



Bioaccumulation of heavy metals by *Phragmites australis* cultivated in synthesized substrates

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Received 25 October 2008; revised 21 March 2009; accepted 17 April 2009

Abstract

Accumulation of heavy metals from various oxides with adsorbed cadmium by wetland plant *Phragmites australis* was studied to evaluate the fate of heavy metals in the sediment of constructed wetlands. Hoagland solution was used as nutrition supply, and single metal oxide with adsorbed cadmium was applied as contaminant to study the accumulation characteristics of cadmium and the substrate metals by *P. australis*. After 45-d treatment, the bioaccumulation degree in root followed the order: $\text{Al}(\text{OH})_3 > \text{Al}_2\text{O}_3 > \text{Fe}_3\text{O}_4 > \text{MnO}_2 > \text{FeOOH}$. Heavy metals absorbed by *P. australis* were largely immobilized by the roots with little translocation to aboveground parts.

Key words: heavy metals; bioaccumulation; metal oxides; adsorption

DOI: 10.1016/S1001-0742(08)62433-X

Introduction

Heavy metal contaminations, induced from anthropogenic activities such as mining, smelting, electroplating and etc., have become a major environmental problem. Hereinto, the mining operation, especially metal ore extraction, is the second source of heavy metal contamination in soil (Singh *et al.*, 2005). Since the Stone Age, mining activities have produced totally about 1150 million tons of heavy metals (copper, lead, cobalt, zinc, cadmium and chromium) on a global scale. According to Ripley *et al.* (1996), when one ton of ore is mined, approximate 0.42 ton of mullock, 0.52 ton of tailing and 0.04 ton of waste residue would be produced and only 0.02 ton of useful materials are remained. Randomly disposed mine wastes resulting from metalliferous mining and processing always tend to release toxic heavy metal into the ambient environment. Subsequently, drainages and mining tailings containing elevated concentrations of metals will degrade large areas of lands and water posing a severe risk on ecosystem and human health.

In mining tailings or sediments of constructed wetland, metal ions are generally associated with particulate matter and accumulate in the bottom sediments which in turn become important sinks and sources of heavy metal contaminants. Sediment is a heterogeneous mixture of dissimilar particles which have been considered a complex assemblage of different organic and inorganic components (Martin *et al.*, 1987) including organic matters and var-

ious minerals. Metals settled in sediments have several association forms such as ion exchange, adsorption, or precipitation (Peijnenburg *et al.*, 1997) which would be the essence to predict the behaviors (bioavailability, toxicity and distribution) of metals in environment (Murakami *et al.*, 2008). Many metal oxides minerals occur as a discrete phase or as coatings on other mineral surfaces in sediments (Axe and Trivedi, 2002). Because these oxides usually have a large surface area, porous structure (for some amorphous phases), and an abundance of binding site, metal ions are easily bound to them (Algan *et al.*, 2004). Alomary (2007) investigated seven metals in surface sediments from 18 sites of Algerian Mediterranean coasts, and cadmium present in “bound to hydroxides” was 23.01% in total extracts. Moreover, significant correlations were found between Cd and Al, Cd and Fe with correlation coefficients of 0.7 and 0.9, respectively, which may result from the high adsorption capacity of Fe and Al oxides (Algan *et al.*, 2004). The waste drainage contain elevated concentrations of metals including Fe, Mn, Al and Cu (Banks *et al.*, 1997) which would easily form metal oxides once reacting with oxygen in liquid or atmosphere during the migrating process.

Phragmites australis (Cav.) Trin. ex Steudel has been used successfully in phytoremediation by constructing artificial wetland (Stoltz and Greger, 2002) due to its excellent tolerances to various contaminants and specific biochemical, physiological and anatomical adaptations which enable it to overcome or avoid the physical chemical hazards of anaerobic soils (Ye *et al.*, 1997; Batty and

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Younger, 2004). The mine tailings enriching sulphides (e.g., pyrite) exposed to oxygen and water can form acid mine drainage (AMD) which may accelerate the release of heavy metals to environment (Stoltz and Greger, 2002). Hence, the use of *P. australis* in constructed wetland may prevent the formation of AMD in mine tailings due to the consumption of oxygen through the root respiration and the created anaerobic environment (Hardej and Ozimek, 2002; Batty and Younger, 2004). Thus, more knowledge of metal bioaccumulation characteristics of *P. australis* should be achieved to successfully utilize plants to improve the mine environment and lessen the release of heavy metals.

Goethite (FeOOH), magnetite (Fe_3O_4), gibbsite ($\text{Al}(\text{OH})_3$), alumina (Al_2O_3) and manganese oxide (MnO_2) are major (hydr)oxide minerals in sediment which fatefully influence the adsorption, fixation, and transportation of heavy metals in sediments (Dong *et al.*, 2000). Therefore, the objective of the present study was to investigate the effect of association between Cd and metal oxides on bioaccumulation characteristics of Cd and metals in oxides as adsorbents in hydrophyte *P. australis*.

1 Materials and methods

All chemicals were of analytical reagent grade. The metal oxides were provided by Sinopharm Chemical Reagent Co., Ltd., China. Cadmium stock solution was prepared by dissolving $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in distilled water at 100 mg/L. All solutions were prepared with distilled water in bottles which were soaked in 0.1 mol/L HNO_3 for at least 24 h to lessen the adsorption by bottle wall. The modified Hoagland solution ($\text{pH } 5.5 \pm 0.2$) was prepared with the following salts (mol/L): $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 3.57×10^{-4} ; H_3BO_3 , 2.31×10^{-5} ; KH_2PO_4 , 9.68×10^{-4} ; KNO_3 , 2.55×10^{-4} ; MgSO_4 , 1.04×10^{-3} ; FeCl_3 , 6.83×10^{-5} ; $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, 7.69×10^{-6} ; MoO_3 , 1×10^{-5} ; $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 1×10^{-5} ; and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 1×10^{-5} .

1.1 Adsorption of Cd on metal oxides

The Cd adsorption experiments were conducted in 2.5 L reactors containing 2 L Hoagland solution. The metal oxide solid of 100 g was mixed with the Hoagland solution and was allowed to equilibrate for 1 h. One hundred milliliters cadmium stock solution (100 mg/L) was added by titration while vigorously stirring to achieve the terminal concentration of 50 mg/kg solid. The system was left to equilibrate in a shaker at 25°C for 24 h. The pH of the solutions was controlled constant at 5.5 using HCl or NaOH. The analysis of residual Cd in solution showed that Cd was completely adsorbed by all oxides. The slurry was then ready for the bioaccumulation tests.

1.2 Hydroponic experiments

Two-year-old seedlings of *P. australis* growing in "clean" wetland were purchased from LJTH Flower Co., China. Roots of seedlings were washed twice with tap water and then distilled water, and cultured into ceramic

buckets (10 cm depth \times 30 cm height, each containing 2 L of 10% Hoagland solution without the addition of heavy metals) for acclimation. Three weeks later, uniform (approximately 25 cm height) healthy seedlings were selected and transplanted into ceramic buckets each containing 2 L of the previously prepared metal oxides-Hoagland solution slurry.

Four seedlings were grown in each of three replicate buckets in each of the substrates. The vessels were arranged in a randomized design. Seedlings were grown in a greenhouse with natural illumination. The media pH was left to drift but monitored once a week after the plant was introduced.

1.3 Dithionite-citrate-bicarbonate extraction

Iron plaque and other metals coating on fresh root surfaces were extracted using a modified dithionite-citrate-bicarbonate (DCB) method (Otte *et al.*, 1989). After 45 d cultivation, each seedling was washed gently once with tap water, and three times with deionized water. The entire root system of each seedling was firstly incubated in 30 mL of 0.03 mol/L sodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$) and 0.125 mol/L sodium bicarbonate (NaHCO_3) and 0.6 g sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$) at 25°C for 60 min. The extract was filtered through a 0.2- μm membrane for analysis.

1.4 Analysis of metal concentrations in plant samples

After DCB extraction, the stems and roots were oven-dried at 80°C to constant weight, and ground to fine powders. The powders were digested in a mixture of $\text{HNO}_3/\text{HClO}_4$ (3/1, V/V), at 150°C for 2 h and 210°C for 1 h, and then dissolved in HNO_3 (5%). The concentrations of Cd, Fe, Al, Mn in the DCB-extracts and in the acid digests were measured by flame atomic absorption spectrometry (FAAS, AA240, Varian USA). A reagent blank and a standard reference material (peach leaves, GBW08501, Chinese National Certified Reference Material) were included to verify the accuracy and precision of the digestion procedure and subsequent analysis.

1.5 Statistical analysis

Data were analyzed by one-way ANOVA using the SPSS Version 11.0 for Windows statistical software package. Data are presented as mean \pm standard error (SE) ($n = 3$), and were tested by least significant difference (LSD) at the 5% level.

2 Results

2.1 Effects of Cd and metal oxide on plant growth

P. australis seedlings were exposed to the concentration of 50 mg/kg metal oxide solid mass in the growth medium to determine the effect of adsorbed Cd on metal accumulation and plant growth expressed as biomass production and allocation. Compared to the control, the growth of plants was slacked exhibiting by the reduction of biomass accumulation ($p < 0.05$) (Table 1). Root/shoot ratio dry mass of seedlings increased, while stem/leaf ratio dry mass

of seedlings prominently increased comparing with the control except for FeOOH treatment.

2.2 Concentration and accumulation of Cd in *P. australis*

The hydroponic-culture experiment using the Hoagland solution showed that the bioaccumulation of absorbed Cd by *P. australis* highly depended upon the type of substrate oxides (Fig. 1). The *P. australis* cultivated in Cd-Al(OH)₃ medium was found accumulating the largest amount of Cd, followed by that in Cd-Al₂O₃ and Cd-Fe₃O₄. The lowest concentration of Cd was observed in the plants cultivated in Cd-FeOOH and Cd-MnO₂. The Cd concentration in roots of *P. australis* under treatments followed a degressive order: Al(OH)₃ > Al₂O₃ > Fe₃O₄ > MnO₂ > FeOOH. The Cd content accumulated in roots was nearly ten folds of that in aboveground parts. The Cd distribution in different parts of the plants followed the decreasing order: root > root surface (DCB-extraction) > stem > leaf. The Cd concentration on root surfaces (DCB-extraction) varied with different metal (hydr)oxides: 30–35 mg/kg for Al(OH)₃, Fe₃O₄ and Al₂O₃; < 20 mg/kg for FeOOH and MnO₂.

2.3 Concentration and accumulation of Fe, Mn, Al in *P. australis*

As an essential element, Fe concentrations collected from plants in different treatments were 529–6213 mg/kg; 115–490 mg/kg; and 613–1014 mg/kg in root, stem and leaf, respectively (Fig. 2). The concentrations of Fe in root followed a degressive order: Fe₃O₄ > FeOOH > MnO₂ > Al(OH)₃ > Al₂O₃. Fe allocation in different parts of the plants followed the decreasing order: root > leaf > root surface (DCB) ≥ stem.

Figure 3 shows the Mn and Al concentrations in different plant parts treated with Cd adsorbed metal oxides systems. Accumulated Mn concentration on the root surfaces (DCB-extraction) was higher than that in other parts of plant with the exception of Cd-MnO₂ treatment in which Mn concentration was extraordinarily greater than others. And Mn concentrations in leaves of *P. australis* of

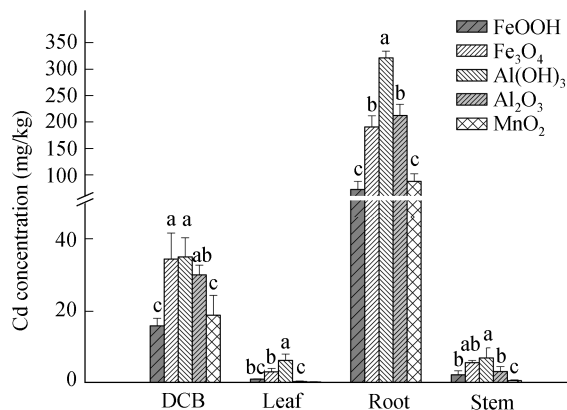


Fig. 1 Cd concentrations in root surface (DCB-extraction), root, stem and leaf of *P. australis* extraction ($n = 3$). Data with different letters are significantly different at $p < 0.05$ level within each group. Error bars represent the mean standard error.

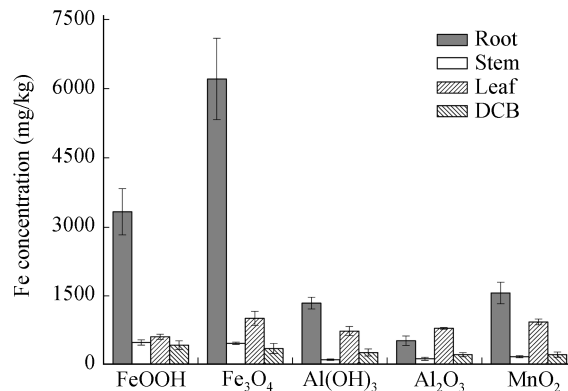


Fig. 2 Fe concentrations in root surface (DCB-extraction), root, stem and leaf of *P. australis* ($n = 3$). Error bars represent the mean standard error.

all treatments were higher than that in stems. As regard to the Al concentrations in plant, significant differences were observed among treatments, and Al concentration in roots of *P. australis* under different treatments followed a degressive order: Al(OH)₃ >> Al₂O₃ > MnO₂ > FeOOH > Fe₃O₄. The Al content accumulated in roots of the plant treated in Cd-Al(OH)₃ was nearly one order of magnitude higher than that in other treatments. Al concentration in root surface (DCB-extraction) was greater than that in roots except samples treated with Al-oxides ($p < 0.05$).

3 Discussion

3.1 Effect of cultivation substrates on Cd bioaccumulation by *P. australis*

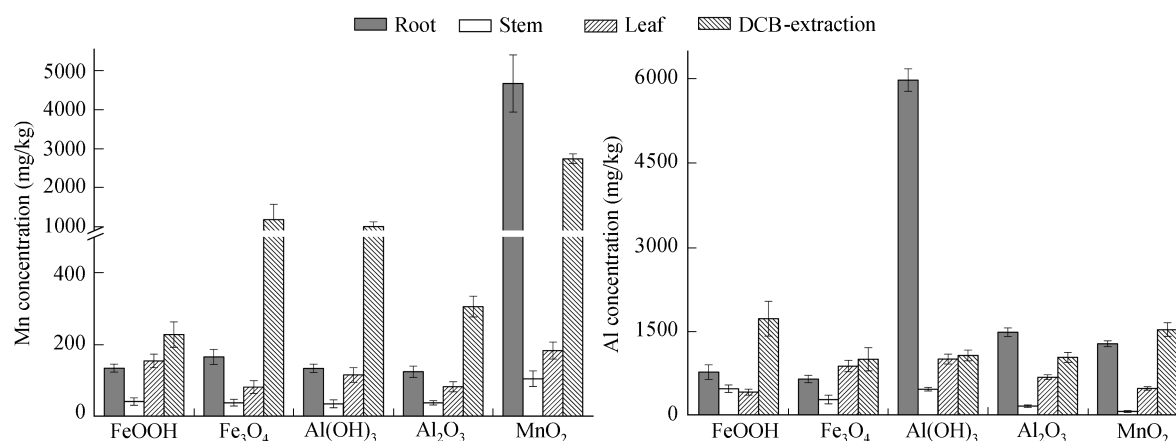
The mobility and bioavailability of heavy metals in environment is largely controlled by their adsorbent substrates. In this study, although the Cd concentration in all treatments was ca. 50 mg Cd/kg oxide solid, the Cd concentration in plant tissues were different which indicated the effect of cultivation substrates on its bioaccumulation. The Cd concentration in the *P. australis* grown in Cd-Al(OH)₃ treatment was about 1.6 times of that in Cd-Fe₃O₄ and Cd-Al₂O₃ systems and about 5 times of that in Cd-FeOOH and Cd-MnO₂ systems. Cadmium associated with aluminum (hydr)oxides was more available than that on Fe and Mn oxides which was probably due to the weak adsorption capability and stability of Al (hydr)oxides. Previous investigation showed that FeOOH adsorbed more Cd than Al₂O₃ under similar conditions (Lai *et al.*, 2002; Sen and Sarzali, 2008). The physicochemical characteristics of metal (hydr)oxides result in the difference of adsorption capacity and stability which in turn would cause the difference of Cd bioaccumulation.

There are various factors that govern the adsorption capacity and bonding strength of metal oxides for Cd ions. Cd ions are associated with metal (hydr)oxides via inner-sphere complexation with hydroxyls, therefore the adsorption is dependent on the density of active sites in the metal (hydr)oxides. Specific surface area is another important factor controlling Cd adsorption. Metal (hydr)oxides with a relative larger specific surface area generally have a

Table 1 Biomass and its allocation between root, shoot and leaf of *P. australis* (g/plant)

Adsorption system	FeOOH	Fe ₃ O ₄	Al(OH) ₃	Al ₂ O ₃	MnO ₂	CK
Root	1.90	1.56	1.67	1.18	1.15	3.15
Stem	2.16	1.70	2.17	1.31	1.77	5.76
Leaf	1.02	0.45	0.65	0.36	0.46	2.24
Root/shoot ratio	0.59	0.73	0.60	0.71	0.52	0.41
Stem/leaf ratio	2.01	3.79	3.32	3.62	3.88	2.57

CK: seedlings without contaminant.

**Fig. 3** Mn and Al concentrations in root surface (DCB-extraction), root, stem and leaf of *P. australis* ($n = 3$). Error bars represent the mean standard error.

higher adsorption capability. Generally, iron oxides exhibit greater specific surface area and adsorption site density than aluminum oxides (Johnson, 1986; Anderson and Benjamin, 1990a, 1990b; Hiemstra *et al.*, 1999; Jordan *et al.*, 2007). The pH of zero point charge (pH_{ZPC}) of metal (hydr)oxides has close relationship with metal adsorption. The surfaces of metal (hydr)oxides would be negatively charged at pH above pH_{ZPC} and positively charged at pH below pH_{ZPC} , which result in the increase of electrostatic attraction or repulsion with metal cations respectively, and lead to a more or less readily adsorption. The pH_{ZPC} of these three set of metal oxides is different: pH 2.8–3.3 for Mn-oxides; 7–8 for Fe-oxides; and 9–9.5 for Al-oxides (Anderson and Benjamin, 1990a, 1990b; Mukal and De Haan, 1992). Hence, Mn-oxides would show electrostatic attraction towards Cd cations as the pH_{ZPC} is below the pH of the cultivation systems (5.5–6.4) in the present study. Iron oxides would show a less electrostatic repulsion towards Cd cations than Al-oxides at the cultivation media pH (Potter and Yong, 1999). Despite being miner phase in sediment, Mn oxides are important oxide minerals and play an important role in controlling the bioaccumulation of Cd in sediments (Turner *et al.*, 2008). Mn-oxide tends to have a greater adsorption capability for Cd ions due mainly to its relatively high specific surface area and low pH_{ZPC} (Catts and Langmuir, 1986). It is reported that for a given salinity, the conditional particle-water distribution coefficient (K_D) of Mn oxides was two orders of magnitude greater than that of Fe oxides (Turner *et al.*, 2008). Therefore, Cd adsorbed on the substrate of Mn-oxides would be more stable against bioaccumulation followed with Fe- and Al-oxides.

3.2 Fates of metals in sediment environments

Heavy metals settled in sediment mostly associate with metal oxides or minerals, but would be mobilized when some condition changed. The mineral compound of Fe, Mn and Al (hydro-)oxides is used as adsorbent in this experiment to simulate natural constitutions in sediments in respect that these elements dominate in the Earth's surface as oxides. Metals of Fe, Mn and Al in adsorbents oxides can be released into liquid phase and accumulated by the plant species with the adsorbate metals when metal oxides are reductively dissolved or the environment of rhizosphere is acidified by organic acids or the discharge of acid mine drainage. Wang *et al.* (2008) reported that probably 13% of total Mn and 64% of total Cd in tailings associated with Fe-Mn oxides and 237 mg/kg Mn, 3.5 mg/kg Cd were accumulated in the roots by *P. australis* grown near the Mn mine tailing. Some studies have shown higher bio-concentration factors in root of *P. australis* than the present work, probably due to the different cultivation conditions such as hydroponics treatment, or longer exposing in previous works (Stoltz and Greger, 2002; Batty and Younger, 2004; Vymazal *et al.*, 2007). Similar root accumulation characteristics of metal or metalloid was also found in *P. australis* for Cu, Zn, As, in *Eriophorum angustifolium* for Cd, Zn, Pb, in *Carex rostrata* for Cu, Zn, As, and in *Salix* for Cu, As (Stoltz and Greger, 2002). Little metals (less than 5%) in *P. australis* were translocated to the aboveground tissues and leaf tissues have the next highest concentrations of Fe, Mn, Al followed by stems (Weis *et al.*, 2004). The elite hydrophytes was widely used

to treat wastewater (Batty and Younger, 2004) or mine tailings (Stoltz and Greger, 2002) due to the outstanding metal tolerance and accumulation ability and the limitation of shoot metal translocation which may lessen metals dispersed into the environment through herbivores or at senescence (Bragato, 2006).

In tailings and minesoils, total metal contents were remarkably high with a range of 666–2400 mg/kg for Mn, 7–110 mg/kg for Cd (González and González-Chávez, 2006) and 88–931 mg/kg for Fe (Li *et al.*, 2007) which were close to the phytotoxic levels of soil. Abundant metals exist in tailings and minesoils as oxides which can be immobilized through the adsorption onto plant roots and other metal oxides or precipitation within the rhizosphere. Once these metals are released to the environment, they could be accumulated by plants as the results shown in Figs. 2 and 3.

In addition, the association of metals on the surfaces of roots probably was another fate of these metals. Metal plaques occur on root surface of aquatic plants or near the rhizosphere, likely resulting from radial oxygen diffusion and subsequent oxidation of metals such as Fe, Mn, and etc. The components of metal plaques were reported as amorphous and crystalline metal oxides (St-Cyr *et al.*, 1993; Snowden and Wheeler, 1995). The plaque deposits were clearly visible as orange-brown or dark-brown coatings on the root surface, extending from 1 cm behind the growing tip along the entire root. Plaques present on root surfaces usually have a high specific surface area and possess –OH functional groups which are capable of reacting with metals and other cations and anions in the environment. Therefore, DCB-extraction concentration results from the present study showed another end-result of metals in sediment environment (Figs. 1 and 3).

4 Conclusions

Bioaccumulation of heavy metals associated with oxides minerals by *P. australis* is largely controlled by the type of substrate.

(1) Bioaccumulation of Cd adsorbed on the metal oxides by *P. australis* was different for different substrate oxide. The Cd concentration in root followed the order of $\text{Al}(\text{OH})_3 > \text{Al}_2\text{O}_3 > \text{Fe}_3\text{O}_4 > \text{MnO}_2 > \text{FeOOH}$.

(2) Heavy metals in sediments both as adsorbents and adsorbates were mostly immobilized by *P. australis* in roots with little translocation to aboveground parts due to root bioaccumulation and plaques adsorption. The limitation of shoot metal translocation may lessen metals dispersed into the environment through herbivores or at senescence.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (No. 40773076), the Ministry of Science and Technology of China through the National Basic Research Program of China (No. 2009CB426301).

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