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BATCH METAL REMOVAL BY PEAT KINETICS AND THERMODYNAMICS

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Abstract—Peat moss, a natural inexpensive material, is able to play an important rôle in treatment processes of metal-bearing industrial effluents since it adsorbs, complexes or exchanges various metal cations. This paper presents kinetics and thermodynamics of batch metal removal reactions by 50 g l⁻¹ (dry wt) eutrophic or oligotrophic peat particles using Cu²⁺, Cd²⁺, Zn²⁺ and Ni²⁺ concentrations ranging from 0.01 to 100 mM.

Metal cation removal reactions are moderately rapid in 10 mM metal unbuffered solutions: the forward kinetic constant ranges between 0.005 and 0.17 M⁻¹ s⁻¹, and equilibrium is reached within about 1 h. Under these conditions of pH (2.2–4.2) and concentrations, apparent binding equilibrium constants were found to range between 2 and 3150 M⁻¹ depending upon the peat origin and the metal cation.

In 0–6.5 pH-buffered metal cation solutions, the four cations binding reactions behaved differently demonstrating that metal binding equilibrium constant decrease in the order Ni²⁺ > Cu²⁺ > Cd²⁺ = Zn²⁺. When pH is higher than 6.7, more than 90% of a 10 mM metal cation solution is removed by 50 g l⁻¹ peat particles and metal binding capacities equal 200 mmol kg⁻¹ dry wt, whatever the metal nature and the peat origin. Except for nickel cation which is very strongly bound to peat, all metal cations are completely released when pH is fixed below 1.5.

Key words—peat, heavy metals, ion exchange, complexation, kinetics, thermodynamics

INTRODUCTION

Surface water is often polluted by the improper disposal of metal-bearing industrial effluents. Numerous approaches have been studied for the development of metal trapping materials. Besides the highly effective artificial chelating polymers containing, for example, thiol functions (Deratani and Sébille, 1981), cheap natural polymeric materials, such as humic substances or peat, have been extensively studied. They indeed strongly adsorb, exchange or complex various metal cations using their carboxylic, phenolic and hydroxylic functional groups (Smith *et al.*, 1977; Wolf *et al.*, 1977; Takamatsu *et al.*, 1978; Sipos *et al.*, 1978; Meisel *et al.*, 1979; Bloom and McBride, 1979). Following Coupal and Lalancette (1976), it has been suggested by several research groups to use peat moss in beds or columns for metal-containing effluent treatment (Poots *et al.*, 1978; Poots and McKay, 1980; Chaney and Hundemann, 1979; McKay 1980; Dissanayake and Weerasooriya, 1981). Before attempting to develop such a peat treatment process in columns, we decided to study the metal removal reactions in batch and determine their kinetics (Gosset *et al.*, 1984) and thermodynamics. We present here results obtained

with metals cations playing an important rôle in water quality, i.e. copper, cadmium, zinc and nickel.

MATERIALS AND METHODS

Peat and reagents

Two types of peat were studied: an oligotrophic peat called "Floratorf" and an eutrophic one called "Heurteauville peat", both being commercially available in France for agricultural purposes.

The metallic salts used were cupric nitrate, cadmium acetate, zinc and nickel chlorides dissolved in slightly acidified distilled water. All metallic salts and chemicals were of analytical grade (Prolabo P.A.).

Peat treatment

In order to homogenize peat samples and to clear them from metallic cations which they could have previously fixed, we pretreated peat in five steps:

- (a) 24 h drying at 100°C;
- (b) dry sieving with a shaker (Prolabo) to 0.5–1.25 or 1.25–5 mm particle size;
- (c) acidification of the sieved samples, 10 g of dry peat being thoroughly shaken for 2 h with 100 ml of 1 M HCl;
- (d) washing with deionized water until filtrate reaches pH 4;
- (e) 24 h drying at 70°C.

When the effect of acidification procedure of peat samples was studied, steps (c) and (d) were avoided. In particle size dependence studies, peat treatment procedure avoided steps (b), (c), (d) and (e).

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All kinetic and thermodynamic batch experiments used the same concentration of peat particles, i.e. 50 g l^{-1} (dry wt).

Kinetic constants determination

Five grams of formerly acidified or non-acidified peat, i.e. including or omitting step (c) in peat treatment procedure, were thoroughly mixed into 100 ml of 10 mM solution of one of the following metallic cations: Cu^{2+} , Cd^{2+} , Zn^{2+} and Ni^{2+} ; peat suspensions were shaken during 2 h at room temperature and 1 ml samples were collected every 15 min and centrifuged during 5 min at 12,000 rpm. Supernatants were analysed using either differential pulse polarography or flame atomic absorption.

The electrochemical assembly contained a static mercury drop electrode (EGG PAR 303) connected to a differential pulse polarograph (EGG PAR 364); 0.2 ml samples were taken from the supernatant and added to 10 ml of deionized water formerly acidified with 0.2 ml of 1 M perchloric acid. Metal determinations were performed by direct differential pulse polarography with initial potentials of +140, -740 and -420 mV/AgCl respectively for copper, zinc + nickel and cadmium and potential sweep rate fixed to -5 mV s^{-1} . The superimposed constant amplitude pulse was 50 mV and the mercury drop period fixed at 1 s. Heavy metals were measured, element per element, using standard addition procedure and recording 2-3 polarograms per solution.

The analysis by acetylene-air flame atomic absorption spectrophotometry was performed with a Perkin-Elmer 2380 and single element hollow cathode lamps. All samples were filtered through a $0.45 \mu\text{m}$ membrane filter (Millipore) before metal determination. Metal concentrations were calculated by averaging 3-5 determinations with the same solution and using calibration curves taking into account a blank and 3 standards.

Thermodynamic constants determination

Two grams of formerly acidified or non-acidified peat, i.e. including or omitting step (c) and (d) in the peat treatment procedure, were thoroughly mixed into 40 ml metal solution during 2 h at room temperature. The initial concentrations of metallic cations were fixed to values ranging between 0.01 and 100 mM. For high free metal concentrations, i.e. using 1-100 mM initial metal concentrations, analysis procedure was direct differential pulse polarography. For determinations of free metal at lower concentrations, we used anodic stripping differential pulse polarography with a preconcentration step of 90 s at -1100 mV/AgCl .

pH dependence

Two and half grams of natural peat, i.e. dried 24 h at 100 C, unsieved and non acidified, were suspended in 50 ml of 10 mM metal cation solutions. pH was adjusted by addition of 1 M perchloric acid or of 1 M sodium hydroxyde. pH was measured at the beginning of reactions and after 1 h of mixing and then readjusted if necessary. Peat particles were stirred for 3 h and centrifuged 5 min at 12,000 rpm. Concentration of metallic cations were determined by flame atomic absorption spectrophotometry on supernatants as previously mentioned.

KINETICS OF METAL BINDING

In order to optimize the residence time of industrial waste water in peat columns, we studied the kinetics of 10 mM metal cation removal by 50 g l^{-1} peat particles in batch experiments. Figure 1 shows the evolution of metal amounts bound to eutrophic peat. As these first experiments were made without buffering pH, solutions in contact with peat presented some pH variations: pH decreases were found to

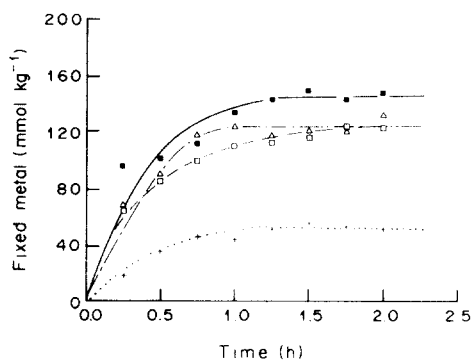


Fig. 1. Kinetics of metal binding reactions on eutrophic peat. 5 g acidified (dry wt) 0.5-1.25 mm peat shaken in 100 ml 10 mM (■) copper, (+) cadmium, (□) zinc and (△) nickel unbuffered solutions: final pH ranged from 2.2 to 4.2.

range between 0.2 and 0.6 pH units whatever the metal and the peat origin. Although we do not intend in such experiments to identify the chemical or physical nature of peat-metal cation interactions, it seems clear that, under these conditions, complexing or adsorption reactions are more important than ion exchange reactions in metal removal processes by peat. Indeed if 1 or 2 protons were released during each metal binding reaction on peat, one should observe a 10 or 20 mM proton concentration increase and a pH shift from 3-4 to approx. 2. Table 1 shows that H/M ratios, i.e. the number of proton released per metal cation bound to peat is always lower than 0.25. Furthermore, the pH variations observed when peat was suspended into 10 mM initial metal ion solutions were similar to those observed when equal amounts of peat were suspended in deionized water, in absence of any metal. Thus pH variations encountered when peat particles are mixed with metal cation solutions result probably from:

the acidic properties of carboxylic and phenolic functional groups present in humic substances (Bloom and McBride, 1979; Boyd *et al.*, 1981);

some ion exchange reactions, i.e. proton release when metal cations bind to peat (Bunzl *et al.*, 1976; Bloom and McBride, 1979; Meisel *et al.*, 1979; Aho and Tummavuori, 1984);

the pH buffering capacity of peat weak acid groups, limiting possible pH variations related to previously mentioned proton release (Attal *et al.*, 1985).

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



with

$$K' = \frac{(\text{PM})}{(\text{P})(\text{M})} = k_1/k_2$$

where

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

Table 1. Metal binding kinetics and equilibrium constants using 50 g l⁻¹ peat in unbuffered 10 mM metal cation solutions

| Peat type | Particle size (mm) | Metal | k_1 (M ⁻¹ s ⁻¹) | k_2 (s ⁻¹) | Cor. coeff. (r ²) | (P) _{in} (mM) | K' (M ⁻¹) | pH (final) | H/M |
|-----------|--------------------|-------|--|--------------------------|-------------------------------|------------------------|-----------------------|------------|--------|
| ac. olig. | 0.5-1.25 | Cu | 0.03 | 10.7 E-4 | 0.60 | 28 | 30 | 3.2 | 0.03 |
| ac. olig. | 1.25-5 | Cu | 0.005 | 1.8 E-4 | 0.75 | 27 | 30 | 3.0 | |
| olig. | nat. | Cu | 0.013 | 3.2 E-4 | 0.85 | 41 | 26 | 2.6 | 0.03 |
| ac. olig. | 0.5-1.25 | Cd | 0.026 | 5.1 E-3 | 0.31 | 5.1 | 39 | 2.8 | 0.23 |
| ac. olig. | 0.5-1.25 | Zn | 0.055 | 9.7 E-3 | 0.77 | 5.6 | 30 | | |
| ac. olig. | 0.5-1.25 | Ni | 0.041 | 1.6 E-2 | 0.74 | 2.6 | 49 | | 0.25 |
| ac. eutr. | 0.5-1.25 | Cu | 0.118 | 3.3 E-4 | 0.96 | 355 | 25 | 2.5 | |
| ac. eutr. | 1.25-5 | Cu | 0.061 | 1.3 E-4 | 0.98 | 483 | 27 | 3.0 | |
| eutr. | nat. | Cu | 0.170 | 0.5 E-4 | 0.98 | 3150 | 20 | 4.2 | 0.0005 |
| ac. eutr. | 0.5-1.25 | Cd | 0.036 | 4.6 E-3 | 0.63 | 7.8 | 46 | 4.0 | 0.01 |
| ac. eutr. | 0.5-1.25 | Zn | 0.060 | 1.7 E-3 | 0.98 | 34 | 52 | | |
| ac. eutr. | 0.5-1.25 | Ni | 0.050 | 1.2 E-3 | 0.74 | 41 | 55 | 2.2 | 0.004 |

(eutr.) eutrophic, (olig.) oligotrophic, (ac.) acidified and (nat.) unsieved and unacidified peat, (H/M) proton/metal exchange ratios, (P)_{in} metal binding capacities estimated by batch metal binding experiments using 100 mM metal cation solutions buffered at pH equal to final pH in this table (Gangneux *et al.*, 1985).

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

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

K' = the apparent conditional stability constant at experimental pH (M⁻¹),

k_1 (M⁻¹s⁻¹) and k_2 (s⁻¹) are the forward and reverse kinetic constant, respectively.

Apparent conditional stability constants K' were calculated taking into account equilibrium concentrations of free (M) and bound (PM) metal and the amount (P)_{in} of metal binding sites on peat. These metal binding capacities (P)_{in} were estimated from bound metal amounts, using higher metal cation concentrations, i.e. 100 mM, in solutions whose pH was buffered between 0 and 6 (Gangneux *et al.*, 1985). Apparent binding constants at pH 2.2-4.2 were found to range between 2 and 3150 M⁻¹, the highest values being obtained for copper removal by eutrophic peat (Table 1).

Binding kinetic constant k_1 was obtained assuming that:

reverse reaction 2 was negligible;

peat-metal cation stoichiometry was constant for all experimental conditions and equal to one metal cation per peat binding site;

overall reaction kinetic was limited by the binding reaction itself and not by diffusion of species;

and by plotting calculated

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

vs time

where

(PM) and (PM)_{lim} are the variable and equilibrium bound metal concentrations (M),

(M)_{in} is the initial free metal concentration (M).

Kinetic plots similar to those presented on Fig. 2 were found to be linear with correlation coefficients higher than 0.7 on 9 curves over 12. When other

assumptions than those listed above were tested, we were not able to obtain such good fit of experimental data. Slopes of these straight lines, giving k_1 , allowed us to calculate the reverse kinetic constant k_2 using previously mentioned apparent stability constant K' (Table 1). Whereas k_1 was found to range between 0.005 and 0.17 M⁻¹s⁻¹, with the highest values for copper removal by eutrophic peat, k_2 values were always smaller than 0.01 s⁻¹. On the few examples tested, unsieved and non acidified oligotrophic or eutrophic peat samples seemed to bind copper more rapidly and efficiently than sieved and acidified ones. This result may be interpreted as a structure modification of this natural matter when acid pre-treated.

Using these values for k_1 and K', we compared the experimental evolution of bound metal (PM) and corresponding calculated curves (where reverse reactions were neglected):

(PM) =

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

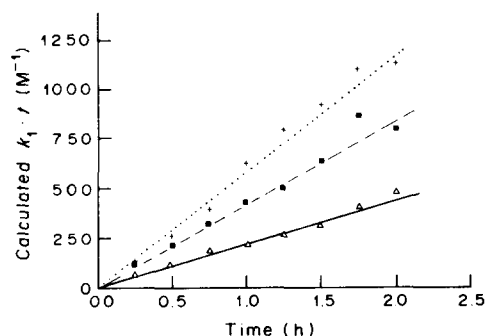


Fig. 2. Eutrophic peat pretreatment and size dependence of copper binding reaction kinetics: determination of forward kinetic constant k_1 . 5 g dry wt (■) unsieved and unacidified or acidified (+) 0.5-1.25 mm or (△) 1.25-5 mm peat suspended in 100 ml 10 mM copper unbuffered solutions. Lines were obtained by least square regression: slopes of these lines and correlation coefficients are given in Table 1.

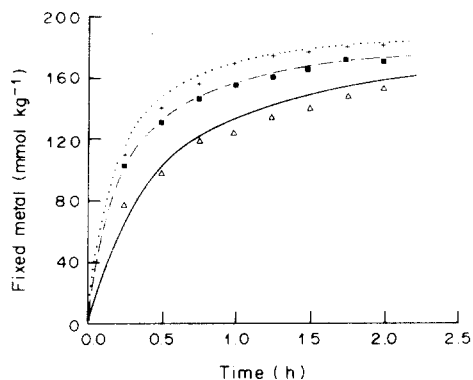


Fig. 3. Calculated and experimental evolution of copper fixed on peat: eutrophic peat pretreatment and size dependence. Lines correspond to calculated fixed copper amounts, taking into account kinetic constants values presented in Table 1. Same symbols as Fig. 2 for experimental data.

As shown on Fig. 3 where such a comparison is presented, agreement is generally good, differences between experimental and calculated data being usually smaller than 6%. Such agreement supports our set of assumptions concerning these kinetics and especially the assumption of a chemical rate limiting step: flow-through experiments in columns should be used to confirm such kinetic behaviour.

Kinetics of metal ion binding by peat has been previously studied by Bunzl (1974a,b) and Bunzl *et al.* (1976) using either continuous or discrete metal cation addition to preacidified sphagnum peat in batch experiments. Reaction kinetics were much more rapid, reaction half-times ranging between 5 and 15 s (instead of 15–30 min in this paper). Such a difference of magnitude in kinetic constants may be related to the large differences in experimental conditions: Bunzl used to shred and sieve peat samples in water to a particle size of 0.2–0.7 mm, and before each experiment 0.5 or 5 g l⁻¹ (wet wt) peat particles were allowed to establish swelling equilibrium in well-stirred deionized water for several hours. Our 24 h drying procedure of non-shredded peat samples may have significantly decreased swelling and metal binding kinetics of much more concentrated peat suspensions (50 g l⁻¹ dry wt).

METAL REMOVAL THERMODYNAMICS

In order to use peat for environmental applications, we found it necessary to determine the peat–metal cation binding isotherms for different unbuffered metal solutions equilibrated with two types of peat samples (Figs 4 and 5). Whatever the peat origin and the metal cation, none of these curves is linear, slopes ranging between 0.5 and 2.0; this seems to indicate that the peat–metal complex stoichiometry and thermodynamic are probably dependent on the free metal concentration and on pH which, in these experiments, may vary due to

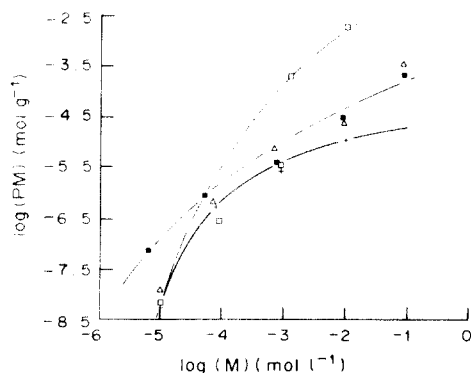


Fig. 4. Metal binding isotherms on eutrophic peat in unbuffered solutions. 2 g (dry wt) acidified 0.5–1.25 mm peat equilibrated with 40 ml deionized water containing metal cations in the 0.01–100 mM initial concentration range. Same symbols as Fig. 1.

unbuffered conditions. Furthermore, no sorption or binding saturation was observed in these unbuffered solutions, even when total metal concentration reached 0.1 M in 50 g l⁻¹ peat suspensions. We frequently observed, especially for oligotrophic peat, that the bound to free metal ratio (PM)/(M) was maximum for total metal concentrations in the 0.1–1 mM range: such a concentration range should correspond to the maximum efficiency of a waste water treatment process using peat columns or batches.

In order to evaluate the occurrence of soluble forms of complexed metal, such isotherms were drawn using either polarographic data, i.e. free and labile species, or atomic absorption data after 0.45 μm filtration, i.e. total soluble concentrations. Differences were generally within the range of reproducibility of such heterogeneous experiments, i.e. about 5%, indicating the negligible importance of soluble humic metal complexes under our experimental conditions. This result is of extreme importance if one thinks of the possible applications of peat columns in waste water treatment: metal binding functions should not dissolve into the flowing

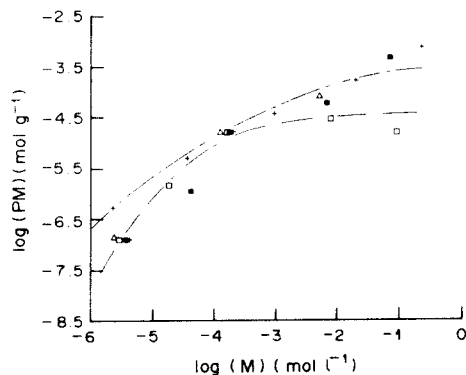


Fig. 5. Metal binding isotherms on oligotrophic peat in unbuffered solutions. 2 g (dry wt) acidified 0.5–1.25 mm peat equilibrated with 40 ml deionized water containing metal cations in the 0.01–100 mM initial concentration range. Same symbols as Figs 1 and 4.

through solutions (Chaney and Hundemann, 1979; Aho and Tummavuori, 1984).

pH DEPENDENCE OF THE METAL REMOVAL THERMODYNAMICS

As equilibrium pH in 50 g l⁻¹ peat suspensions had been found to range between 2.2 and 4.2 in the previously mentioned unbuffered solutions (Table 1), we decided to study more precisely the pH dependence of metal removal thermodynamics. Competition between proton and metal ion exchange or complexation is an indirect method to compare their energetics (Stumm and Morgan 1981). We found that such experiments need several pH adjustments with small additions of strong acid or base: indeed several hours are necessary to obtain a stable pH in a solution in contact with peat (Attal *et al.*, 1986); the addition of metal cations and/or strong acid or base does not seem to decrease significantly the time which is necessary for peat to equilibrate its acido-basic functions.

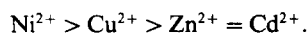
We have observed that pH presents a strong influence on metal ion binding equilibria when the total concentration of metal cation equals 10 mM. Indeed the percentage of metal extraction, i.e. (PM)/[(PM) + (M)] ratio, varies from 0 to almost 100% within 4–5 pH units (Figs 6 and 7 in Table 2). This study was performed at pH lower than 6.5 in order to prevent precipitation of metal hydroxides. Independently of peat origin three important results were obtained in relation to metal cation:

nickel is the most strongly fixed, even in very acidic media;

above pH 3 copper binding is very similar to nickel, but below pH 3 copper may be completely released from peat;

cadmium and zinc present a similar pH dependence and are less strongly fixed than the two other cations.

Taking into account pH values for 50% metal binding capacities, equilibrium constants may be compared:



Except for nickel and copper respective positions, these results are in good agreement with metal-humic substances previous results (Bunzl *et al.*, 1976; Giesy, 1983).

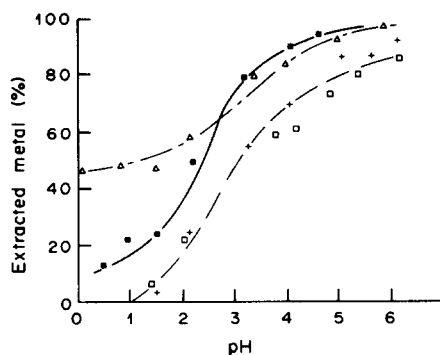


Fig. 6. pH dependence of the metal uptake of eutrophic peat. 2.5 g unsieved and unacidified peat equilibrated with 50 ml 10 mM metal cation solutions either acidified by 1 M perchloric acid or alcalinised by 1 M sodium hydroxide: (■) copper, (+) cadmium, (□) zinc or (△) nickel solutions.

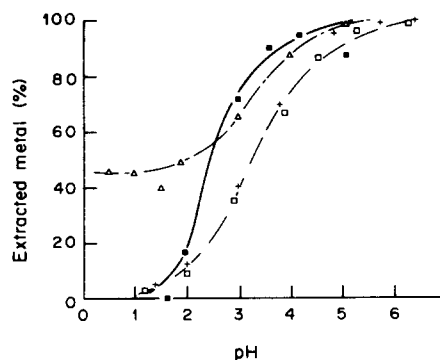


Fig. 7. pH dependence of the metal uptake of oligotrophic peat. Same symbols as Fig. 6.

Although these experiments enable the comparison of the respective metal-peat binding energetics, they also show clearly that the maximum binding capacities in 10 mM metal cation solutions are very similar for the different metals and peats: all values range between 180 and 200 mmol kg⁻¹ dry wt (Table 2). Such a result is not obvious when metal binding experiments are achieved in unbuffered media of pH ranging from 2.2 to 4.2 (Figs 1–5). It demonstrates that metal-peat interactions present the same stoichiometries and that the available binding capacities are similar for eutrophic and oligotrophic peat. The same pH dependence of metal distribution coefficient was demonstrated by Aho and Tummavuori (1984).

Table 2. pH dependence of metal removal by 50 g l⁻¹ dried, unsieved and unacidified peat equilibrated with 10 mM metal cation solutions: pH values for 10, 50 and 90% extraction and maximum capacities observed

| Metal cation | Eutrophic peat | | | | Oligotrophic peat | | | |
|--------------|----------------|-----------|-----------|---|-------------------|-----------|-----|---|
| | pH values for | | | Maximum capacity (mmol kg ⁻¹) | pH values for | | | Maximum capacity (mmol kg ⁻¹) |
| 10% extr. | 50% extr. | 90% extr. | 10% extr. | | 50% extr. | 90% extr. | | |
| Cu | 0.2 | 2.2 | 4.0 | 190 | 1.8 | 2.5 | 3.6 | 190 |
| Cd | 1.5 | 3.1 | 5.6 | 180 | 2.0 | 3.3 | 4.7 | 200 |
| Zn | 1.5 | 3.1 | 6.7 | 170 | 2.0 | 3.3 | 4.7 | 200 |
| Ni | 0 | 1.2–1.6 | 4.5 | 190 | 0 | 1.6–2.0 | 4.0 | 200 |

who worked with peat columns: they found copper binding capacities ranging between 200 and 300 mmol kg⁻¹ using 0.0025 mM Cu²⁺ solutions. Previously, Bunzl *et al.* (1976) had found apparent ion exchange capacities of sphagnum peat at pH 4 equal to 500 mmol Zn²⁺ kg⁻¹ dry wt, 600 Cd²⁺ and 650 Cu²⁺ using 0.01 to 0.5 mM metal solutions. All these metal binding capacities are somewhat smaller than those obtained recently by Gangneux *et al.* (1985) using 100 mM metal cation buffered solutions and 50 g l⁻¹ dry wt eutrophic and oligotrophic peat suspensions: 650–780 mmol Cu²⁺ g⁻¹ dry wt and 1000–1300 mmol Cd²⁺, Zn²⁺ or Ni²⁺ kg⁻¹.

Finally, some metal removal and recovery experiments were performed with copper solutions: within the experimental range of error, i.e. about 5%, the amount of metal fixed on peat, as estimated from the metal removal in solution, was equal to the amount of metal released during the acidification step.

CONCLUSION

Four major results were found during these batch experiments with eutrophic and oligotrophic peat:

(1) Peat is able to strongly bind copper, cadmium, zinc and nickel cations in solution, a maximum capacity of about 200 mmol kg⁻¹ dry wt being obtained at pH larger than 6.7 when the initial metal concentrations equal 10 mM.

(2) The metal removal efficiency in unbuffered solutions is significant in a very large concentration range, i.e. from 0.01 to 100 mM, the maximum extraction ratios being obtained in the 0.1–1 mM range.

(3) Batch reaction rates are such that a residence time seems necessary for a complete treatment of solutions on columns; thus, very thin peat layers or beds as proposed by Lalancette in its French patent of 1972 seem very unlikely to achieve a complete metal removal by complexation, adsorption or ion-exchange.

(4) Except for nickel cation which seems so strongly complexed on peat that at pH 1.2–2 half of the maximum capacity is attained, copper, cadmium and zinc may be easily removed from peat during an acid treatment.

Taking into account the data obtained during these batch experiments, 40 l peat columns have been constructed and their hydrodynamic and chemical properties and characteristics are under investigation.

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