New insights into the sorption mechanism of cadmium on red mud

Lei Luo^{a,b}, Chenyan Ma^c, Yibing Ma^{b,*}, Shuzhen Zhang^a, Jitao Lv^a, Mingqi Cui^c

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

^b Ministry of Agriculture Key Laboratory of Plant Nutrition and Nutrient Cycling, Institute of Agricultural Resources and Regional Planning, Chinese Academy of Agricultural Sciences, Beijing 100081, China

^c State Key Laboratory of Synchrotron Radiation, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100039, China

Cadmium can be strongly sorbed and partially forms inner-sphere complexes on red mud.

ARTICLE INFO

Article history:

Received 1 October 2010

Received in revised form

7 February 2011

Accepted 9 February 2011

Keywords:

Cadmium

Red mud

Sorption

XANES

Sequential extraction analysis

ABSTRACT

Effectiveness and mechanism of cadmium (Cd) sorption on original, acidified and ball milling nano-particle red muds were investigated using batch sorption experiments, sequential extraction analysis and X-ray absorption near edge structure (XANES) spectroscopy. The maximum sorption capacity of Cd was 0.16, 0.19, and 0.21 mol/kg for the original, acidified, and nano-particle red muds at pH 6.5, respectively. Both acidification and ball-milling treatments significantly enhanced Cd sorption and facilitated transformation of Cd into less extractable fractions. The Cd *L*_{III}-edge XANES analysis indicated the formation of inner-sphere complexes of Cd similar to XCdOH (X represents surface groups on red mud) on the red mud surfaces although outer-sphere complexes of Cd were the primary species. This work shed light on the potential application of red mud to remediate Cd-contaminated soils and illustrated the promising tool of XANES spectroscopy for speciation of multicomponent systems of environmental relevance.

© 2011 Elsevier Ltd. All rights reserved.

1. Introduction

Cadmium (Cd), as a highly mobile and toxic trace element, has been exerting a great pressure on environmental safety due to its increasingly higher input flux from anthropogenic sources (Luo et al., 2009). Appropriate remediation technologies for the contaminated environments become necessary. It is known that the fate of Cd is controlled by its sorption reactions and speciation in the environment. Therefore much attention has been paid to its sorption reactions and speciation in immobilizing materials for remediation (Hamon et al., 2002; Basta and McGowen, 2004; Zhang et al., 2010). Understanding how the contaminant interacts with and competes for sorption sites in immobilizing materials is critical to predicate accurately the fates of contaminants and remediate effectively the contaminated soils.

Red mud is an alkaline oxide-rich residue generated by aluminum production from bauxite and often used as an amendment material to immobilize trace metal contaminants in soils in laboratory studies (Lombi et al., 2002a,b; Brown et al., 2005; Santona et al., 2006). Based on sequential extraction analysis and biological experiments, it was reported that the application of red

mud could transform bioavailable fractions of heavy metals including Cd (i.e. in exchangeable fraction) into less bioavailable fractions possibly through specific chemisorption and thus decrease their phytotoxicity (Lombi et al., 2002a,b; Santona et al., 2006). It is therefore expected that red mud can be an effective immobilizer for Cd contaminants in soil environments. However, due to the heterogeneous composition of red mud and the limit of analytical techniques, the exact mechanisms of Cd sorption on red mud are still to be explored (Hamon et al., 2002; Lombi et al., 2002b), which will cast doubt on the stability and persistence of the immobilizing material.

It was proposed that Cd could be sorbed by specific adsorption via inner-sphere complexation and/or non-specific adsorption via outer-sphere complexation, depending on its surface loading and sorbent types (Brummer et al., 1988; Gräfe et al., 2007). In many cases, these reaction mechanisms are proposed based on macroscopic data, lacking direct microscopic evidence (Serrano et al., 2009). Recently, X-ray absorption spectroscopy (XAS) has been increasingly applied to investigate the sorption mechanisms and speciation of trace elements in mineral and plant samples (Randall et al., 1999; Waychunas et al., 2003; Gräfe et al., 2007; Isaure et al., 2010). Particularly, X-ray absorption near edge structure (XANES) spectroscopy is expected to meet the need of the detection limit and provide the information of complexation and speciation of Cd in environmental samples (Waychunas et al., 2003; Gräfe et al.,

* Corresponding author.

E-mail address: ybma@caas.ac.cn (Y. Ma).

2007; Isaure et al., 2010). To our knowledge, it has not been used so far to investigate Cd sorption reactions in red mud probably due to the limits of high energy required by *K*-edge and low sensitivity at *L_{III}*-edge of Cd absorption spectra.

Red mud is a fine-textured mixture and principally composed of aluminum and iron oxides and hydroxides. Consequently, red mud is expected to show high surface reactivity to Cd contaminants apart from its alkaline pH (Lombi et al., 2002b; Santona et al., 2006). Additionally, grain size of red mud is also expected to affect the affinity and reaction mechanisms of the immobilizer for Cd contaminants. The aims of this study were therefore to clarify the sorption characteristics of Cd by red mud with acidification and nano-particle ball milling treatments, examine the immobility of Cd sorbed on the red muds, and then thoroughly identify the reaction mechanism and sorption species of Cd on the red muds using sorption experiments, sequential extraction analysis and XANES spectroscopy.

2. Materials and methods

2.1. Red mud

Red mud from the stockpiles of Shandong Aluminum Industry Co., Ltd. (Shandong, China) was dried overnight at 105 °C, ground and sieved (<0.25 mm). An aliquot of the red mud was treated by ball milling (nano-particle milling) in order to examine the effect of grain size on Cd sorption by the red mud. Also another aliquot was acid-treated by washing twice with HCl (0.1 mol/L for 4 h at the ratio 1:25 (w/v) of red mud/solution), then thoroughly washed with deionized water and dried overnight at 105 °C. The acidification treatment was used to investigate its feasibility when applied to neutral environments and compare the effect of acidification on the characteristics of the red mud.

The chemical composition of red mud was measured by ICP-OES (PerkinElmer, USA) after aqua regia digestion; pH was measured in a 1:5 suspension of solid and water; particle size distribution was characterized by laser particle analyzer (Malvern Mastersizer 2000, Malvern, UK); the specific surface area was measured by the N₂ BET method with an ASAP 2020 analyzer (Micromeritics Co.); and the cation exchange capacity (CEC) was determined with BaCl₂-triethanolamine following standard methods. X-ray diffraction (XRD) analysis was performed using a PAN-Analytical X'Pert Pro X-ray diffractometer equipped with a Cu source (Cu K α). In addition, amorphous aluminum and iron oxides were extracted with 0.2 mol/L ammonium oxalate at pH 3.0 (Sparks, 1996).

2.2. Sorption experiments

Sorption isotherms were conducted at pH 6.5 and 25 °C. Triplicate 0.5 g red mud samples were equilibrated with 20 mL of background electrolyte solution containing Cd²⁺ concentration ranging from 0.01 to 10.0 mmol/L in 45 mL polypropylene centrifuge tubes. The wide concentration range was used in order to examine accurately the capacity and mechanisms of Cd²⁺ sorption on the red mud. The pH of red mud suspensions was adjusted with HNO₃ prior to the addition of Cd stock solution and maintained at 6.5. The final concentrations of background electrolyte were kept at 0.01 mol/L with KNO₃. The mixtures were shaken at 100 rpm on a reciprocal shaker for 48 h and subsequently centrifuged at 7200 $\times$ g for 20 min at 25 °C before filtering through a 0.45 μ m Millipore membrane.

To examine the effect of ionic strength on Cd sorption on red mud, two ionic concentrations (0.01 or 0.1 mol/L KNO₃) were adopted. To avoid obvious variations of ionic strength during pH adjustment, the acid-treated red mud was applied in the ionic strength effect experiment.

Cadmium concentrations were analyzed by ICP-OES. Cadmium sorption was calculated from the difference between the amount added and the amount remaining in the solution. The sorption data were described by the Freundlich model:

$$S = K_f C_e^n \quad (1)$$

where *S* is the amount of Cd sorbed (mg/kg), *C_e* is the concentration of Cd in equilibrium solution (mg/L), and *K_f* and *n* are related to the capacity and intensity of sorption, respectively.

The points of zero charge (PZCs) as well as the ζ potential affected by Cd sorption at the present condition (pH 6.5) for the red mud were determined with a zeta potential analyzer (Zetasizer 2000, Malvern, UK) as described previously (Luo et al., 2006). In addition, the microtopography and chemical contents of the red mud sorption samples were determined by SEM with an EDAX KEVEX level 4 (Hitachi S-3500N). Before the analysis, the sorption samples were thoroughly washed with deionized water and freeze-dried.

2.3. Sequential extraction analysis

The immobility of Cd retained in red mud was examined by a modified sequential extraction procedure. According to the procedure, Cd retained in the red mud sorption samples (with initial Cd concentrations of 0.2, 1.0, 2.0 6.0 and 10.0 mmol/L, prepared as described in the section of *Sorption Experiments*) were operationally fractionated into four forms designated as water soluble (WS-Cd), CH₃COONH₄ (NH₄Ac) extractable (NH₄Ac-Cd), EDTA extractable (EDTA-Cd) and residual fractions (Res-Cd) (Sparks, 1996; Basta and Gradwohl, 2000; Santona et al., 2006). Detailed information of the sequential extraction procedure was provided in Table S1 in the Supplementary Information (SI). After each step, the samples were centrifuged and filtered through 0.45 μ m filter to separate the liquid and solid phases. The filtrate from each step of the sequential extraction procedure was stored for Cd analysis. The data shown are the mean of three replicates.

2.4. XANES spectroscopy analysis

Cadmium *L_{III}*-edge (3538 eV) XANES spectra were collected at the 4B7A beam-line of the Beijing Synchrotron Radiation Facility, China. Spectra were collected in fluorescence mode with a Si(Li) detector. The red mud sorption samples (with initial Cd concentrations of 1.0 and 6.0 mmol/L) at pH 4.5 (for the acid-treated red mud only) and at pH 6.5 were prepared according to the procedures as described in the section of *Sorption Experiments*. In addition, Cd reference compounds of oxide, hydroxide, nitrate and carbonate phase, and hydroxylchloride (Cd(OH)Cl) and Cd sorption samples on goethite and Fe(OH)₃ (similar to the preparing procedures for red mud) were also prepared for XANES fingerprint analysis. Cd(OH)₂ and CdCO₃ were prepared following the methods of Gräfe et al. (2007), and Cd(OH)Cl was synthesized according to Cudennec et al. (2000). Three or more scans were averaged for each sample and reference compound.

Processing of XANES data and least-square linear combination fitting (LCF) analyses were carried out using Athena software (Ravel and Newville, 2005). Principle component analysis (PCA) was conducted using SixPACK software, and a set of spectra is decomposed into the minimum number of unique components that exist in a set of mixed spectra can be derived (Ressler et al., 2000). Linear combination fitting of the Cd *L_{III}*-edge XANES spectra was performed in the region between 3518 and 3590 eV. In addition, *ab initio* XANES calculations using FEFF 8 for Cd(OH)Cl were also performed to simulate the spectrum (Waychunas et al., 2003; Ravel and Newville, 2005). The crystal structure data were obtained from Cudennec et al. (2000).

3. Results and discussion

3.1. Red mud characteristics

The red mud, produced from Bayer procedure, exhibited an alkaline pH of 10.8 (Table 1). The contents of heavy metals including Cu, Cr, Ni, Pb and Zn in the original red mud (RM₀) were below the national environmental standards in agricultural soils in China (SEPAC, 2006), and Cd was lower than 0.01 mg/kg. Over 90% of the red mud particles fall below 20 μ m in particle size. The acidified red mud (RM_a) showed a pH of 7.2 and exhibited a significantly higher surface area (39.7 m²/g). The higher specific surface area was probably due to the cleaning effect of acidification and the increased number of pores with lower diameter (2.0–6.0 nm). After treated with ball milling, the average particle size of the red mud was as low as 112 nm (RM_{nano} for short later), meanwhile its surface area was significantly increased from 21.6 (of RM₀) to 77.4 m²/g.

Table 1
Properties of red mud.

pH	10.8	SSA N ₂ -BET (m ² /g)	21.6
CEC (mmol(+))/kg	112.6		
<i>Macro element composition (% dry weight)</i>			
Si	9.4	Mg	0.72
Fe	21	Ti	1.4
Al	12	K	0.25
Ca	3.0	Na	7.0
<i>Trace metal concentration (mg/kg, dry weight)</i>			
Cd	<0.01	Ni	4.2
Cr	133	Pb	119
Cu	31	Zn	94

X-ray diffraction results revealed that hematite, goethite, gibbsite and quartz are the predominant crystal minerals in the red mud (Fig. S1 in SI). In addition, the red mud also contained minor amorphous oxides. The acidification treatment did not significantly change the crystal mineral composition of the red mud.

3.2. Sorption isotherms

Cadmium sorption isotherms on red mud with different treatments are shown in Fig. 1, together with the corresponding values of the Freundlich parameters (K_f and n). The sorption data fit well with the model ($r^2 > 0.980$). It is noteworthy that at the relative low initial Cd concentrations (≤ 1.0 mmol/L), the sorption ratios of Cd^{2+} are always larger than 80%, and even at an initial concentration of 10.0 mmol/L, the sorption ratios are not lower than 40%, with a maximum sorption of about 0.16 mol Cd/kg for RM_0 .

Compared with RM_0 , RM_{nano} showed significantly higher sorption capacity for Cd^{2+} ($p < 0.01$), which was probably due to the increased surface area of RM_{nano} and the newly exposed sorption sites from the destroyed micro-structure of iron- and aluminum-oxides after treated with ball milling (Figs. S2 and S3 in SI). It is interesting that RM_a also showed an increased sorption capacity compared with RM_0 (Fig. 1), which is probably related to the HCl activation of some sorption sites once occupied by other metal ions and the refreshment of micro-structure of red mud (Wang et al., 2008).

At higher ionic strength, the sorption of Cd^{2+} tended to decrease, particularly at higher initial Cd concentrations (> 1.0 mmol/L) (Fig. 2). Effect of ionic strength is often linked to distinguishing sorption reaction types on adsorptive interfaces. The ionic strength-dependent Cd^{2+} sorption might be attributed to the weakly complexation of Cd like outer-sphere surface species on the red mud (Sparks, 1995; Goldberg and Johnston, 2001). The elevation of ionic strength could increase the net surface positive charges of the red mud at pH (6.5) below its PZC (8.5), which could drive the competition of Cd^{2+} for the sorption sites and change the ζ potential in the sorption plane, thus decreasing the Cd^{2+} sorption on the red mud (Naidu et al., 1994). Therefore, it can be presumed that Cd^{2+} was sorbed probably through ion exchange reaction with the positive charges from exchangeable sites and formed outer-sphere complexes (Angove et al., 1997; Srivastava et al., 2005; Serrano et al., 2009). However, Naidu et al. (1994) observed that

Fig. 1. Cadmium (Cd^{2+}) sorption isotherms (dots) on red mud (RM) with different treatments (pH 6.5, suspension density = 25 g/L) and best fit of the Freundlich model (lines) and the relevant parameters.

Fig. 2. Effect of ionic strength on Cd^{2+} sorption by the acidified red mud.

Cd^{2+} sorption was increased with the increase of ionic strength at pH below the PZC and attributed the phenomena to the fact that the specific sorption rather than simple ion exchange occurred in the sorption plane. Therefore, the unambiguous information about sorption mechanisms of Cd on red mud still needs to be supplied by other additional evidence.

3.3. Sequential extraction analysis

The sequential extraction results showed that the proportions of WS-Cd and NH_4Ac -Cd to total sorbed Cd increased and the proportion of Res-Cd decreased with the increase of the initial Cd concentrations (Fig. 3), indicating the sites for both specific sorption and exchangeable reactions were gradually saturated with the increasing Cd loadings. It is noteworthy that the residual fraction accounted for over 50% of the Cd sorbed in the red mud. Generally, the proportions of different fractions were in the order: Res-Cd (50–67%) $>$ EDTA-Cd (19–30%) $>$ NH_4Ac -Cd (8.9–24%) $>$ WS-Cd (0.06–4.4%), and obvious variations occurred to the different treatments of red mud. Compared with RM_0 and RM_a , lower proportions of WS-Cd and higher proportion of Res-Cd in RM_{nano} suggested that the ball milling treatment led to a significant decrease in extractability of Cd retained by red mud, and that Cd formed stable complexes in the RM_{nano} by providing additional sorption sites for Cd contaminants. The fraction of EDTA-Cd remained less variable for the RM_a and RM_{nano} and obviously lower than that of the RM_0 ($p < 0.05$), implying the enhanced immobilization by the treatments since the EDTA-Cd was generally associated with the relatively immobile and not readily bioavailable fraction (Ma and Uren, 1998; Santona et al., 2006). The sequential extraction results suggested that the red mud, especially treated with nano-particle milling, would no doubt exhibit potential implications in remediation of Cd contaminated soils because of its stronger affinity for Cd.

3.4. XANES spectroscopy analysis

The XANES spectra of Cd compounds show a dramatic dependence on local electronic structure and first neighbor coordination environment as shown in Fig. 4. Valid speciation information can be obtained by performing PCA and LCF analyses on the spectra of the sorption samples (Ressler et al., 2000; Isaure et al., 2010). In this study, PCA was performed to define the number of components in the normalized spectra of the eight sorption samples and the results revealed that two significant components accounted for 91%

Fig. 3. Cadmium fractions of water soluble (WS), NH₄Ac and EDTA extractable, and residual (Res-Cd) from the red mud (RM) with different treatments.

of the variance in the energy spectra. The PCA reconstructions with CdO and CdCO₃ were eliminated automatically during the calculation process, while the reconstructions with Cd(NO₃)₂ (Cd²⁺ for short later), Cd(OH)₂, and Cd(OH)Cl spectra were more successful with the SPOIL values below 3, indicating the presence in the sorption samples of Cd species bearing structural similarity to these standard compounds. In addition, based on the key features in the XANES regions shown in Fig. 4 (marked with arrows), the presence

of CdCO₃ and CdO could be also excluded. Thus, the XANES spectra of the sorption samples were fitted using a least-squares algorithm to obtain linear combinations of edge spectra from the three spectra. Cd(OH)Cl was chosen as a reference compound because many studies have proposed that Cd(OH)Cl-like compound was formed on clay minerals during Cd sorption (Lackovic et al., 2002; Gräfe et al., 2007; Serrano et al., 2009). Additionally, the experimental spectrum shape of the compound was well reproduced by FEFF calculation: intensities and positions of the features are satisfactory (Fig. S4 in SI), indicating the reliability of the synthesized compound.

In the LCF analysis, the two most statistically significant fit scenarios are: (1): 61% Cd²⁺ and 39% Cd(OH)Cl (as shown in Fig. 4a and Table S2), and (2) 68% Cd²⁺ and 32% Cd(OH)₂ for the RM₀ sample at low Cd loading (1.0 mmol/kg). Actually, no large amount of Cd(OH)₂ could form in the experimental conditions since Cd predominately presented as Cd²⁺ at pH 6.5. In addition, inclusion of Cd(OH)₂ or any other compound as the third component in the sorption samples improved the fit less than 16%.

It was proposed that Cd²⁺ could be sorbed to surface hydroxyl groups in Fe- and Al-oxyhydroxide minerals at neutral pH based on surface complexation model via the following reactions (Lackovic et al., 2002; Srivastava et al., 2005; Serrano et al., 2009):

and/or

where SOH represents the functional groups from both Fe- and Al-oxyhydroxide minerals. While the formation of the outer-sphere complex might occur via the following reaction (Srivastava et al., 2005; Serrano et al., 2009):

where SH represents ion exchange sites.

The formation of XCd(OH) is reasonable (X represents surface groups on red mud) since the degree of dissociation of a water molecule adsorbed on mineral surface is 10⁷ times higher than in liquid water (Frenkel, 1974). The greater affinity of hydroxyl metal ions from dissociation over metal ions is also apparent due to the lower degree of hydration of the former which leads to both steric and electrostatic favoritism in the sorption process (Ma and Uren, 1998; Naidu et al., 1994). It is necessary to note that formation of the two complexes could occur simultaneously (Lackovic et al., 2002; Serrano et al., 2009).

According to the proposed surface complexation model and the LCF results, it is reasonable to conclude that Cd²⁺ sorbed on the RM₀ as a mixture of outer-sphere complexes (about 65% Cd²⁺) and polynuclear complexes analogous to XCd(OH) (about 35%) which is assumed to be inner-sphere complexes (Gräfe et al., 2007). In addition, similar XANES spectra between goethite and red mud sorption samples (Fig. S5) also indicated that inner-sphere complexation occurred to the red mud since Cd²⁺ is believed to form inner-sphere complexes on goethite (Randall et al., 1999). Similar fit results were also obtained from the treated red mud samples (Fig. 4a and Table S2), while a slight increase in the proportion of inner-sphere complexes occurred to the samples. The formation of the inner-sphere complexes at pH 6.5 can also be evidenced by the decreased occurrence of the inner-sphere complexes at relatively low pH (Fig. 5). At lower pH, the formation of Cd(OH)⁺ in either liquid or sorbent surface would be limited by higher H⁺ concentration. As a result, relatively more hydrated Cd²⁺

Fig. 4. Cadmium L_{III} -edge XANES spectra (a) and corresponding first derivatives (b) of sorption samples on different red mud (RM) and reference compounds: A, CdCO_3 ; B, CdO ; C, $\text{Cd}(\text{OH})_2$; D, $\text{Cd}(\text{NO}_3)_2$; E, $\text{Cd}(\text{OH})\text{Cl}$; F, $\text{RM}_{\text{nano}} + 1.0 \text{ mmol/L Cd}$; G, $\text{RM}_{\text{nano}} + 6.0 \text{ mmol/L Cd}$; H, $\text{RM}_a + 1.0 \text{ mmol/L Cd}$; I, $\text{RM}_a + 6.0 \text{ mmol/L Cd}$; J, $\text{RM}_o + 1.0 \text{ mmol/L Cd}$; K, $\text{RM}_o + 6.0 \text{ mmol/L Cd}$ and the LCF results (open circles).

might be sorbed as outer sphere complexes (Srivastava et al., 2005) and the sorption capacity also significantly decreased (data not shown).

In addition, Cd sorption species in the red mud samples were slightly affected by Cd sorption loadings. At higher sorption loadings, the proportion of inner-sphere complexes was slightly decreased probably due to the increasing saturation of the specific sorption sites in the red mud (Table S2), which was consistent with the sequential extraction results to a certain extent since the inner-sphere complexes are believed to be relatively stable in soil environment (Calmano et al., 2001). Although no direct data of XANES spectra on Cd sorption at lower loadings ($<1.0 \text{ mmol/L}$) was available due to the detection limit, it is reasonable to conclude that

more inner-sphere complexes will occur for Cd on the red mud at the lower Cd loadings since more surface hydroxyl groups are available and less competition occurs to the hydroxyl Cd^{2+} at lower loadings.

It is necessary to note that the residual-Cd plus EDTA-Cd fractions from the sequential extraction results are obviously higher than the inner-sphere complex fractions based on the XANES analysis. Considering the redistribution among the remaining fractions during the extraction procedure (Calmano et al., 2001) and the uncertainty of the linear combination method (Ressler et al., 2000), it can be assumed that the results from the two methods were consistent. In addition, the XANES data only provide first neighbor coordination environment around Cd because of the

Fig. 5. Cadmium L_{III} -edge XANES spectrum of sorption sample in the acidified red mud (RM_a) at pH 4.5 and the LCF results (open circles). The weighted components and corresponding residual (the value is present in parentheses) are displayed below the fit.

short k range (Waychunas et al., 2003). Due to the lower sensitivity of both the intermediate energy X-ray and the extended X-ray absorption fine structure (EXAFS) analysis, the EXAFS data of the sorption samples displayed poorly and thus failed to provide the fine structure information of the complexes, which still needed further investigation.

4. Conclusion

The red mud showed a great affinity for Cd, and ball milling treatment, as an economical technique, significantly enhanced the sorption effectiveness. As indicated by sequential extraction analysis and XANES analysis, a large proportion of Cd formed persistent compounds, among which a fraction of inner-sphere complexes of Cd occurred in the red mud. The proportion of the inner-sphere complexes tends to be enhanced at lower Cd loadings while it was decreased at lower pH. In fact, the concentrations of Cd in soil environment are far below the concentrations adopted in the present study. It is therefore expected that the red mud, particularly with ball-milling treatment, can exert a significantly immobilizing effect on Cd in soils and be used to remediate Cd-contaminated soils effectively. At the same time, the results exhibited important implications for reducing waste disposal and giving new value to the industrial wastes by converting them into a potential immobilizing material.

Acknowledgements

This work was funded by the National Key Project of Scientific and Technical Supporting Programs (2006BAD17B04), the National High Technology Research and Development Program of China (2006AA06Z360), and the Special Fund of Agro-scientific Research in the Public Interest (200903015).

Appendix. Supplementary information

Supplementary information associated with this article can be found in the online version, at doi:10.1016/j.envpol.2011.02.019.

References

- Angove, M.J., Johnson, B.B., Wells, J.D., 1997. Adsorption of cadmium (II) on kaolinite. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 126, 137–147.
- Basta, N.T., Gradwohl, R., 2000. Estimation of Cd, Pb, and Zn bioavailability in smelter-contaminated soils by a sequential extraction procedure. *Journal of Soil Contamination* 9, 149–164.
- Basta, N.T., McGowen, S.L., 2004. Evaluation of chemical immobilization treatments for reducing heavy metal transport in a smelter contaminated soil. *Environmental Pollution* 127, 73–82.
- Brown, S., Christensen, B., Lombi, E., McLaughlin, M., McGrath, S., Colpaert, J., Vangronsveld, J., 2005. An inter-laboratory study to test the ability of amendments to reduce the availability of Cd, Pb, and Zn in situ. *Environmental Pollution* 138, 34–45.
- Brummer, G., Gerth, J., Tiller, K.G., 1988. Reaction kinetics of the adsorption and desorption of Ni, Zn and Cd by goethite I. Adsorption and diffusion of metals. *Journal of Soil Science* 39, 35–52.
- Calmano, W., Mangold, S., Welter, E., 2001. An XAFS investigation of the artefacts caused by sequential extraction analyses of Pb-contaminated soils. *Fresenius Journal of Analytical Chemistry* 371, 823–830.
- Cudennec, Y., Riou, A., Grault, Y., Lecerf, A., 2000. Synthesis and crystal structures of Cd(OH)Cl and Cu(OH)Cl and relationship to brucite type. *Journal of Solid State Chemistry* 151, 308–312.
- Frenkel, M., 1974. Surface acidity of montmorillonites. *Clays and Clay Minerals* 22, 435–441.
- Goldberg, S., Johnston, C.T., 2001. Mechanisms of arsenic adsorption on amorphous oxides evaluated using macroscopic measurements, vibrational spectroscopy, and surface complexation modeling. *Journal of Colloid Interface Science* 234, 204–216.
- Grfe, M., Singh, B., Balasubramanian, M., 2007. Surface speciation of Cd (II) and Pb (II) on kaolinite by XAFS spectroscopy. *Journal of Colloid Interface Science* 315, 21–23.
- Hamon, R.E., McLaughlin, M.J., Cozens, G., 2002. Mechanisms of attenuation of metal availability in in situ remediation treatments. *Environmental Science and Technology* 36, 3991–3996.
- Isaure, M.P., Sarret, G., Harada, E., Choi, Y.E., Marcus, M.A., Fakra, S.C., Geoffroy, N., Pairs, S., Susini, J., Clemens, S., Manceau, A., 2010. Calcium promotes cadmium elimination as vaterite grains by tobacco trichomes. *Geochimica et Cosmochimica Acta* 74, 5817–5834.
- Lackovic, K., Angove, M.J., Wells, J.D., Johnson, B.B., 2002. Modeling the adsorption of Cd(II) onto Muloorina illite and related clay minerals. *Journal of Colloid Interface Science* 257, 31–40.
- Lombi, E., Zhao, F.J., Wieshammer, G., Zhang, G., McGrath, S.P., 2002a. In situ fixation of metals in soils using bauxite residue: biological effects. *Environmental Pollution* 118, 445–452.
- Lombi, E., Zhao, F.J., Zhang, G., Sun, B., Fitz, W., Zhang, H., McGrath, S.P., 2002b. In situ fixation of metals in soils using bauxite residue: chemical assessment. *Environmental Pollution* 118, 435–443.
- Luo, L., Zhang, S.Z., Shan, X.Q., Jiang, W., Zhu, Y.G., Liu, T., Xie, Y.N., McLaren, R.G., 2006. Arsenate sorption on two Chinese red soils evaluated using macroscopic measurements and EXAFS spectroscopy. *Environmental Toxicology and Chemistry* 25, 3118–3124.
- Luo, L., Ma, Y.B., Zhang, S.Z., Wei, D.P., Zhu, Y.G., 2009. An inventory of trace element inputs to agricultural soils in China. *Journal of Environmental Management* 90, 2524–2530.
- Ma, Y.B., Uren, N.C., 1998. Dehydration, diffusion and entrapment of zinc in bentonite. *Clays and Clay Minerals* 46, 132–138.
- Naidu, R., Bolan, N.S., Kookana, R.S., Tiller, K.G., 1994. Ionic-strength and pH effects on the sorption of cadmium and the surface charge of soils. *European Journal of Soil Science* 45, 419–429.
- Randall, S.R., Sherman, D.M., Ragnarsdottir, K.V., Collins, C.R., 1999. The mechanism of cadmium surface complexation on iron oxyhydroxide minerals. *Geochimica et Cosmochimica Acta* 63, 2971–2987.
- Ravel, B., Newville, M., 2005. ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. *Journal of Synchrotron Radiation* 12, 537–541.
- Ressler, T., Wong, J., Roos, J., Smith, I.L., 2000. Quantitative speciation of Mn-bending particulates emitted from autos burning (methylcyclopentadienyl)manganese tricarbonyl-added gasolines using XANES spectroscopy. *Environmental Science and Technology* 34, 950–958.
- Santona, L., Castaldi, P., Melis, P., 2006. Evaluation of the interaction mechanisms between red muds and heavy metals. *Journal of Hazardous Materials* 136, 324–329.
- Serrano, S., O'Day, P.A., Vlassopoulos, D., Garca-Gonzlez, M.T., Garrido, F., 2009. A surface complexation and ion exchange model of Pb and Cd competitive sorption on natural soils. *Geochimica et Cosmochimica Acta* 73, 543–558.
- Sparks, D.L., 1995. *Environmental Soil Chemistry*. Academic Press, San Diego, CA.
- Sparks, D.L., 1996. *Methods of Soil Analysis. Part 3: Chemical Methods*. SSSA and ASA, Madison, WI.
- Srivastava, P., Singh, B., Angove, M.J., 2005. Competitive adsorption behavior of heavy metals on kaolinite. *Journal of Colloid Interface Science* 290, 28–38.
- State Environmental Protection Administration of China (SEPAC), 2006. *Farmland Environmental Quality Evaluation Standards for Edible Agricultural Products (HJ 332-2006)*. China Environment Press, Beijing.
- Wang, S.B., Ang, H.M., Tad, M.O., 2008. Novel applications of red mud as coagulant, adsorbent and catalyst for environmentally benign processes. *Chemosphere* 72, 1621–1635.
- Waychunas, G.A., Fuller, C.C., Davis, J.A., Rehr, J.J., 2003. Surface complexation and precipitate geometry for aqueous Zn(II) sorption on ferrihydrite: II. XANES analysis and simulation. *Geochimica et Cosmochimica Acta* 67, 1031–1043.
- Zhang, Z.Z., Li, M.Y., Chen, W., Zhu, S.Z., Liu, N.N., Zhu, L.Y., 2010. Immobilization of lead and cadmium from aqueous solution and contaminated sediment using nano-hydroxyapatite. *Environmental Pollution* 158, 514–519.