governed by two major factors: the adjusted pH and the copper present in the solution initially. This phenomenon could also be represented as a functional relationship of these two parameters, given by:

$$pH_{fin} = f(pH_{in} C_0^{-1})$$

Copper Removal

The maximum adsorption capacity (X_m) found for the peat used in this current study was 16.4 mg/g (Table 2). This value is very comparable with the results from earlier studies using unmodified peat, at a range of concentrations (0.5 to 50 g/l), in both batch and continuous tests. Table 2 shows that these values ranged from 2.6 to 25.4 mg/g with the average being 13.5 mg/g. Table 2 also shows that peats which had been acid-treated had significantly higher capacities.

The efficiency of copper removal by peat is controlled by the adjusted pH of the reaction mixture. Figure 7 demonstrates this effect and shows that, as the pH is increased from 2.00 to 5.00, the removal increases. However, increases above pH 4.00 produce less of an effect than was achieved between 2.00 and 4.00. This effect was most pronounced at low concentrations. The linear relationship with a correlation coefficient of 0.996 can be expressed as:

$$R = \frac{pH_{in} - \gamma}{\alpha + \beta(pH_{in} - \gamma)}$$

α, β and γ are characteristics of the copper removal/pH curve. $1/\beta$ is defined as the plateau value of R, γ is the pH value when $R = 0$ and $1/\alpha$ is the tangent to the curve when $R = 0$.

The values for α, β and γ at the various C_0 concentrations are shown in Table 3.

The relationship between the copper removal (R) and the initial copper concentrations at different initial pH values is shown in Figure 8. A double logarithmic plot of the data showed that there were linear relations with correlation coefficients of more than 0.96 (Table 4).

This means, therefore, that there is an inverse functional relationship which can be expressed, at any particular pH, as:

$$R = mC_0^{-n}$$

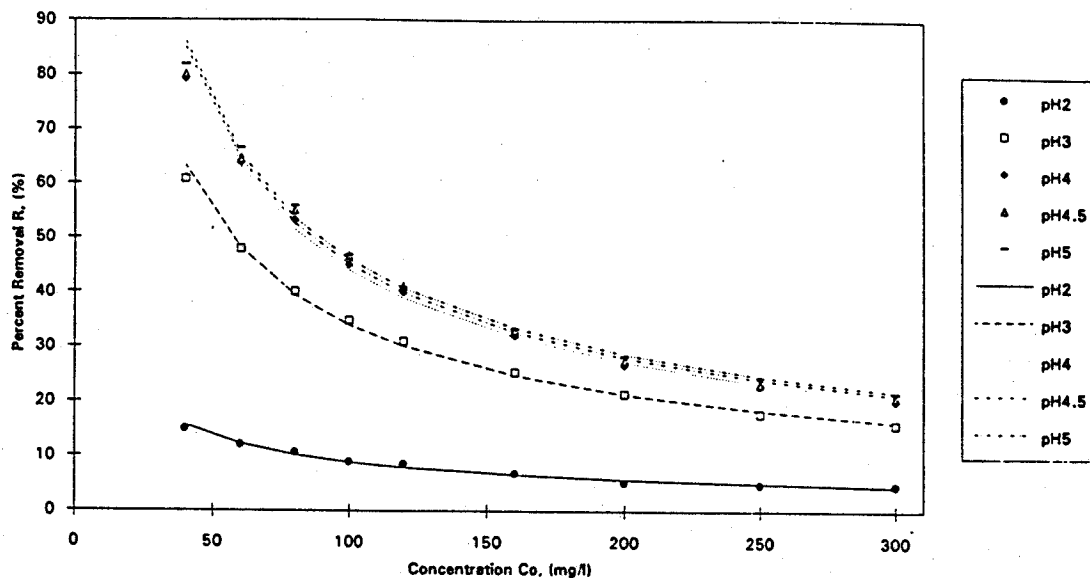The values for m and n are given in Table 4.

Figure 8. Effect of varying the initial concentration on copper removal at different pH_{in}.

Table 4. Constants for the copper removal/C_O relationship at different pH_{in} values.

pH	Proportionality constant	n	Corr Coeff r^2
2	1.41×10^2	0.601	0.988
3	5.45×10^2	0.608	0.983
4	6.56×10^3	0.595	0.962
4.5	6.44×10^3	0.586	0.959
5	6.38×10^3	0.580	0.960

The efficiency of copper removal by peat is controlled by the initial pH of the reaction mixture and the initial copper concentrations. Figure 9 demonstrates this effect and shows that the efficiency of copper removal (R) increases with increasing pH_{in} and decreasing initial copper concentrations. The relationships between α, β and γ and the initial copper concentration were linear

with correlation coefficients greater than 0.968. The relationship can be expressed as:

$$\alpha = 8.85 \times 10^{-5} C_O + 2.64 \times 10^{-3}$$

$$\beta = 1.04 \times 10^{-4} C_O + 6.76 \times 10^{-3}$$

$$\gamma = -1.80 \times 10^{-4} C_O + 1.90$$

Substituting for α, β and γ, R can be represented as:

$$R = \frac{1.80 \times 10^{-4} C_O + pH_{in} - 1.90}{1.87 \times 10^{-8} C_O^2 - 1.08 \times 10^{-4} C_O + 1.04 \times 10^{-4} C_O(pH_{in}) + 6.76 \times 10^{-3}(pH_{in}) - 1.02 \times 10^{-2}}$$

This equation can then be used to derive the percent copper removal at any given initial coppeer concentrations and adjusted pH value. The three dimension plot of the equation is shown in Figure 9.
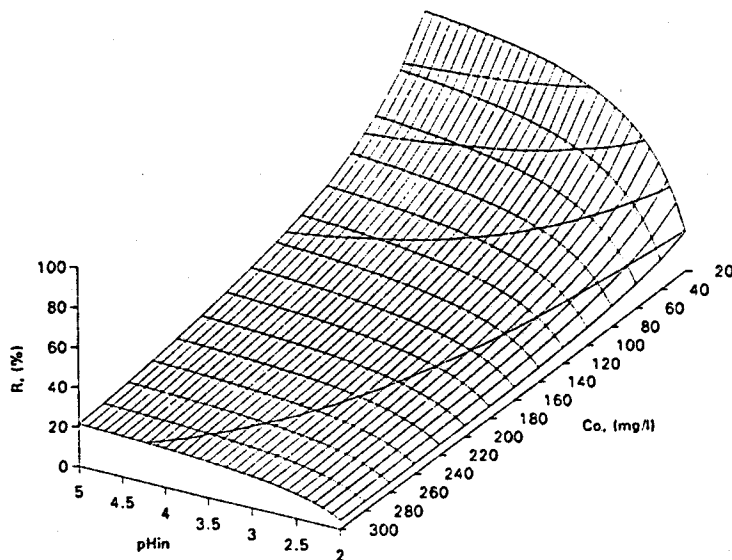

Figure 9. Effect of the initial copper concentration and different pH_{in} on copper removal.
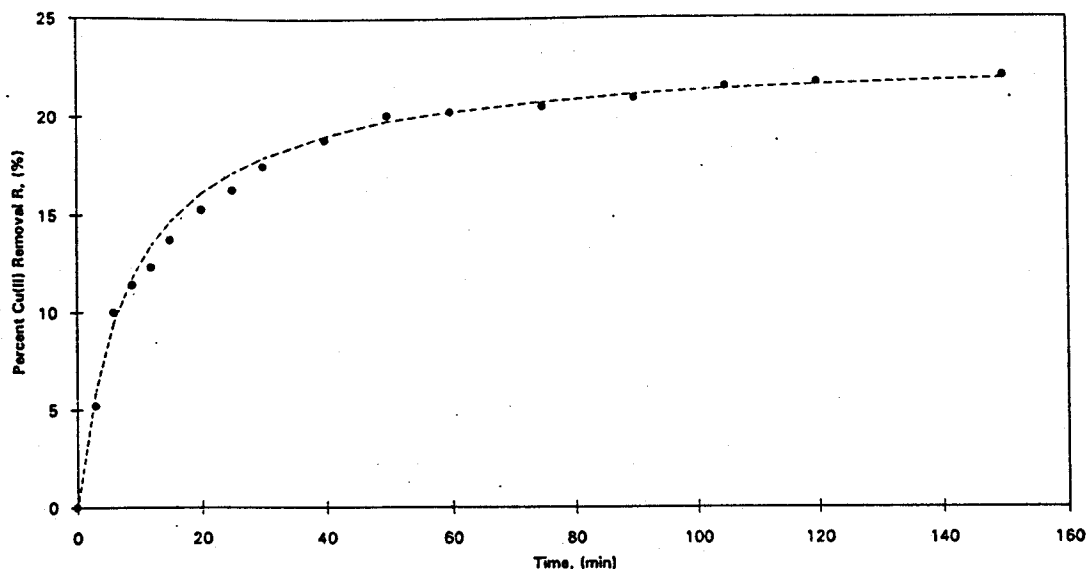
Figure 10. Copper removal in relation to time.

Kinetics of Copper Removal

The effect of contact time on the Cu(II) removal was investigated using an initial copper concentration of 1000 mg/l and a solution pH of 5.00. The results are presented in Figure 10 and show that, initially, there is a rapid uptake of copper with most of the removal being achieved within 30–40 minutes. However, an effective equilibrium was reached only after 108 minutes. This could well suggest that intra particle diffusion is the limiting factor in this latter portion of the process. The copper removal/time relationship can be described as:
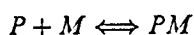
$$R = \frac{T}{0.375 + 0.0432 \times T}$$

where

R = copper removal, %;

T = reaction time, min.

In the absence of stoichiometric data, the simplest way to describe the metal removal by peat is:

$$P + M \Longleftrightarrow PM$$

with $K = (PM)/(P)(M) = k_1/k_2$
where

(P) = the concentration of peat binding sites, M;

(M) = the concentration of free metal in solution, M;

(PM) = the concentration of metal bound to peat, M;

K = the apparent conditional stability constant, M^{-1}

$k_1(M^{-1}s^{-1})$ and $k_2(s^{-1})$ are the forward and reverse kinetic constants respectively. Based on this equation, Gosset *et al.*[9] developed a technique for obtaining the binding kinetic constant, k_1. This required the following assumptions:

- reverse reaction (k_2) is negligible;
- peat metal anion stoichiometry was constant for all experimental conditions and equal to one metal ion per binding site;

- overall kinetics were limited by the binding reaction itself and not the diffusion of species.

Gosset *et al.*[9] then developed an expression to describe these reactions:

$$k_1 t = \frac{1}{(PM)_{lim} - (M)_{in}} \ln \frac{(M)_{in}}{(PM)_{lim}} \frac{(PM)_{lim} - (PM)}{(M)_{in} - (PM)}$$

where

(PM) and $(PM)_{lim}$ are the variable and equilibrium bound metal concentration, M;
$(M)_{in}$ is the initial free metal concentration, M.

Thus, by plotting $(k_1 t)$ against time (t), values of k_1 can be calculated. With the current data, the relationship was found to be linear with a correlation coefficient of 0.982 (Table 5). The quality of this correlation supports the set of assumptions concerning the kinetics and especially the assumption of a chemical rate limiting step. However, flow-through experiments in columns should be used to confirm such kinetic behaviour.

The equation can be rearranged as:

$$(PM) = (M)_{in} \frac{exp\{[(M)_{in} - (PM)_{lim}]k_1 t\} - 1}{\frac{(M)_{in}}{(PM)_{lim}} exp\{[(M)_{in} - (PM)_{lim}]k_1 t\} - 1}$$

Thus, it can be used to calculate the concentration of copper adsorbed at any given time in a batch reactor. However, it does not take into account the effect of peat dose and the pH although similar relationships could be developed by evaluating k_1 values as a function of pH and adsorbent dose rate.

Table 5. Kinetic constants of adsorption.

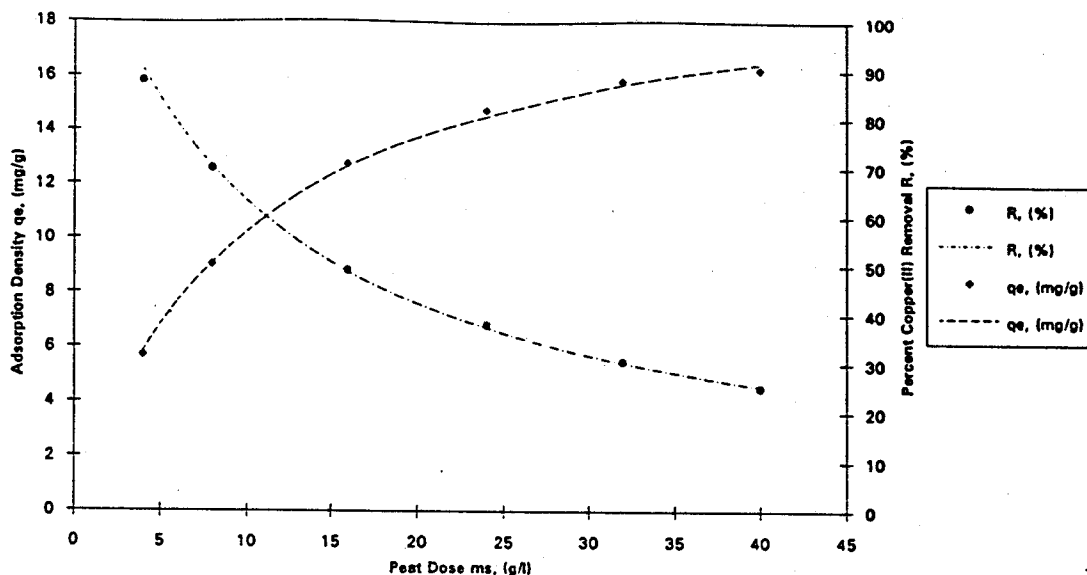| C_O (mM)	Corr Coeff r^2	k_1 $(M^{-1}s^{-1})$	Saturation time (min)	Removal (%)
15.8	0.982	0.120	50	50.0

Figure 11. Variation of adsorption density (q_e) and percent copper removal (R) in relation to peat dose (m_s).

Effect of Peat Dose on Adsorption

The effect of varying the peat dose (m_s) using an initial copper concentration of 200 mg/l is shown in Figure 11. It can be seen that the removal increases with increasing adsorbent doses for the given initial copper concentration. This is to be expected because, for a fixed initial solute concentration, increasing adsorbent doses provide greater surface area (or adsorption sites). The data in Figure 11 can be used to derive a mathematical relationship (using the boundary conditions $m_s = 4.0$ to 40 g/l). The relationship, which has a correlation coefficient as high as 0.999 is:

$$R = \frac{m_s}{8.81 \times 10^{-2} + 8.72 \times 10^{-3} m_s}$$

The above equation can be used to predict the percent copper removal for any peat dose within the test limits at pH 5.00 and initial copper concentration $C_O = 200$ mg/l.

The adsorption density curve in Figure 11 indicates that adsorption densities decreased from 15.9 mg/l to 4.52 mg/l when the peat doses were increased from 4 to 40 g/l. This leads to the conclusion that, in order to obtain the optimum peat dose, higher copper concentrations should be tested in conjunction with high doses. The relationship between adsorption density (q_e) and the peat dose (m_s) was found to have a high correlation coefficient (0.999) and to have the form:

$$q_e = \frac{1}{4.40 \times 10^{-2} + 4.36 \times 10^{-3} m_s}$$

CONCLUSIONS

The initial part of the study, based on the derivation of conventional Langmuir and Freundich isotherms, produced results which were comparable with earlier copper/peat studies. The data from these isotherms, together with the results from the adsorption/time studies were used to:

(a) test new mathematical relationships derived in earlier studies;
(b) develop new mathematical expressions which could be used to predict the adsorption of copper by peat.

Taken overall, this study has shown that, despite the fact that the characteristics of peat will vary depending on their source, the adsorption properties of peat in relation to copper could, as a first approximation, be thought of as invariable. Certainly, the fact that the expression derived by Gosset et al.[9] can also be applied to the current data would support this hypothesis. Nevertheless, it is a philosophy which must be tested. In particular, the general applicability of the various mathematical expressions and the errors likely to occur when they are used as general equations will need to be appraised.

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