Mechanisms of competitive adsorption of Pb, Cu, and Cd on peat

Fei Qin ^{a,b}, Bei Wen ^a, Xiao-Quan Shan ^{a,*}, Ya-Ning Xie ^c, Tao Liu ^c,
Shu-Zhen Zhang ^a, Shahamat U. Khan ^d

^a State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences,
Chinese Academy of Sciences, P.O. Box 2871, Beijing 100085, China

^b Department of Biology, College of Art and Science, Beijing Union University, Beijing 100049, China

^c Beijing Synchrotron Radiation Laboratory, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, China

^d Department of Chemistry and Biochemistry, MSN 3E2, George Mason University, 4400 University Drive, Fairfax, VA 22030-4444, USA

Received 1 July 2005; accepted 29 December 2005

*X-ray absorption spectroscopic study provided an evidence for the competitive adsorption
mechanism of Pb, Cu, and Cd on peat.*

Abstract

Combined use of batch equilibration adsorption and X-ray absorption spectroscopy (XAS) was employed to study the mechanisms of competitive adsorption of Pb, Cu, and Cd on Danish and Heilongjiang peat in single- and multi-solute systems. The adsorption capacity and initial adsorption rate on the same peat in single-solute systems followed the order Pb > Cu > Cd. Both the adsorbed amount of each metal (q'_m) and its initial adsorption rate were decreased in multi-solute systems. It was observed that the adsorbed amounts of metals at low-energy adsorption sites ($q_{m,1}$) decreased pronouncedly compared to those at high-energy adsorption sites ($q_{m,2}$), indicating that the competitive adsorption of Pb, Cu and Cd occurred mainly at the low-energy adsorption sites. XAS study revealed that both Pb and Cu were coordinated in peat predominantly to carboxylic moieties without excluding the hydroxyl groups, thereby providing an insight into the mechanism of competitive adsorption of Pb and Cu on peat.

© 2006 Elsevier Ltd. All rights reserved.

Keywords: Peat; Heavy metals; Competitive adsorption; Kinetics; X-ray absorption spectroscopy

1. Introduction

Heavy metals are generally considered as a threat toward humans health and ecosystems because of their potentially high toxicity. Unlike organic pollutants, heavy metals do not undergo biological degradation and tend to accumulate in the organisms, thereby eventually entering the food chains. Lead, copper, and cadmium belong to the group of serious hazardous heavy metals. Due to their high toxicity various government agencies have imposed strict and more stringent environmental legislations on wastewater discharges. Removal of heavy metals from wastewater has been a subject of major concern to scientists for many years.

Among various methods applied for the removal of colloidal and dissolved heavy metals from aqueous solutions, adsorption onto low cost particulate media, such as peat, now offers an attractive, inexpensive option. Peat is a natural substance with lignin, cellulose, and humic materials as its major constituents (Yonebayashi et al., 1994). These constituents feature the presence of polar functional groups such as aldehydes, ketones, and carboxylic, hydroxylic, phenolic acid groups in their molecular structure, which can all be involved in heavy metal adsorption. Because of the polar character of peat, it appears to have a good potential for adsorption of metals and polar organic molecules.

In general, contaminated water contains more than one heavy metal. From the point of view of environmental protection, adsorption studies from multi-metal systems to which much work has been dedicated are imperative. Mohan and

* Corresponding author. Tel.: +86 10 62923560; fax: +86 10 62923563.

E-mail address: xiaoquan@rcees.ac.cn (X.-Q. Shan).

Singh (2002) and Ko et al. (2004) used Langmuir and Freundlich models, and Sip equation to examine the competitive adsorption of metals on activated carbon and bone char in multi-solute systems. Jeon et al. (2003) and Hanzlík et al. (2004) studied the adsorption kinetics of metals on hematite, natural carbonaceous materials and peat, respectively. Xiao and Thomas (2004) and Serrano et al. (2005) investigated the competitive adsorption of metals based on the batch equilibration adsorption and adsorption kinetic studies. However, the above-mentioned studies were based only on macroscopic observations. Very little information is available on the adsorption sites involved in the competitive adsorption of heavy metals and no direct evidence has been provided for the competitive adsorption of metals on peat.

X-ray absorption spectroscopy (XAS) has been shown to be a versatile structural probe for studying the local environmental conditions for the adsorption of metals and metalloids on different matrices. XAS provides unique structural data that cannot be duplicated by other methods. Xia et al. (1997) used XAS to demonstrate the formation of inner-sphere complexes of Pb and Cu with soil humic substances. Strawn et al. (1998) combined the kinetic study with XAS to investigate the interaction between Pb and aluminum oxides. They found that Pb formed an inner-sphere bidentate complex and the local atomic structure surrounding Pb was not changed with time. Lin et al. (2004) used XAS to explain the increased sorption of Cu and phosphate in binary solute systems. Ramstedt et al. (2005) combined batch adsorption and XAS to examine the co-adsorption of Cd and glyphosate at water–manganite interface. They observed that binary inner-sphere PMG–manganite, Cd(II) manganite surface complexes and ternary Cd(II)–PMG–manganite species were formed.

To our knowledge it seems that there is no report on the combined use of batch equilibration adsorption method with XAS to probe the mechanisms of competitive adsorption of heavy metals on peat. Therefore, the aim of this study was to reveal the mechanisms of the competitive adsorption of Pb, Cu, and Cd on Danish and Heilongjiang peat in single- and multi-solute systems by using an equilibrium adsorption method in combination with XAS.

2. Materials and methods

2.1. Peat characterization

Heilongjiang peat (China) was purchased from Beijing Forestry University and Danish peat was supplied by Northeast China Normal University. They were dried for 24 h at 105 °C, then sieved to pass through a 100-mesh sieve and finally homogenized. The typical characteristics of peat were determined by the methods of Nelson and Sommers (1996) and Sumner and Miller (1996). Elemental analysis was performed using a FLASH EA1112 micro-analyzer. Humification degree of peat was expressed by the ratio of C to N (C/N) (Balabane and van Oort, 2002). The selected properties of peat are listed in Table 1.

2.2. Effect of pH on Pb, Cu, and Cd adsorption on peat

A portion of the peat sample (0.100 g) was mixed with 20 ml of 0.01 mol l⁻¹ NaNO₃ in a 50 ml polypropylene centrifuge tube. Suspension pH values of approximately 2–8 were attained by adding either HNO₃ or

Table 1
Selected characteristics of peat

Characteristics	Danish peat	Heilongjiang peat
pH	4.10	6.45
C (%)	45.9	32.8
N (%)	0.68	2.12
H (%)	5.64	3.71
C/N	67.5	15.5
CEC (cmol kg ⁻¹)	61.7	53.4
OM (%)	59.5	48.6
DOC (μg g ⁻¹)	104	117
BET surface area (m ² g ⁻¹)	13.3	9.67

NaOH. During the shaking, the pH values were measured at certain intervals and readjusted if necessary. An aliquot of Pb, Cu, and Cd (50 μl) as nitrate salts was then added to get the initial metal concentration of 1 × 10⁻⁴ mol l⁻¹, pH of the suspension was adjusted again and then shaken for another 24 h. At the end of the shaking period, the pH of suspension was measured and then filtered through a 0.45 μm cellulose acetate membrane. The experiments were carried out in duplicate.

2.3. Adsorption isotherms

Single, binary and ternary solute adsorption of Pb, Cu and Cd by peat was performed by a batch equilibrium technique at room temperature. Briefly, 0.100 g of peat and 20 ml of Cu(NO₃)₂, Cd(NO₃)₂, or Pb(NO₃)₂ solution were added in 50 ml polypropylene centrifuge tubes. A soil background electrolyte of 0.01 mol l⁻¹ NaNO₃ was used and the pH of the system was maintained at 6.0. For Pb, Cu and Cd adsorption in binary and ternary solute systems, the initial molar concentration of each metal was the same as that in single-solute systems. The samples were shaken end-over-end for 24 h, centrifuged at 4000 g for 30 min and then filtered. The adsorbed amounts of metals were calculated by the difference between the initial and final concentrations remaining in the equilibrium filtrate after adsorption. All the measurements were made in duplicate. For each sample, an experiment without adsorbent was performed to test possible adsorption and/or precipitation of metals onto the container walls. Preliminary experiments showed that metal losses due to the adsorption onto the container walls and to the filter paper were negligible. The adsorption isotherm experiments were repeated in triplicate and the average values were reported.

2.4. Adsorption kinetics

Pb, Cu, and Cd adsorption kinetics in single- and multi-solute systems on peat were also conducted by batch equilibrium method detailed in Section 2.3. The initial concentration of each metal was 2 mmol l⁻¹. After the samples were shaken end-over-end for 24 h, the suspensions were filtered and the metal concentrations in the filtrates were determined. The adsorption kinetic experiments were performed in triplicate.

2.5. Metal analysis

The concentrations of Pb, Cu, and Cd in the filtrates after adsorption were determined by inductively coupled plasma mass spectrometry (ICP-MS, PQ3, Fisons Instruments, UK). The operating conditions were optimized and ¹¹⁵In was used as internal standard to compensate for matrix suppression and signal drifting during metal determination. The detailed operating conditions of ICP-MS were reported previously (Wang et al., 2003).

2.6. X-ray absorption spectra measurements and data analyses

Wet pastes (Danish peat) obtained after adsorption of Cu and Pb as described above were loaded into Teflon sample holders and sealed with Kapton

tape. XAS spectra at Cu K-edge (8979 eV) and Pb L₃-edge (13,066 eV) were obtained at the 4W1B beamline of the Beijing Synchrotron Radiation Facility (BSRF) using a Si (111) double crystal monochromator. The storage ring was operated at 2.2 GeV with a beam current of 80 mA. To suppress the unwanted harmonics, the monochromatic crystal faces were detuned, reducing the incident beam by 30%. The XAS spectra for all adsorption samples were recorded in fluorescence mode at room temperature. The reference compounds of Cu(OH)₂, Cu(CH₃COO)₂, Pb(CH₃COO)₂ and α-PbO powders together with Cu(NO₃)₂ and Pb(NO₃)₂ aqueous solutions were recorded in transmission mode. Three scans were collected and averaged for each sample to obtain a signal-to-noise ratio sufficiently high for EXAFS analysis. Energy calculation was monitored with a Cu or Pb metal foil.

Data analysis was performed with WinXAS2.1 following standard procedures. A polynomial preedge function and a cubic spline were subtracted from each averaged spectrum and the data normalized. Resulting data of Cu and Pb were Fourier transformed over k range 2–12 Å⁻¹ and 2–11 Å⁻¹, respectively. For the fitting of Cu, the coordination number (N) was fixed while the scale factor (S_0^2), atomic distance (R), energy offset (E_0), and Debye–Waller factor (σ^2) were allowed to float freely. For the fitting of Pb, the scale factor (S_0^2) was fixed to 0.8 (Ostergren et al., 2000). Phase shifts and backscattering amplitudes were obtained from the theoretical calculation using FEFF7.0.

2.7. Adsorption models

2.7.1. Adsorption isotherms

The adsorption equilibrium models of Langmuir one-site, Langmuir two-site and Freundlich models were used. The above three models are given, respectively, as follows:

$$q_e = \frac{b q_m C_e}{1 + b C_e} \quad (1)$$

$$q_e = \frac{b_1 q_{m,1} C_e}{1 + b_1 C_e} + \frac{b_2 q_{m,2} C_e}{1 + b_2 C_e} \quad (2)$$

$$q_e = K_F C_e^{1/n} \quad (3)$$

where C_e (mmol l⁻¹) and q_e (mmol g⁻¹) are the equilibrium adsorbate concentrations in the aqueous and solid phases, respectively; q_m is the maximum adsorption capacity (mmol g⁻¹); $q_{m,1}$ and $q_{m,2}$ are the maximum populations of adsorption sites for two different sites, respectively; b , b_1 , and b_2 are the adsorption equilibrium constants; K_F is the equilibrium constant indicative of adsorption capacity and $1/n$ is the adsorption constant whose reciprocal is indicative of adsorption intensity. For the fitting of Langmuir two-site model, the total adsorption maximum capacity, q'_m , should be:

$$q'_m = q_{m,1} + q_{m,2} \quad (4)$$

2.7.2. Adsorption kinetic models

Pseudo-second-order model developed earlier by Ho and McKay (2000) for the adsorption systems of divalent metal ions using sphagnum moss peat was adopted. Its rate law is expressed as:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \quad (5)$$

Integrating Eq. (5) for the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, Eq. (5) was rearranged to obtain a linear form:

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

where q_e and q_t are the amounts of solute adsorbed by adsorbent at equilibrium and at time t , k is the rate constant. In the limit $q_t/t \rightarrow 0$, the initial adsorption rate, h , is given by $h = k q_e^2$. Thus Eq. (6) can be rearranged to obtain

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \quad (7)$$

The plot of t/q_t against t of Eq. (7) should give a linear relationship with a slope of $1/q_e$ and an intercept of $1/h$, or $1/k q_e^2$.

The goodness of fitting of the above-mentioned models was verified using the approaches of Alves and Lavorenti (2004) by the following equation:

$$S.E. = \left[\sum (q - q^*)^2 / (n - 2) \right]^{1/2} \quad (8)$$

where S.E. represents standard error, q is the measured metal adsorbed; q^* is the predicted metal adsorbed by models; and n is the number of experimental points.

3. Results and discussion

3.1. Effect of pH on the adsorption of Pb, Cu, and Cd on peat

Adsorption of Pb, Cu, and Cd increased with the increase of pH from 2 to 8 (Fig. 1). There was no obvious difference in adsorption of metals on the Danish and Heilongjiang peat. The pH value, at which 50% of the initial heavy metal ions were adsorbed, termed as pH₅₀ (Wang and Xing, 2004), is a measure of the relative affinity of metal cations for adsorbent surface. Lower pH₅₀ indicates higher affinity of metals for the adsorbent surface. The results suggest that the affinity of Pb for peat were higher than that of Cu and Cd. The respective

Fig. 1. Effect of pH on Pb (▲), Cu (■) and Cd (★) adsorption on (a) Danish and (b) Heilongjiang peat.

optimum pH for adsorption of Pb, Cu, and Cd on peat was graphically determined as 4, 4, and 6, which correlated with the results of Brown et al. (2000) and Ringqvist et al. (2002). The different maximum adsorption pH of Pb, Cu, and Cd highlights the importance of pH in the treatment of wastewaters containing different metals. In the following adsorption isotherm and kinetic studies, the pH of the systems was adjusted to 6.0.

3.2. Adsorption isotherms of Pb, Cu, and Cd on peat in single-solute systems

Langmuir one-site, Langmuir two-site, and Freundlich models fit the adsorption isotherms of Pb, Cu and Cd on peat in single-solute systems. The fitting parameters and S.E. are summarized in Table 2. It will be noted that the best fitting was obtained by the Langmuir two-site model. The Freundlich model adequately described the experimental data, but not better than the Langmuir one-site and Langmuir two-site models. This is in agreement with the work by Sharma and Forster (1993). The Langmuir two-site model was developed on the basis of the Langmuir one-site model to solve the heterogeneity problem of adsorption sites. It has been successfully applied to represent equilibrium adsorption data of Cd onto bone char (Cheung et al., 2001), and Pb onto activated carbon (Machida et al., 2004). Table 2 shows that the adsorption capacities (q'_m) were higher for Danish peat than those for Heilongjiang peat. This preference of adsorption exhibited by Danish peat over Heilongjiang peat was due mainly to the higher CEC, organic matter content and BET surface areas (Table 1). For the three metals, the adsorption capacity followed the order of Pb > Cu > Cd, which may be attributed to their different adsorption affinities. The adsorption affinities

are tentatively correlated to their properties such as hydrated radius, electronegativity and softness.

The equilibrium constant b_2 value was much higher than b_1 , indicating that the surface of peat was heterogeneous. The high-energy sites with high equilibrium constant (b_2) had a significantly higher affinity than that for low-energy sites with low equilibrium constant (b_1). The high-energy sites on which metals were tightly held had a low adsorption maximum ($q_{m,2}$), accounting for 30.1%, 26.0% and 23.5% of total Pb, Cu or Cd adsorption on Danish peat, respectively. The low-energy sites on which metals were loosely held had a high adsorption maximum ($q_{m,1}$). As can be seen from Table 2, the adsorption equilibrium constant (b_2) of Danish peat was higher than that of Heilongjiang peat. Therefore, Danish peat not only had a higher overall adsorption capacity than that of Heilongjiang peat, but it also contained sites with higher binding energy for metals.

3.3. Adsorption isotherms of Pb, Cu, and Cd on peat in multi-solute systems

The competitive adsorption isotherms in binary and ternary solute mixtures on peat are shown in Fig. 2. It was observed that Pb was always favorably adsorbed on peat over Cu and Cd, and Cu over Cd in the multi-solute systems. This was consistent with the adsorption isotherms in single-solute systems. Since the adsorption isotherms of Pb, Cu and Cd in single-solute systems fit the Langmuir two-site model well, this model was also used to simulate the competitive adsorption isotherms of Pb, Cu, and Cd in binary and ternary solute systems (Fig. 2). The Langmuir two-site model also yielded best fit for Pb and Cu adsorption on peat in binary and ternary solute systems. However, it failed in the case of Cd, especially in

Table 2
Single-solute isotherm parameters with error analysis for Pb, Cu, and Cd adsorption on Danish and Heilongjiang peat (q_m , $q_{m,1}$, $q_{m,2}$ and q'_m : mmol g⁻¹; b , b_1 and b_2 : l mmol⁻¹)

Parameters	Danish peat			Heilongjiang peat		
	Pb	Cu	Cd	Pb	Cu	Cd
Langmuir one-site model						
q_m	0.573	0.536	0.447	0.428	0.402	0.285
b	32.4	13.5	3.07	27.2	16.3	4.18
R^2	0.946	0.967	0.964	0.991	0.986	0.960
S.E.	0.0350	0.0243	0.0187	0.0104	0.0123	0.0130
Langmuir two-site model						
$q_{m,1}$	0.415	0.400	0.364	0.251	0.231	0.246
b_1	3.68	2.48	0.508	4.90	3.98	0.694
$q_{m,2}$	0.267	0.226	0.183	0.208	0.195	0.118
b_2	194	70.4	16.5	105	35.8	27.2
q'_m	0.682	0.626	0.547	0.459	0.426	0.364
R^2	0.999	0.999	0.999	0.993	0.994	0.997
S.E.	0.00432	0.00314	0.00321	0.00984	0.00825	0.00357
Freundlich model						
K_F	0.579	0.484	0.303	0.380	0.348	0.206
$1/n$	0.253	0.289	0.379	0.222	0.245	0.317
R^2	0.955	0.957	0.990	0.847	0.884	0.982
S.E.	0.0317	0.0279	0.00976	0.0435	0.0351	0.00871

Fig. 2. Single- and multi-solute adsorption of Pb, Cu, and Cd on (a) Danish and (b) Heilongjiang peat. Symbols are the experimental data and solid lines are Langmuir two-site model fitting.

ternary solute systems. Therefore, only the fitting parameters of Pb and Cu are tabulated in Table 3. When compared with their adsorption in single-solute systems, the individual adsorption capacity (q_m) of all the three metals showed obvious decrease both in binary and in ternary solute systems. Furthermore, the decrease in the adsorption capacity was greater in ternary solute systems as compared to binary solute systems. These results indicated a competition between metals for adsorption sites. Both the adsorption maximum ($q_{m,1}$) on the low-energy sites and the adsorption maximum ($q_{m,2}$) on the

high-energy sites of multi-solute systems decreased as compared to those in single-solute systems. Moreover, $q_{m,1}$ decreased to a much larger degree than $q_{m,2}$, thereby indicating that the mutual competitive effect of Pb, Cu and Cd mainly took place on the low-energy sites. As metals on the low-energy sites were loosely held, they were easy to be replaced by other metal ions.

As can be seen from Fig. 2, the adsorbed Pb and Cu increased rapidly with increase in Pb and Cu equilibrium concentrations at the initial step, and then increased slowly with

Table 3

Single- and multi-solute isotherm parameters of Langmuir two-site model with error analysis for Pb, and Cu adsorption on Danish and Heilongjiang peat ($q_{m,1}$, $q_{m,2}$ and q'_m : mmol g⁻¹; b_1 and b_2 : l mmol⁻¹)

Adsorption systems	$q_{m,1}$	b_1	$q_{m,2}$	b_2	q'_m	R^2	S.E. $\times 10^3$	q_i^{mix}/q_i^0
Danish peat								
Pb	0.415	—	0.267	—	0.682	—	—	—
Pb (Pb–Cd)	0.380	3.15	0.242	175	0.622	0.999	31.4	0.912
Pb (Pb–Cu)	0.284	2.41	0.213	199	0.497	0.996	9.37	0.728
Pb (Pb–Cu–Cd)	0.296	3.60	0.176	180	0.472	0.990	17.6	0.692
Cu	0.400	—	0.226	—	0.626	—	—	—
Cu (Cu–Cd)	0.354	1.24	0.213	40.9	0.567	0.997	16.5	0.906
Cu (Pb–Cu)	0.105	1.40	0.210	54.2	0.315	0.990	9.27	0.503
Cu (Pb–Cu–Cd)	0.101	1.70	0.205	53.6	0.306	0.986	3.52	0.489
Heilongjiang peat								
Pb	0.251	—	0.208	—	0.459	—	—	—
Pb (Pb–Cd)	0.234	2.60	0.202	90.4	0.436	0.997	5.68	0.950
Pb (Pb–Cu)	0.0967	3.05	0.195	98.7	0.292	0.999	32.8	0.636
Pb (Pb–Cu–Cd)	0.128	3.15	0.153	116	0.281	0.997	5.01	0.612
Cu	0.231	—	0.195	—	0.426	—	—	—
Cu (Cu–Cd)	0.216	1.06	0.201	39.4	0.417	0.993	7.25	0.979
Cu (Pb–Cu)	0.0144	2.13	0.181	40.6	0.195	0.992	4.07	0.458
Cu (Pb–Cu–Cd)	0.0207	2.50	0.147	39.6	0.168	0.995	2.71	0.394

further increase in Pb and Cu equilibrium concentrations. The trend was somewhat different for Cd, although the adsorbed Cd increased rapidly with increasing Cd equilibrium concentration at the initial stage. The adsorbed Cd reached a maximum and then decreased with increasing equilibrium solution concentration. Our results are consistent with the competitive adsorption of Pb, Cu, and Cd on microporous titanosilicate ETS-10 (Lv et al., 2005). At low initial metal equilibrium concentrations, the amounts adsorbed for two or three metal ions increased rapidly with increasing concentration due to the abundant adsorption sites of peat. Therefore, over this metal concentration range the competitive effects were not pronounced. As the metal concentrations increased further, metals with higher affinity compete with metals with lower affinity for the adsorption sites of peat. When metals compete for the same adsorption sites of an adsorbent, metals with a greater affinity (strongly adsorbed species) could displace others with a lower affinity (weakly adsorbed species) (Christophi and Axe, 2000). Among the three metal ions, Cd had the lowest affinity. When Pb, Cu and Cd co-existed at higher concentration levels, Pb and Cu competed with Cd for the adsorption sites of peat, thereby resulting in decreased adsorption of Cd.

Mohan and Singh (2002) investigated the mutual effects of metals on their adsorption in multi-solute systems by measuring the ratio of the adsorption capacity of one metal in multi-solute systems, q_i^{mix} , to that of given metal in single-solute systems, q_i^0 . If $q_i^{\text{mix}}/q_i^0 > 1$, metal i enhanced the adsorption of other metal ion(s). If $q_i^{\text{mix}}/q_i^0 = 1$, metals had no effects on each other. If $q_i^{\text{mix}}/q_i^0 < 1$, metal i competed with other metals for the adsorption sites of adsorbents. As shown in Table 3, the values of q_i^{mix}/q_i^0 were < 1 , which further demonstrated the competitive adsorption of Pb, Cu and Cd in the multi-solute systems. These results are in agreement with the work of Mohan and Singh (2002).

The mutual competitive effect of Pb, Cu, and Cd in binary and ternary solute systems is evident from Fig. 2 and Table 3. Moreover, Pb, Cu, and Cd had different competitive effect. Compared to its adsorption in single-solute systems, the adsorption capacity (q'_m) of Pb on Danish peat was reduced by 30.8% in Pb–Cu–Cd, by 27.1% in Pb–Cu and by 8.80% in Pb–Cd systems. Similarly, the adsorption capacity (q'_m) of Cu on Danish peat was decreased by 51.1% in Pb–Cu–Cd, by 49.7% in Pb–Cu and by 9.42% in Cu–Cd systems, compared to Cu adsorption capacity in single-solute systems. Although Langmuir two-site model does not fit Cd adsorption in multi-solute systems, Fig. 2 shows clearly that Cd adsorption decreased more pronouncedly in binary and ternary solute systems than Pb and Cu. These results showed that the adsorption capacity of Pb was reduced to a less extent than that of Cu and Cd. The competitive ability of Pb, Cu, and Cd followed the order Pb $>$ Cu $>$ Cd. Ma et al. (1994) also reported that Cu diminished Pb adsorption more significantly than did Cd. The different suppression effect can be attributed to the different affinity of co-existed ion(s) for the binding sites. The affinity sequence of Pb $>$ Cu $>$ Cd described in the pH effect section earlier accounted for their unequal competitive effect in different systems. Such different competitive effects were reported in the natural carbonaceous materials for Ag–Cd and Ag–Cu systems (Hanzlík et al., 2004), and in the activated carbon for Hg–Pb, Hg–Cd, Hg–Ca, Pb–Cd, Pb–Ca and Cd–Ca systems (Xiao and Thomas, 2004).

When two or more metal ions are present together, they may increase, decrease or not change the metal-ion adsorption capacity of the adsorbent. The data in Table 3 indicate that total adsorption of Pb and Cu on Danish peat in Pb–Cu system (0.812 mmol g⁻¹) was higher than Pb adsorption capacity (0.682 mmol g⁻¹) or Cu adsorption capacity (0.626 mmol g⁻¹) in their respective single-solute solutions. Similarly, the total adsorption capacity of Pb

and Cu ($0.778 \text{ mmol g}^{-1}$) on Danish peat in Pb–Cu–Cd system was higher than Pb ($0.682 \text{ mmol g}^{-1}$), Cu ($0.626 \text{ mmol g}^{-1}$) or Cd ($0.547 \text{ mmol g}^{-1}$) adsorption capacity in single-solute systems. These results suggest that the total adsorption capacity of metals in binary and ternary solute systems increases, but individual metal adsorption will decrease due to metal interaction and competition for adsorption sites. This conclusion was supported by the work of Hanzlík et al. (2004).

3.4. Adsorption kinetics of Pb, Cu, and Cd on peat in single- and multi-solute systems

The adsorption of Pb, Cu, and Cd onto peat in both single- and multi-solute systems showed typical biphasic kinetics with a rapid adsorption of Pb, Cu, and Cd on peat at the initial step followed by a slower one, although some differences were observed between metals (Fig. 3). This biphasic kinetics may be

Fig. 3. Single- and multi-solute kinetics for Pb, Cu, and Cd adsorption on (a) Danish and (b) Heilongjiang peat. Error bars represent standard deviation of triplicate measurements.

attributed to the heterogeneity of the adsorption sites of peat. Aringhieri et al. (1985) ascribed the initial faster rate to a rapid diffusion of ions from solution to external adsorbent surface, and the slower adsorption rate in the second stage was probably due to the diffusion of metal ions into porous structure of the adsorbent.

For all the adsorption systems, the adsorbed amounts of Pb were always higher than those of Cu and Cd. The pseudo-second-order model fits the kinetics of Pb, Cu and Cd in single- and multi-solute systems with good correlation coefficients ($R^2 \geq 0.999$). The parameters calculated from the slopes and the intercepts along with S.E. are listed in Table 4. Table 4 indicates that pseudo-second-order kinetic model showed low S.E. (1.05×10^{-3} – 6.24×10^{-3}). Thus the pseudo-second-order model described the experimental data well. It should be pointed out that the pseudo-second-order model has been successfully used by Ho and McKay (1998), Chiron et al. (2003) and Ho (2003). The good fitting of pseudo-second-order kinetic model for our experimental data indicated an activated adsorption mechanism (Ho and McKay, 1998). The initial adsorption rate of Danish peat was higher than that of Heilongjiang peat. This may be attributed to higher BET surface area of Danish peat, thus more adsorption sites were available for metals. It can also be attributed to the higher affinity of metals for Danish peat than that for Heilongjiang peat as demonstrated by the isotherm studies. For the same peat, the initial adsorption rate h followed the descending order of $\text{Pb} > \text{Cu} > \text{Cd}$, indicating that Pb was initially more rapidly adsorbed on Heilongjiang and Danish peat than Cu and Cd in single- and multi-solute systems. Similar adsorption phenomena of Pb and Cd on soils were observed by Serrano et al. (2005) from single and binary solute systems.

The adsorbed amounts of Pb, Cu, and Cd decreased in binary and ternary systems when compared with their adsorption in single-solute systems as depicted with the results of adsorption isotherms. The initial adsorption rate (h) decreased in the binary and ternary systems compared to those in the single-solute systems (Table 4). The total metal concentration of the binary and ternary systems was higher than that of

single-solute systems while the concentration of individual metal was the same as that of single-solute systems. On the basis of the magnitude of the repulsive electrostatic forces existing between ions in the bulk solution it appears that the adsorption of metals in the multi-solute systems would not be favorable kinetically or thermodynamically (Pardo-Botello et al., 2004). Gündoğan et al. (2004) also found that the initial adsorption rate decreased with the increase of Cu initial concentration in the Cu–peat system.

3.5. X-ray absorption measurements

In order to elucidate the mechanisms of competitive adsorption of Cu, Pb and Cd on peat XAS was used to examine whether these metals were coordinated via the same ligand groups. XANES and EXAFS were used to probe the local atomic environment of Cu and Pb adsorbed onto peat. However, due to the practical limitation of energy range available in Beijing Synchrotron Radiation Laboratory no XAS study was performed for Cd.

3.5.1. Cu K-edge XANES and EXAFS

The normalized K-edge XANES spectra and their first derivatives for adsorbed Cu on peat and reference model compounds are shown in Fig. 4a and b, respectively. The XANES spectra are very similar (Fig. 4a). Their first derivative spectra have two different inflections, peaks α and β , located at 8980 and 8985 eV, corresponding to $1s \rightarrow 4d$ and $1s \rightarrow \text{continuum}$ transitions, respectively (Fig. 4b). The first derivative showed a weak preedge feature due to $1s \rightarrow 3d$ transition. The intensity of the preedge was sensitive to the presence of a center of symmetry, and its intensity increased with distortions from symmetry due to the increase of p–d orbital mixing (Hahn et al., 1982). The β peak represents the main adsorption transition ($1s \rightarrow \text{continuum}$). The α peak is influenced by the degree of axial distortion and covalence of the equatorial ligands bonded to Cu(II) ions (Palladino et al., 1993; Lee et al., 2005). The reduced α peak intensity has been attributed to a transition arising from $1s \rightarrow 4p_z$ excitation

Table 4

Pseudo-second-order kinetic parameters for the adsorption of Pb, Cu, and Cd on Danish and Heilongjiang peat in single- and multi-solute systems (q_e : mmol g⁻¹; k : g mmol⁻¹ h⁻¹; h : mmol g⁻¹ h⁻¹)

Adsorption systems	Danish peat				Heilongjiang peat			
	q_e	k	h	S.E. $\times 10^3$	q_e	k	h	S.E. $\times 10^3$
Pb	0.377	317	45.0	2.24	0.371	265	36.4	3.12
Pb (Pb–Cd)	0.361	194	25.3	1.08	0.327	104	11.1	4.27
Pb (Pb–Cu)	0.339	145	16.7	1.89	0.255	144	9.35	1.65
Pb (Pb–Cu–Cd)	0.319	136	13.9	1.07	0.234	120	6.58	1.51
Cu	0.352	220	27.2	1.05	0.353	192	23.9	3.49
Cu (Cu–Cd)	0.327	138	14.7	2.13	0.297	129	11.4	1.17
Cu (Pb–Cu)	0.273	134	10.0	3.74	0.177	180	5.63	1.90
Cu (Pb–Cu–Cd)	0.248	138	8.48	2.48	0.150	105	2.34	2.36
Cd	0.260	140	9.47	3.64	0.211	58	2.58	6.24
Cd (Cu–Cd)	0.148	109	2.40	4.12	0.0886	186	1.46	3.03
Cd (Pb–Cd)	0.112	104	1.31	1.93	0.0689	193	0.919	1.22
Cd (Pb–Cu–Cd)	0.035	124	0.153	1.33	0.0233	113	0.0614	2.21

Fig. 4. Normalized XANES spectra (pre- and near-edge region) of adsorbed Cu on peat (Cu–peat) and other reference compounds (a) and corresponding first derivatives (b), EXAFS spectrum (χ -function) of the Cu adsorbed onto peat (c), Fourier transformation (RSF) of the EXAFS spectrum (d) and first-shell fit of the EXAFS function of the adsorbed Cu on peat (e). Solid and dotted lines in (e) represent the experimental first-shell filtered data and the best fit, respectively. Experimental phase and amplitude functions were extracted from the EXAFS spectrum of the $\text{Cu}(\text{CH}_3\text{CO}_2)_2$ reference compound.

combined with strong ligand-to-metal charge transfer (Shadle et al., 1993). Therefore, the decreased α peak intensity for adsorbed Cu on peat compared to aqueous Cu^{2+} (Fig. 4b) suggests that the stronger field of water molecules in the tetragonal plane exchanged with a different field of organic moieties (carboxylic and hydroxyl functions) from peat particles.

The diminished α peak of adsorbed Cu on peat in comparison with aqueous Cu^{2+} spectrum suggests that peat was sterically hindered due to their three dimensional structure. When Cu^{2+} approached, it cannot bond in the equatorial plane with the same degree of angular overlap as water. Thus, it can be concluded that Cu(II) formed inner-sphere complex (Flogéac et al., 2004).

The $\chi(k)k^3$ spectrum of adsorbed Cu to peat and its corresponding radial structural function (RSF), derived from Fourier transformations, are presented in Fig. 4c and d, respectively. The weighted EXAFS spectrum showed oscillations of about equal amplitude across the entire k range, but it also amplified spectral noise at high k . The position of the peaks in the RSF corresponded to relative distances (uncorrected for phase shift) between Cu and oxygen atoms in local coordination shells. The strongest peak occurring at 1.53 Å in Fig. 4d,

corresponded to first Cu–O shell. The adsorbed Cu onto peat fit first-shell-EXAFS signal well (Fig. 4e), indicating that Cu(II) ions were coordinated to four equatorial oxygen atoms and two axial oxygen atoms. The average Cu–O_{eq} bond length is 1.94 Å, and the Cu–O_{ax} bond length is 2.34 Å. The results of four short equatorial bonds and two elongated axial bonds were due to the Jahn–Teller effect of Cu(II), which were consistent with many EXAFS studies involving Cu(II) (Flogeac et al., 2004; Palladino et al., 1993).

Fig. 5. Normalized XANES spectra (pre- and near-edge region) of adsorbed Pb on peat (Pb-peat) and other reference compounds (a) and corresponding first derivatives (b), EXAFS spectra (c) and Fourier transform (RSF) (d) of EXAFS for Pb adsorbed on peat together with reference compounds. First-shell fit of the EXAFS function of the adsorbed Pb on peat (e). Solid and dotted lines in (e) represent the experimental first-shell filtered data and the best fit, respectively. Experimental phase and amplitude functions were extracted from the EXAFS spectrum of the Pb(CH₃CO₂)₂ reference compound.

Analysis of the XANES and EXAFS data on Cu(II) adsorbed on peat, Cu in reference compounds of Cu(OH)₂, Cu(CH₃CO₂)₂ and Cu(NO₃)₂ aqueous solution (Fig. 4b) suggests that the coordination environment of Cu(II) adsorbed on peat strongly resembles that of Cu(CH₃CO₂)₂, where Cu(II) was bonded primarily to carboxylic moieties. We can also suggest that probably Cu(II) was also bonded to phenolic group of peat, without excluding the hydroxyl groups. This conclusion is supported by the works of Alcacio et al. (2001) and by ¹³C CPMAS NMR spin lattice relaxation rate measurements (Schilling and Cooper, 2004).

3.5.2. Pb L₃-edge XANES and EXAFS

The sensitivity of Pb L₃-edge XANES to the first-shell coordination has been documented previously in detail (Strawn and Sparks, 1999). Marked differences in near-edge features have been observed and Pb is present in different coordination environments. The XANES (Fig. 5a) of Pb and its first derivative (Fig. 5b) showed a distinct shoulder around 13,010 eV in α-PbO, which has been assigned to 2p → 6s electronic transitions possibly arising from multiple scattering of the photoelectron from the neighboring atoms (Bargar et al., 1997). This feature was weak in adsorbed Pb on peat. This distinct difference in Pb L₃-XANES spectra between adsorbed Pb on peat and that of α-PbO suggests that the coordination environment of Pb in peat was unlikely the same as that in α-PbO. Background-subtracted *k*³-weighted EXAFS functions and their Fourier transform of adsorbed Pb on peat and other reference compounds are presented in Fig. 5c and d, respectively. The *k*³-weighted EXAFS functions of adsorbed Pb on peat and other reference compounds exhibited a strong sinusoidal beat pattern that was typical of first neighbor O-shell backscattering. The complex χ structure of α-PbO was due to the contributions from second shell Pb atoms. For the χ structure of adsorbed Pb on peat there was a large decrease in the amplitude of the signal at *k* > 6 Å⁻¹. This was ascribed to the dampening of the EXAFS signal of structural and thermal disorder (Strawn and Sparks, 1999). The χ structure of EXAFS data was Fourier transformed to yield radial structure function (RSF). For Pb²⁺ (aq), Pb(CH₃CO₂)₂ and adsorbed Pb onto peat there was only a broad peak centered at ~1.7 Å (Fig. 5d). The broad peak was from typical O backscattering in the first coordination shell of the Pb atoms. The large width of these peaks indicated a high degree of disorder. The fitting of this first peak (Fig. 5e) led to 2.7 oxygen atoms at 2.28 Å with σ² = 0.006 Å². This result was similar to Pb adsorption on aluminum oxide reported by Bargar et al. (1997). The coordination number was particularly low as expected because of the highly structural disorder of the Pb coordination shells. The L₃-edge XANES spectra (Fig. 5a and b), EXAFS functions (Fig. 5c) and corresponding radial structure function (Fig. 5d) appeared to be very similar for adsorbed Pb on peat and Pb(CH₃CO₂)₂. They presented relatively similar amplitudes (Fig. 5c), which indicated Pb coordination on peat mostly through carboxylic moieties.

In summary, the XAS spectroscopic studies suggest that the coordination environment of Cu(II) adsorbed on peat strongly

resembles that of Cu(CH₃CO₂)₂, where Cu(II) was bonded primarily to carboxylic moieties. The adsorbed Pb on peat was primarily bonded to carboxylic ligands of peat. The above results provided an evidence for the observed competitive adsorption of Cu and Pb.

4. Conclusions

The adsorption isotherms of Pb, Cu, and Cd on peat in single- and multi-solute systems were simulated with Langmuir two-site model satisfactorily. The adsorption capacity of Pb, Cu, and Cd on Danish peat was higher than that of Pb, Cu, and Cd on Heilongjiang peat. In the binary and ternary solute systems, adsorption capacity of peat for each metal decreased due to competitive effect. The competitive effect of Pb, Cu and Cd occurred mainly at the low-energy sites as the adsorbed amounts of Pb, Cu and Cd in multi-solute systems decreased to a large extent at the low-energy sites (*q*_{m,1}) than at the high-energy sites (*q*_{m,2}). Different metal exerted different competitive effect on the adsorption of other metals. The competitive ability of Pb, Cu, and Cd followed the order Pb > Cu > Cd. The pseudo-second-order kinetic model best described the adsorption kinetics of Pb, Cu, and Cd on peat in single- and multi-solute systems. Danish peat had higher adsorption rate for Pb, Cu and Cd in single-solute systems than Heilongjiang peat. In the multi-solute systems, both the adsorbed amounts and the initial adsorption rates of Pb, Cu, and Cd decreased compared to those in the single-solute systems. XAS spectroscopic study offered a direct evidence for similar binding environment of Pb and Cu on peat, mainly through carboxyl group, without excluding hydroxylic group. This study provides an insight into the mechanisms of competitive adsorption of Pb, Cu and Cd on peat by a combination of macroscopic batch equilibration method and XAS.

Acknowledgements

This work was funded by the National Natural Science Foundation of China (Grant Number 20237010).

References

- Alcacio, T.E., Hesterberg, D., Chou, J.W., Martin, J.D., Beauchemin, S., Sayers, D.E., 2001. Molecular scale characteristics of Cu(II) bonding in goethite–humate complexes. *Geochim. Cosmochim. Acta* 65, 1355–1366.
- Aringhieri, R., Carrai, P., Petruzzelli, G., 1985. Kinetics of Cu²⁺ and Cd²⁺ adsorption by an Italian soil. *Soil Sci.* 139, 197–204.
- Alves, M.E., Lavoretti, A., 2004. Sulfate adsorption and its relationships with properties of representative soils of the São Paulo State, Brazil. *Geoderma* 118, 89–99.
- Balabane, M., van Oort, F., 2002. Metal enrichment of particle organic matter in arable soils with low metal contamination. *Soil Biol. Biochem.* 34, 1513–1516.
- Bargar, J.R., Brown Jr., G.E., Parks, G.A., 1997. Surface complexation of Pb(II) at oxide–water interfaces: I. XAFS and bond-valence determination of mononuclear and polynuclear Pb(II) sorption products on aluminum oxides. *Geochim. Cosmochim. Acta* 61, 2617–2638.
- Brown, P.A., Gill, S.A., Allen, S.J., 2000. Metal removal from wastewater using peat. *Water Res.* 34, 3907–3916.

- Cheung, C.W., Chan, C.K., Porter, J.F., McKay, G., 2001. Film-pore diffusion control for the batch sorption of cadmium ions from effluent onto bone char. *J. Colloid Interface Sci.* 234, 328–336.
- Chiron, N., Guilet, R., Deydier, E., 2003. Adsorption of Cu(II) and Pb(II) onto a grafted silica: isotherms and kinetic models. *Water Res.* 37, 3079–3086.
- Christophi, C.A., Axe, L., 2000. Competition of Cd, Cu, and Pb adsorption on goethite. *J. Environ. Eng.* 126, 66–74.
- Flogeac, K., Gullion, E., Aplincourt, M., 2004. Surface complexation of copper(II) on soil particles: EPR and XAFS studies. *Environ. Sci. Technol.* 38, 3098–3103.
- Gündoğan, R., Acemioğlu, B., Alma, M.H., 2004. Copper(II) adsorption from aqueous solution by herbaceous peat. *J. Colloid Interface Sci.* 269, 303–309.
- Hanzlík, J., Jehlička, J., Šebek, O., Weishauptová, Z., Machovič, V., 2004. Multi-component adsorption of Ag(I), Cd(II) and Cu(II) by natural carbonaceous materials. *Water Res.* 38, 2178–2184.
- Hahn, J.E., Scott, R.A., Hodgson, K.O., Doniach, S., Desjardins, S.R., Solomon, E.I., 1982. Observation of an electric quadrupole transition in the X-ray absorption spectrum of a Cu(II) complex. *Chem. Phys. Lett.* 88, 595–598.
- Ho, Y.S., 2003. Removal of copper ions from aqueous solution by tree fern. *Water Res.* 37, 2323–2330.
- Ho, Y.S., McKay, G., 1998. Sorption of dye from aqueous solution by peat. *Chem. Eng. J.* 70, 115–124.
- Ho, Y.S., McKay, G., 2000. The kinetics of sorption of divalent metal ions onto sphagnum moss peat. *Water Res.* 34, 735–742.
- Jeon, B.H., Dempsey, B.A., Burgos, W.D., Royer, R.A., 2003. Sorption kinetics of Fe(II), Zn(II), Co(II), Ni(II), Cd(II) and Fe(II)/Me(II) onto hematite. *Water Res.* 37, 4135–4142.
- Ko, D.C.K., Cheung, C.W., Choy, K.K.H., Porter, J.F., McKay, G., 2004. Sorption equilibria of metal ions on bone char. *Chemosphere* 54, 273–281.
- Lee, Y.J., Elzinga, E.J., Reeder, R.J., 2005. Cu(II) adsorption at the calcite–water interface in the presence of natural organic matter: kinetic studies and molecular-scale characterization. *Geochim. Cosmochim. Acta* 69, 49–61.
- Lin, S.H., Kao, H.C., Cheng, H.C., Juang, R.S., 2004. An EXAFS study of the structures of copper and phosphate sorbed onto goethite. *Colloids Surf. A* 234, 71–75.
- Lv, L., Hor, M.P., Su, F.B., Zhao, X.S., 2005. Competitive adsorption of Pb²⁺, Cu²⁺, and Cd²⁺ ions on microporous titanosilicate ETS-10. *J. Colloid Interface Sci.* 287, 178–184.
- Ma, Q.Y., Traina, S.J., Logan, T.J., Ryan, J.A., 1994. Effects of aqueous Al, Cd, Cu, Fe(II), Ni, and Zn on Pb immobilization by hydroxyapatite. *Environ. Sci. Technol.* 28, 1219–1228.
- Machida, M., Kikuchi, Y., Aikawa, M., Tatsumoto, H., 2004. Kinetics of adsorption and desorption of Pb(II) in aqueous solution on activated carbon by two-site adsorption model. *Colloids Surf. A* 240, 179–186.
- Mohan, D., Singh, K.P., 2002. Single- and multi-component adsorption of cadmium and zinc using activated carbon derived from bagasse – an agriculture waste. *Water Res.* 36, 2304–2318.
- Nelson, D.W., Sommers, L.E., 1996. Methods of Soil Analysis, Part 3, Chemical Methods. In: *Soil Science Society Book Series*, vol. 5. American Society of Agronomy, Madison, WI, pp. 961–1010.
- Ostergren, J.D., Brown Jr., G.E., Parks, G.A., Persson, P., 2000. Inorganic ligand effects on Pb(II) sorption to goethite (α -FeOOH). II. Sulfate. *J. Colloid Interface Sci.* 225, 483–493.
- Palladino, L., Della Longa, S., Reale, A., Belli, M., Scafati, A., Onori, G., Santucci, A., 1993. X-ray absorption near edge structure (XANES) of Cu(II)-ATP and related compounds in solution: quantitative determination of the distortion of the Cu site. *J. Chem. Phys.* 98, 2720–2726.
- Pardo-Botello, R., Fernández-González, C., Pinilla-Gil, E., Cuerda-Correa, E.M., Gómez-Serrano, V., 2004. Adsorption kinetics of zinc in multicomponent ionic systems. *J. Colloid Interface Sci.* 277, 292–298.
- Ramstedt, M., Norgren, C., Shchukarev, A., Sjöberg, S., Persson, P., 2005. Co-adsorption of cadmium(II) and glyphosate at the water–manganite (γ -MnOOH) interface. *J. Colloid Interface Sci.* 285, 493–501.
- Ringqvist, L., Holmgren, A., öborn, I., 2002. Poorly humified peat as an adsorbent for metals in wastewater. *Water Res.* 36, 2394–2404.
- Schilling, M., Cooper, W.T., 2004. Identification of copper binding sites in soil organic matter through chemical modifications and ¹³C CPMAS NMR spectroscopy. *Environ. Sci. Technol.* 38, 5059–5063.
- Serrano, S., Garrido, F., Campbell, C.G., García-González, M.T., 2005. Competitive sorption of cadmium and lead in acid soils of central Spain. *Geoderma* 124, 91–104.
- Shadle, S.E., Penner-Hahn, J.E., Schugar, H.J., Hedman, B., Hodgson, K.O., Solomon, E.I., 1993. X-ray absorption spectroscopic studies of the blue copper site: metal and ligand K-edge studies to probe the origin of the EPR hyperfine splitting in plastocyanin. *J. Am. Chem. Soc.* 115, 767–776.
- Sharma, D.C., Forster, C.F., 1993. Removal of hexavalent chromium using sphagnum moss peat. *Water Res.* 27, 1201–1208.
- Strawn, D.G., Scheidegger, A.M., Sparks, D.L., 1998. Kinetics and mechanisms of Pb(II) sorption and desorption at the aluminum oxide–water interface. *Environ. Sci. Technol.* 32, 2596–2601.
- Strawn, D.G., Sparks, D.L., 1999. The use of XAFS to distinguish between inner- and outer-sphere lead adsorption complexes on montmorillonite. *J. Colloid Interface Sci.* 216, 257–269.
- Sumner, M.E., Miller, W.P., 1996. Methods of Soil Analysis, Part 3, Chemical Methods. In: *Soil Science Society Book Series*, vol. 5. American Society of Agronomy, Madison, WI, pp. 1201–1230.
- Wang, W.S., Shan, X.Q., Wen, B., Zhang, S.Z., 2003. Relationship between the extractable metals from soils and metals taken up by maize roots and shoots. *Chemosphere* 53, 523–530.
- Wang, K., Xing, B., 2004. Mutual effects of cadmium and phosphate on their adsorption and desorption by goethite. *Environ. Pollut.* 127, 13–20.
- Xia, K., Bleam, W., Helmke, P.A., 1997. Studies of the nature of Cu²⁺ and Pb²⁺ binding sites in soil humic substances using X-ray absorption spectroscopy. *Geochim. Cosmochim. Acta* 61, 2211–2221.
- Xiao, B., Thomas, K.M., 2004. Competitive adsorption of aqueous metal ions on an oxidized nonporous activated carbon. *Langmuir* 20, 4566–4578.
- Yonebayashi, K., Pechayapisit, J., Vijarnsorn, P., Zahari, A.B., Kyuma, K., 1994. Chemical alterations of tropical peat soils determined by Waksman's proximate analysis and properties of humic acids. *Soil Sci. Plant Nutr.* 40, 435–444.