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Adsorption of Cd, Cu, Ni, Pb and Zn on *Sphagnum* peat from solutions with low metal concentrations

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Abstract

This work investigates adsorption of metal ions on *Sphagnum* peat from solutions with environmentally relevant concentrations of metals. The peat moss is intended as an alternative, low-cost filter material for contaminated waters. Adsorption of Cd, Cu, Ni, Pb and Zn was studied in batch tests, and adsorption isotherms were determined. The kinetics of adsorption was analyzed using a second-order model and rate constants were calculated. An empirical model for predicting adsorption of metal ions at a given time was derived from these constants. Metal ions were removed in the descending order Pb>Cu>Ni>Cd>Zn. Relationship between the affinities of the metals to the peat active sites with chemical properties for the metals were indicated by the results. In addition, equilibration studies were performed at constant pH and ionic strength. The experimental data fitted the Freundlich equation. Both the uptake of metals and the Freundlich constants increased in line with increasing pH. The Freundlich exponent declined with higher initial concentrations, suggesting adsorption to sites with lower activity. © 2007 Elsevier B.V. All rights reserved.

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Keywords: Adsorption; Heavy metals; Sphagnum peat; Freundlich isotherm

1. Introduction

Peat moss has been studied as a material for the purification of contaminated waters for over 25 years. It has a high adsorption capacity for heavy metals compared to other natural adsorbent materials [1–3]. The adsorption capacity of peat has been found to depend on the type of peat studied and solution properties, such as pH, metal ion concentration, ionic strength and the presence of other ligands.

The mechanisms for adsorption of metal ions on peat suggested in the literature include physical adsorption, ion exchange, chelating, lone pair electron sharing, chemical reaction with phenolic hydroxyls and similar species [2]. Humic and fulvic acids are considered to be the main metal binding ligands. Evidence of metal complexation involving carboxylic groups, mainly due to the formation of inner-sphere complexes, has been found [4,5]. Experimental data have shown that base cations in the peat matrix and protons in humic substances can be exchanged for metal ions from the solution [6]. The number of protons released per divalent metal ion adsorbed was found to be less than 1 [7,8], 2 [6], or over 2 [9]. Values <1 were attributed to incomplete reaction/adsorption of the metal ions or displacement of other metal ions, whereas values >2 were ascribed to the deprotonation of hydrated metal ions. The aim of most studies on metal adsorption has been to estimate the maximum adsorption capacity of peat. Thus, the metal concentrations used were much higher than those generally observed in natural waters and wastewater. The range of heavy metal concentrations used in previous research is $10-7000 \text{ mg} \text{ l}^{-1}$ [6,10–12], while wastewater typically contains metals at microgram levels and the most contaminated leachates may contain up to $3 \text{ mg } l^{-1}$ of heavy metals, except Zn that may reach $100 \text{ mg} \text{ } \text{l}^{-1}$ [13]. The concentration of metal ions may affect the mechanisms of metals binding to humic acids [8]. Since the results published to date have mainly been obtained using very high metal concentrations, research on adsorption of metals on peat at low metal concentrations,

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as in the work presented in this paper, is needed in order to contribute to a more complete understanding of adsorption mechanisms. Concentrations of metals used in this study are in the range $0.1-5 \text{ mg l}^{-1}$.

Due to the complex structure and chemical composition of peat and difficulties in maintaining strictly controlled experimental conditions, the knowledge of metal adsorption is of an empirical nature. In addition, the results are largely interpretative and vary between studies. In the present work, results from batch experiments, where conditions have been strictly controlled and restricted to change in only one variable at a time, are presented. The ionic strength and pH were kept constant, the initial metal concentration was equal, but the amount of peat and thus the number of active sites varied.

2. Materials and methods

2.1. Kinetic studies

Kinetic experiments are performed to assess the uptake rates and contact times needed for completion of adsorption reactions and can be used to optimise the residence time of contaminated waters in treatment systems.

Gosset et al. [7] developed an empirical expression for the removal of metals by peat, which assumes that desorption is negligible, the peat-metal stoichiometric ratio equals one and the overall kinetics being limited only by the binding reactions and not by the diffusion of species. The expression has been simplified further into a pseudo-second-order model [14]:

$$q_{\rm t} = \frac{q_{\rm e}^2 kt}{(1+q_{\rm e}kt)}\tag{1}$$

when $t \rightarrow 0$, the initial sorption rate becomes

$$h = kq_{\rm e}^2 \tag{2}$$

In these equations, k is the equilibrium rate constant of adsorption $(g \mu g^{-1} \min^{-1})$, q_e is the amount of metal ion sorbed at equilibrium $(\mu g g^{-1})$, h is the initial adsorption rate $(\mu g g^{-1} \min^{-1})$, and q_t is the amount of metal ion on the surface of the adsorbent at time t ($\mu g g^{-1}$).

Eq. (3) can be re-arranged to yield:

$$\frac{t}{q_{\rm t}} = \frac{1}{kq_{\rm e}^2} + \frac{1}{q_{\rm e}}t\tag{3}$$

If the pseudo-second-order kinetics is applicable to the adsorption system, the plot of t/q_t against t of Eq. (3) gives a linear relationship. The values q_e and k can be determined from the slope and intercept on the Y-axis of the plot.

The pseudo-second-order model has been applied successfully to adsorption of metals on peat and was used in this study [15,16].

2.2. Equilibrium studies

The simplest mathematical model describing adsorption is an isotherm equation. The two most commonly used are the Lang-

muir and Freundlich equations. The Langmuir isotherm model has limited applicability at low liquid-phase concentrations [17]. In this study, the metal concentrations were low, and the Langmuir isotherm was thus found to be inapplicable. The Freundlich isotherm was employed, since it adequately describes adsorption in dilute solutions.

The Freundlich isotherm equation may be written as:

$$q = K_{\rm F} C^n \tag{4}$$

or in linear form

$$\log q = \log K_{\rm F} + n \log C \tag{5}$$

where *q* is the solid-phase $(\mu g g^{-1})$ and *C* the liquid-phase concentration $(\mu g l^{-1})$; K_F is the Freundlich unit-capacity coefficient $(\mu g g^{-1})$ and $n (\mu g l^{-1})$ the adsorption exponent, representing the energy distribution of the process. The values of K_F and *n* can be determined from the intercept and slope of the plot of log *q* versus log *C*.

2.3. Adsorption experiments

Six series of adsorption experiments were conducted using a batch laboratory procedure with a variable *L/S* ratio and constant initial concentration of adsorbate:

- 1. Kinetic experiments, pH 4.0.
- 2. Evaluation of the reproducibility of the experimental methodology, pH 4.0.
- 3. Study of the effect of peat pre-treatment by water-washing, pH 4.0.
- 4. Study of the effect of the buffer solution, pH 4.0.
- 5. Study of pH influence on adsorption at pH 4 and 5.6.
- 6. Study of the effect of metal concentration on adsorption, pH 7.0.

Single-metal solutions were used in all the experiments in order to eliminate competition between metals and study mechanisms of adsorption for each metal. Research on adsorption of metals onto peat from multi-metal solutions and real contaminated water is presented elsewhere [3]. Three different pH conditions, i.e. 4.0, 5.6 and 7, were used in order to study influence of pH on adsorption. The pH of contaminated waters lies usually in the range 4.5–8 [13]. Most of the experiments were conducted at pH 4 as peat buffers contaminated waters to around pH 4 [3].

The kinetic experiments were run for a total of 30 h. Samples for metal analysis were taken every 10 min during the first half hour, followed by every 30 min for 2.5 h, and then every third hour. Experiments 2–6 were run for 12 h. Peat amounts of 0.1, 0.25, 0.5, 1 and 2 g and 500 ml of 100 μ g l⁻¹ single-metal solutions were used in all experiments. The metal solutions with Me²⁺-ions were prepared from high purity ICP-MS standards of 1000 mg l⁻¹ metal nitrate. Experiments 1 and 5 were conducted for Cd, Cu, Zn, Ni and Pb, whereas experiments 2–4 were only carried out for Pb. Cadmium solutions of 0.1, 0.2, 0.5, 1 and 5 mg l⁻¹ were used in Experiment 6. Final solutions were filtrated through 0.45 μ m acetate cellulose filters, preserved by 1% of supra-pure HNO₃ and stored at +4 °C until analysis. The metal concentrations in the solutions were measured by ICP-MS. A multi-element standard (Merck XI CertiPUR) was employed for calibration and 1 mg l⁻¹ rhodium solution as an internal standard.

2.4. Adsorbent material

The physical and chemical properties of the peat were characterized using standard procedures [18]. The peat was dried at $50 \,^{\circ}$ C, ground, sieved and the 0.25–0.5 mm particles were used. The peat was washed with ultra pure water in order to remove soluble organic matter.

2.5. Adsorbates

Adsorbate solutions were buffered with sodium acetate in order to obtain stable pH conditions. Sodium acetate was considered the most appropriate buffer system for the present study, based on results of speciation simulations by CHEAQS Pro software[19] and findings from a literature review. This buffer forms two complexes, the MeCH₃COO⁺ and Me(CH₃COO)₂. However, the metal-acetate complexes have large dissociation constants [20], which indicates that they will dissociate when free metal ions are removed from the solution due to adsorption on the peat.

Solutions with 0.02, 0.05 and 0.07 M sodium acetate as a buffer did not maintain the pH of the experimental peat mixtures constant. Instead, the peat was treated with a 0.25 M buffer for 30 min, which was then removed by filtering and mixed with a 0.02 M buffer solution. This pre-treatment procedure made it possible to keep the pH of the experimental solutions stable. The influence of the acetate buffer on adsorption of metals on peat was investigated by comparing the adsorption of Pb in three systems: one without a buffer and with manually controlled pH, one with peat pre-treated with 0.25 M buffer with subsequent manual control of the pH, and one with peat equilibrated in 0.25 M buffer and used in a Pb adsorption experiment in 0.02 M buffer. A 2% increase in Pb uptake was obtained in the system comprising peat pre-treated with 0.25 M acetate buffer. Other effects of buffer pre-treatment are an additional release of soluble organic acids and a cation exchange where H⁺ in carboxylic and hydroxyl groups is substituted by Na⁺. Depending on the increase in pH as a result of buffer treatment, the peat macromolecules will become more negatively charged. The molecules will repel each other and the structures will be more uncurled, resulting in a greater number of active sites for adsorption of metals.

2.6. Reproducibility of the experimental procedure

The reproducibility of the general experimental method was evaluated by carrying out two sets of experiments in triplicate. In these experiments adsorption of Pb at pH 4 by untreated as well as water-washed peat was studied. Relative standard deviations (RSD) were calculated for the experimental and derived data. Since the RSD values obtained were all below 1%, the main part of the work was performed with washed peat and in single experiments.

3. Results and discussion

3.1. Physical and chemical characteristics of Sphagnum peat

The physical and chemical properties of the untreated peat are presented in Table 1. The material has an acidic pH, high moisture content and a low decomposition level, as indicated by the von Post scale. It has a low bulk density and high hydraulic conductivity, which indicates good permeability and suitability as a filtering medium. The trace metal content is low and comparable to that in the peat used by other authors [10-12]. The measured cation exchange capacity (CEC) is considerably lower than that of other peat types described in the literature. This is probably due to the lower degree of degradation of this peat. The organic acids in the peat consist of 78% humic and 22% fulvic acids. If the peat had been more decomposed, the fulvic acid content would have been greater. Since the specific surface area and the content of proton donating groups of a typical fulvic acid are almost twice that of a humic acid, it could have resulted in a higher cation exchange and adsorption capacity.

3.2. Kinetics

The adsorption process was said to be in steady state or equilibrium when no changes in the metal concentration of the solution greater than 0.5% of the initial concentration were

Table 1

Physical and chemical characteristics	of Sphagnum peat from Southwest Sweden ^a
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Decomposition degree ^b	pН	Water content (%)	Bulk density $(g \text{ cm}^{-3})$	Fiber content (%)	Hydraulic conductivity ^c (cm min ⁻¹)	CEC ^d (meq kg ⁻¹) DS	Humic acids (%)	Fulvic acids (%)
H3	4.0	83.6	0.095	77.5	0.034	309	78.0	22.0
Metal content $(\mu g g^{-1}) DS$		Cr 1.20	Zn 59.3	Pb 11.4	Ni 4.00	Cu 23.0	Cd 0.40	Fe 1430

^a Ljungby.

^b von Post scale.

^c Saturated hydraulic conductivity.

^d Cation exhange capacity.



Fig. 1. Experimental and modelled data of adsorbed amount of metal ions vs. time.

observed. In the case of Pb, steady state was reached in 20 min and for Cd and Cu in 1 h, whereas for Ni and Zn it took 1.5 and 2 h, respectively. Most authors agree on an equilibration time of 20–60 min for divalent metals in adsorption experiments [1]. In the present work, a contact time of 12 h was chosen to ensure that equilibrium was reached.

Using the experimental data to construct a plot of t/q_t versus t, see Fig. 1, yielded a linear relationship, which indicates that pseudo-second-order kinetics is applicable to the adsorption system studied. The regression coefficients were all 1.00, showing that the data employed in this study fit the model very well. A comparison with published data obtained for high metal concentrations $(25-200 \text{ mg l}^{-1})$ [14] shows that the pseudo-second-order model describes adsorption of metals better at low concentrations $(0.1-5 \text{ mg l}^{-1})$ than at high ones. This can be confirmed by analysis of the model, derived from the expression obtained by [7] and allowing the equilibrium liquid-phase concentration to approach zero, similar to the experimental conditions in this study. These findings suggest that chemical adsorption is the main active sorption mechanism.

The constants in the pseudo-second-order model (Eq. (3)) were determined from the slopes and intercepts of the plots and are presented in Table 2. The values of the initial sorp-

tion rates, *h* in Eq. (2), were found to decrease in the order Pb > Cd > Cu > Ni > Zn, with Pb having about a five times higher initial adsorption rate than the rest of the metals. The order was found to be the same using mass or molar unit. The adsorption capacity was nearly identical for all metal ions. A slight decrease in the order $Cu \ge Pb > Cd > Ni > Zn$ was observed. The adsorption capacities obtained in the equilibrium experiments were found to decrease in the same order.

Based on the excellent fit with experimental data, the pseudosecond-order model was used to predict sorption rates for metal adsorption on peat. The empirically obtained kinetic constants were used in Eq. (1), and the rate expressions obtained were employed to derive values of the amount of metals adsorbed, q_t , at a given time t as presented in Table 2.

3.3. Equilibrium studies

Experimental data were evaluated by means of the Freundlich isotherm model. It was found that this model describes the adsorption processes relatively well, with regression coefficients (R^2) close to 1, as shown in Table 3.

The uptake of metal ions decreased in the order Pb > Cu > Ni > Cd > Zn. These differences in affinity to the sorbent surface can be due to dissimilar adsorption mechanisms. Humic and fulvic acids are considered to be the main metal binding ligands in peat, and the major binding sites are carboxylic and phenolic functional groups. However, other less abundant functional groups, containing nitrogen or sulphur, may also be active [21]. The binding of Cu is believed to differ from other metals, as it forms ring shaped complexes with multi-dentate chelating compounds, in contrast to Pb, Cd and Ni, which exhibit 1:1 stoichiometric relations [22,23]. In addition, most of the Cu binding in peat is attributed to phenolic sites, whereas carboxylic sites dominate in the binding of Pb, Ni and Zn.

The different affinity of certain metal ions to adsorption sites in peat can also be explained by their chemical properties [24,25]:

1. The size or ion radius (*r*) and charge (*z*) of the metal ion, which can be expressed as the ionic potential (Ip = z/r).

1.000

1.000

Rate expression^e (q_t =)

16.19

(1+0.689t)10.90t

 $\frac{10.90t}{(1+0.436t)}$

 $\frac{10.21t}{(1+0.422t)}$

 $\frac{1}{(1+2.084t)}$

(0.382t)

- 2. The electronegativity of the element.
- 3. A classification based on

10.21

51.69

Second-ord	Second-order rate constants for adsorption of metals onto peat						
	$k^{\rm a}$ (g µg ⁻¹ min ⁻¹)	$q_{\rm e}^{\rm b}$ (µg g ⁻¹)	$h^{\rm c}$ (µg g ⁻¹ min ⁻¹)	<i>R</i> ^{2d}			
Cd	0.029	23.50	16.19	1.000			
Cu	0.017	25.02	10.90	1.000			
Zn	0.017	22.63	8.657	0.9990			

24.17

24.81

^a k = equilibrium rate constant of adsorption.

0.017

0.084

^b q_e = amount of metal ion adsorbed at equilibrium.

^c \hat{h} = initial adsorption rate.

^d R^2 = regression coefficient.

 $e_{q_t} = \frac{q_e^2 kt}{(1+q_e kt)}.$

Table 2

Ni

Ph

Metal pH 4.0					pH 5.6						
	Uptake	ke Adsorption constants		R ^{2d}	Uptake (%)	Adsorption constants					
(%) ^a	$\overline{K_{\mathrm{F}}^{\mathrm{b}}}$	n ^c	-	K _F		n					
Cd	95.2	1.83	1.15	0.999	99.1	4.85	1.24	0.969			
Cu	97.6	3.03	1.46	0.839	97.3	2.88	1.46	0.840			
Zn	92.2	1.33	1.27	0.992	99.4	4.39	0.81	0.962			
Ni	96.8	2.35	1.08	0.998	98.7	4.00	1.44	0.957			
Pb	99.3	6.02	1.19	0.620	99.6	9.06	1.66	0.955			

Table 3	
Removal efficiency and Freundlich coefficients of metal adsorption onto per	at

^a % = percentage adsorbed.

^b $K_{\rm F}$ = Freundlich unit-capacity coefficient (µg g⁻¹).

^c n = Freundlich exponent (g l⁻¹).

^d R^2 = regression coefficient.

a. The electron configuration of the cations.

- b. The hard and soft acid and base (HSAB) behaviour of cations and ligands.
- 4. Ligand field stabilization energy (LFSE) effects in the metal-peat complexes.

Table 4 summarizes the above-mentioned characteristics of the metals used in this study as well as the corresponding stability constants for metal-humic acid [26] metal-fulvic acid complexes [27]. The series of affinities from the result of this study is in good agreement with experimentally obtained stabilisation constants for metal-humic/fulvic acids complexes.

The Irving–Williams order [28] is based on empirical observation and related to both the increase in effective nuclear charge in line with atomic number, due to imperfect shielding by the electrons, and ligand field stabilization energy (LFSE) effects [29]. The results of this study are in agreement with

the Irving–Williams order for Ni²⁺ < Cu²⁺ > Zn²⁺. Copper and nickel ions that form complexes with high-spin configurations (Table 4) are subject to the LFSE effects and have a strong tendency to form stable complexes with peat. Cadmium and zinc ions form complexes in low-spin configurations and thereby more unstable complexes with peat than Cu²⁺ and Ni²⁺. According to the theory of hard and soft acids and bases (HSAB) [30] the class C cations [31] Pb²⁺, Cu²⁺ and Ni²⁺ form stronger complexes with humic/fulvic acids than class B cations such as Cd²⁺ and Zn²⁺. The affinity of the metals to a certain ligand on the peat surface can also be expected to increase in line with increasing electronegativity (Table 4), which seems to be true for Cu²⁺, Ni^{2+,} Cd²⁺ and Zn²⁺, but not Pb²⁺.

In general, the tendency of cations to form inner-sphere complexes with a given ligand increases with increasing ionic potential (Ip, charge to radius ratio). For a group of divalent metal ions this means that the smaller the radius of the ion, the more

Table 4

The affinity order of the metal complex formed with peat in terms of stability constants and the chemical characteristics of the metal ions

Characteristics

	Metal ions in peat co	mplex, affinity order:						
Stability constants with humic acids ^a	$Pb^{2+} > Cu^{2+} > Ni^{2+} > Cd^{2+} > Zn^{2+}$							
	3.66	5.25	3.20	2.78	2.74			
Stability constants with fulvic acids ^b	-	3.3/3.4	3.1/3.2	_	2.4/2.3			
Electron configuration	5d ¹⁰ 6s ² 6p ⁰	$3d^{9}4s^{0}$	$3d^84s^0$	4d ¹⁰ 5s ⁰	3d ¹⁰ 4s ⁰			
LFSE ^c – electron configuration in complexes ^d	_	High-spin config- uration \rightarrow stable complexes	High/low-spin configuration → stable or unstable complexes	Low-spin configura- tion → unstable complexes	Low-spin configura- tion → unstable complexes			
Electronegativity ^e Pauling scale	1.60	2.00	1.91	1.69	1.65			
Schwarzenbach's classes f	-	Class C	Class C	Class B	Class B			
Pearson's HSAB ^g	Between hard/soft	Between hard/soft	Between hard/soft	Soft	Soft			
Ionic radius ^e (pm)	119	73	69	95	74			
Ionic potential ^e	1.68	2.74	2.90	2.11	2.70			

^a log *K*, *I* = 0.1, pH 3.5 (Pandey [26]).

^b log *K*, *I*=0.1, pH 3.5(Faust and Hunter [27]).

^c LFSE = ligand field stabilization energy.

^d In square planar, octahedral or tetrahedral complexes.

^e Langmuir [24], Ip = charge to radius ratio.

f Schwarzenbach [31].

^g HSAB = hard and soft acids and bases (Pearson [30]).

likely it is to be found in an inner-sphere complex within peat active sites. Inner-sphere complexes are usually much stronger than ion pairs, e.g. outer-sphere complexes associated with a hydrated cation and an anion held by long-range electrostatic forces. This does not apply exactly to the data upon which this work is based, thus indicating the importance of other properties. For example, despite its low Ip, the Pb²⁺-ion exhibits a great affinity to peat, probably due to binding to specific chelating groups in the peat. The strong affinity of lead ions to peat may also be explained by their borderline acid properties, or the fact that the two electrons in the 6th level electronic layer are easily divided by a ligand in a complex. Due to the large ion size of Pb²⁺, the electrons are easily polarised and to a lesser degree retained by the nucleus. Lead may also be sterically trapped in the peat macromolecules because of the large size of the ion.

3.4. pH dependence

Three pH levels were used in the present experiments; i.e. 4.0, 5.6 and 7. Adsorption of all the five metals was studied at pH 4.0 and 5.6 but only Cd adsorption was studied at pH 7. The results indicate that the Freundlich constants and the uptake of metals increase with increasing pH (Table 3). The release of H⁺/Na⁺ from carboxylic and phenolic groups increases with increasing pH, and negatively charged macromolecules also repel each other, making a greater number of active sites available for adsorption of other metal ions. The metal uptake trends obtained at pH 4.0 and 5.6 were somewhat different, which may suggest other adsorption mechanisms, as the activation of sites on peat is pH dependent. At pH 4.0, metal ions were adsorbed in the descending order Pb > Cu > Ni > Cd > Zn, which is in good agreement with other results reported [12,14,32,33]. The order of adsorption capacity at pH 5.6 was Pb>Cd>Zn>Ni>Cu. The higher Cd adsorption combined with constant Cu adsorption may be due to several reasons. Cadmium adsorption to phenolic groups is favored at high pH and low Cd concentrations [8]. Adsorption of Cu is more specific and less dependent on pH and concentration levels and reaches a maximum in the pH range 4-5 [34].

3.5. Effect of initial metal concentration

Results reported for metal binding on peat humic acids suggest that the binding mechanisms may depend on the metal ion concentration [8]. The contribution of carboxylic and phenolic sites to the overall Cd, Ca and Cu binding on peat humic acid at pH 6 and 8 is that Cd and Cu were mainly bound to carboxylic sites at high concentrations and to phenolic sites at low concentrations. Benedetti et al. [8] also showed that adsorption mechanisms are reflected in changes in H⁺/Me²⁺ molar exchange ratios. This ratio was found to be lower than 1 for Cd and Ca and decreases from 0.9 to 0.3 with increasing metal concentration. The same trend was found for Cu, but the exchange ratio was always larger than 1, ranging from 1.8 to 1.3.

No significant trend in adsorption capacity K_F with increasing concentration of Cd was found in the present work, as shown in Fig. 2 and Table 5. On the other hand, the Freundlich



Fig. 2. Freundlich isotherms of Cd adsorption on peat at pH 7 for different initial concentrations.

Table 5

Cadmium uptake and Freundlich coefficients for various initial concentrations

Cd, C_0 (µg l ⁻¹)	$K_{\rm F}$	n	R^2	Adsorbed (%)
100	5.00	1.39	0.97	97.3
200	4.84	1.11	0.98	96.6
500	6.21	0.76	0.95	94.6
1000	3.91	0.98	0.96	92.7
5000	5.57	0.75	0.97	86.6

exponent n, characterizing preferential adsorption, decreased with increasing concentration, which is in agreement with other results reported in the literature [17]. A possible explanation may be that, at low metal concentrations, metal ions are initially adsorbed by the high affinity sites, but at higher concentrations they also have to occupy sites with lower affinity. The uptake decreased slightly with higher initial concentration as adsorption sites became increasingly saturated.

3.6. Precision of the methodology

The pre-treatment of the peat by washing with water greatly improved the reproducibility of the experimental data. The relative standard deviation (RSD) level decreased about 10 times after washing. In the case of experiments carried out with dry peat, the values of equilibrium concentration *C* varied between 10 and 30%, whereas the percentage of adsorbed metal and the amount of metal adsorbed at equilibrium (*q*) varied between 0.2 and 2.2%. The values of K_F and *n* varied between 15 and 18%. In the experiments conducted with washed peat, *C* only varied between 2 and 5%, the percentage of adsorbed metal and *q* between 0.02 and 0.2% and the K_F , *n* values between 7 and 8%. It was observed that RSD was lower for experimental data, i.e. *C*, the percentage of adsorbed metal and *q*, than for data derived by linear approximation (K_F and *n*).

4. Conclusions

Kinetic and equilibrium studies on metal ion adsorption on peat moss were carried out under carefully controlled parameters. Adsorption of five metals in single-component dilute solutions at pH 4 and 5.6 was adequately described by the Freundlich isotherm equation, and Freundlich constants were obtained. The affinity of the metal ions to adsorption sites decreased in the order Pb > Cu > Ni > Cd > Zn, which accorded well with the results reported by other authors. In addition, the possible influence of some properties of the metal ions on their affinity to the adsorption sites and their binding mechanisms were discussed.

The adsorption of Cd showed a decrease in the Freundlich exponent with increasing metal ion concentration in the water phase, which suggests that less favourable sites on the peat are increasingly used at higher ion load. The metal adsorption capacity of the peat generally increased in line with pH.

The kinetics of adsorption followed the pseudo-second-order model, and rate constants were calculated using that model. From these constants, empirical rate equations were derived for prediction of the adsorption capacity of metal ions at a given time. The fit of experimental data to the pseudo-secondorder model obtained in this study was better than others reported in the literature. This suggests that the model better describes adsorption at low than at high metal concentrations.

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