SIMULTANEOUS REMOVAL OF SOME HEAVY METALS AND ARSENIC FROM AQUEOUS SOLUTIONS BY *Phragmites australis*

Tran Thi Huyen Nga*, Nguyen Thi Hoang Ha

VNU University of Science, Vietnam National University, 334 Nguyen Trai, Hanoi, Vietnam

*Email: tranthihuyennga@hus.edu.vn

Received: 5 May 2016; Accepted for publication: 26 June 2016

ABSTRACT

In this study, *Phragmites australis* (common reed) was transplanted into solutions added with different concentrations of Mn, Zn, Cd, Pb, and As for 30 days in the laboratory (10 days of incubation and repeated three times without changing the plant) to assess the removal of these metals and its accumulation in the plant. The results showed that high removal efficiency was achieved by growing *P.australis*. The highest daily removal rates of heavy metals and As were obtained after 1 day of new solution addition. The highest concentrations of Mn, Zn, Cd, Pb, and As in the plant roots were 3920, 1020, 90.9, 1350, and 183 mg kg–1 dry wt., respectively; those in the stems were 465, 108, 26.4, 227, and 74.0 mg kg^{-1} dry wt.; and those in the leaves were 716, 150, 18.1, 157, and 88.3 mg kg^{-1} dry wt. The results of this study indicated that *P. australis* has the ability to remove simultaneously these metals from water, making it a potential species for phytoremediation of wastewater from Pb-Zn mine.

Keywords: arsenic, heavy metals, *Phragmites australis*, phytoremediation, removal.

1. INTRODUCTION

Mining activities including exploitation and processing have generated considerable amounts of waste materials to the surrounding environment [1]. One of the largest Pb-Zn and long-term operation mine in northern Vietnam has been reported to be contaminated with heavy metals and As [2]. Mn and Zn are essential micronutrients for normal plant metabolism, playing an important role in plant growth [3]; however, they are toxic when present in high concentrations [4]. Cd, Pb, and As are not known to be essential elements to plants [3]. Mn, Zn, Cd, Pb, and As are toxic to normal plants at concentrations of 300–500, 100–400, 5–30, 30–300, and 5–20 mg/kg, respectively [5]. Of particular concern, water from the main stream in the Pb-Zn mine is directly used for irrigation by rural communities located around the mine [6]. Considering their pressing threat to human and animal health, the appropriate treatment of these metals is of great environmental importance. A variety of treatment methods have been developed for the elimination of these metals from water, including coagulation, adsorption, ion exchange, electrocoagulation, and biological processes; however, many of these methods are costly and require major investments in equipment and facilities [7]. Phytoremediation has emerged as a cost-effective, long-lasting, and environment-friendly technology for the treatment of waters contaminated with heavy metals [8].

Aquatic macrophytes have great potential for the phytoremediation of water contaminated with heavy metals and As [7, 9]. *Phragmites australis* (common reed, Poaceae) is one of the most widely distributed species in the world. In addition, this plant species is well adapted with contaminated environments and is a potential candidate for phytoremediation of heavy metals [10, 11].

The objectives of the present study are to examine (1) simultaneous removal of Mn, Zn, Cd, Pb, and As from water by *P. australis*; and (2) the potential use of this plant species in phytoremediation of wastewater from Pb-Zn mine.

2. MATERIALS AND METHODS

2.1. Experimental plant, growth condition, and heavy metal preparation

P. australis was collected and washed thoroughly with tap water followed by Milli-Q water to remove sediments, and placed into 30 L experimental tanks (56.4 cm x 37.9 cm x 20.5 cm) filled with 10 L of Milli-Q water, where it received 16 h of white fluorescent light per day. The air and water temperatures were kept constant (24 ± 1 ^{0}C) during the experiment.

Five metal ions (Pb, Zn, Mn, Cd, and As) were added as standard solutions ($Pb(NO_3)_2$, $Zn(NO_3)_2$, $Mn(NO_3)_2$, Cd $(NO_3)_2$ and Na_2HAsO_4). The reagents were dissolved in Milli-Q water to obtain the desired contamination levels. The resulting solutions were adjusted to pH=7 with NaOH and HNO_3 using the Horiba D54 pH meter.

2.2. Experimental setup and sampling

The laboratory experiment was carried out over 30 days. All laboratory experiments were repeated in duplicated. Experiments were performed as following:

Tank A: *P. australis* (200 g fresh weight) was grown in a tank containing no metals as plant control.

Tank B: Heavy metals and As were simultaneously added to the tanks to make the final concentrations of Mn, Zn, Cd, Pb, and As were 20, 6.0,0.5,20, and 1.0 mg/l, respectively. *P. australis* (200 g fresh weight) was grown in the tank. The desired contamination levels in tank B were set the same as metal concentrations in direct wastewater of the largest Pb-Zn mine in northern Vietnam.

Tank C: Heavy metals and As were simultaneously added to the tanks to make the final concentrations ofMn, Zn, Cd, Pb, and As were 4, 1.5, 0.1, 0.6, and 0.4mg/l, respectively. *P. australis* (200 g fresh weight) was grown in the tank. The desired contamination levels in tank C were set the same as metal concentrations in outlet wastewater of two reservoirs of the largest Pb-Zn mine in northern Vietnam.

Tank D and E: the same metal concentrations were generated with tank B and C, respectively; however, no plant was transplanted for metal control.

The plants were exposed to the solutions for 10 days, then the solutions were decanted and replaced with fresh metal solutions. This process was repeated three times. Water samples for metal analysis were collected before and at 1 day, 2 days, 3 days, 4 days, 7 days, and 10 days of incubation. Plant samples were collected at the start and end of the experiment.

2.3. Elemental analysis of plant and water samples

P.australis was well rinsed with deionized water and dried in a ventilated oven at 80^0C for 48 hours. The dried samples were ground into fine powder using a mortar mill. Plant samples (50 mg per each) were digested with mixture (H_2O_2: HNO_3 =1:5) for atomic absorption spectroscopy (AAS) analysis. Elemental analysis of plant and water samples was performed by the AAS (240FS and VGA77, Agilent) at the Faculty of Geology, VNU University of Science.

2.4. Statistical analysis

Statistical analyses of experimental data were performed using SPSS 15.0. All data were tested for goodness of fit to a normal distribution, using a Kolmogorov–Smirnow one-sample test. Evaluation of significant differences among treatments was performed using one-way ANOVA followed by Tukey's post-hoc test, with $p < 0.05$ indicating statistical significance.

3. RESULTS AND DISCUSSION

3.1. Removal of heavy metals from solutions

Concentrations of heavy metals and As showed a rapid decline over the period of the experiment (Fig. 1) for every initial concentration and 3 times (10 days per each) of replaced solutions. The initial concentrations of Mn, Pb, Zn, As, and Cd in tank B were 20.0, 20.0, 6.0, 1.0, and 0.5 mg/l, respectively; which decreased to 14.2, 16.1, 4.6, 0.9, and 0.4 mg/l after 1 day of incubation and 6.9, 8.8, 2.4, 0.4, and 0.2 mg/l at the 10^{th} day of the experiment. The initial concentrations of Mn, Pb, Zn, As, and Cd in tank C were 4.0, 0.6, 1.5, 0.4, and 0.10 mg/l, respectively; which decreased to 0.3, 0.3, 0.5, 0.3, and 0.08 mg/l after 1 day of incubation and 0.03, 0.05, 0.07, 0.13, and 0.03 mg/l at the 10^{th} day of the experiment.

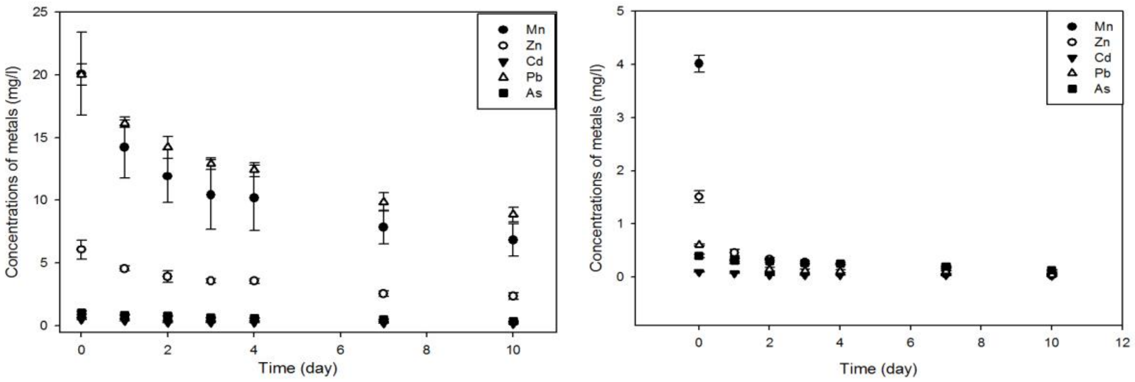

Figure 1. Concentrations of heavy metals and As in Tank B(left) and C (right).

The highest removal rate of heavy metals and As from water was obtained after 1 day of incubation (for every time the metal solutions was replaced) (Fig. 2). The removal rate of Mn, Zn, Cd, Pb, and As from Tank B solution after one day of incubation was 29.2, 24.8, 20.4, 19.6, and 14.9%, respectively; that from Tank C solution was 92.2, 69.7, 24.7, 48.8, and 18.8%. The cumulative removal rate of Mn, Zn, Cd, Pb, and As after 10 days of incubation from tank B solution was 65.9, 60.8, 63.1, 55.7, 62.5%, respectively; that from tank C solution was 99.2, 95.6, 69.5, 92.0, and 66.9%. Arsenic was gradually removed from water solutions during the experiment. In contrast, considerably high amounts of heavy metals were removed from solutions after 2 days of incubation, indicating the sufficient time period for constructed wetland design. The result of metal control (Tanks D and E) demonstrated that the percentage of As, Pb, Cd, Zn, and Mn removed by the plant was 83.7–99.7, 75.1–91.7, 29.8–54.5, 29.2–64.1, and 0.7–32.0%, respectively. This result indicated that other amount of metal removal from solutions was possibly due to natural precipitation and adsorption into natural rock in tanks.

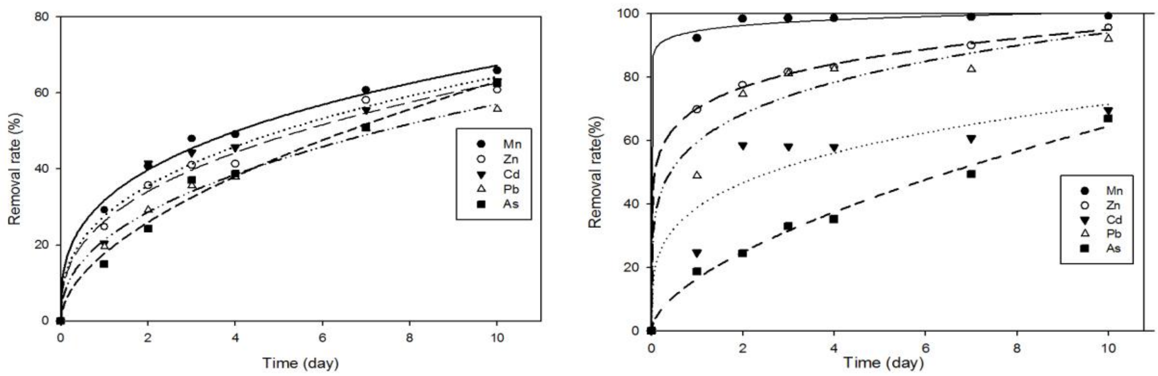

Figure 2. Cumulative removal rates of heavy metals and As in Tank B (left) and C (right).

3.2. Accumulation of heavy metals in *P. australis*

Table 1. Concentrations of heavy metals and As in *Phragmitesaustralis* (mg kg–1 dry wt.).

Metal	Plant part	Initial	Tank A	Tank B	Tank C
Mn	Root	253±21	259±54	3920±150	1140±44
	Stems	34.5±3.5	39.3±1.9	465±39	113±9
	Leaves	32.2±3.1	38.0±8.4	716±40	122±13
Zn	Root	90.4±11.9	94.8±15.6	1020±50	327±37
	Stems	35.9±3.0	37.5±3.7	108±17	81.4±4.7
	Leaves	53.1±7.2	58.8±8.7	150±12	95.3±10.6
Cd	Root	5.87±1.24	7.93±1.23	90.9±9.6	26.8±4.2
	Stems	4.44±0.62	5.41±0.49	26.4±7.6	7.59±0.81
	Leaves	5.04±0.38	5.61±0.90	18.1±1.0	8.43±0.60
Pb	Root	70.1±7.2	77.7±5.9	1350±50	169±13
	Stems	48.4±3.4	58.4±4.1	227±23	128±12
	Leaves	49.2±4.7	56.5±8.8	150±16	157±18
As	Root	25.9±2.6	22.9±5.0	183±21	70.2±8.3
	Stems	15.8±1.2	16.5±2.6	74.0±5.8	66.0±7.2
	Leaves	21.5±2.4	22.9±5.7	63.7±5.0	88.3±5.4

Values present means±standard deviations (N=3–9)

The highest concentrations of Mn, Zn, Cd, Pb, and As in the plant roots were 3920, 1020, 90.9, 1350, and 183 mg kg–1 dry wt., respectively; those in the stems were 465, 108, 26.4, 227, and 74.0 mg kg–1 dry wt.; and those in the leaves were 716, 150, 18.1, 157, and 88.3 mg kg–1 dry wt. (Table 1). Concentrations of Mn, Zn, Cd, Pb, and As in *P. australis* growing in tanks B and C were significantly higher than the initial concentration ($p < 0.05$) by factors of approximately 15, 11, 15, 19, and 7, respectively. In addition, concentrations of heavy metals in the plant roots were significantly higher than those in the stems and leaves ($p < 0.05$) (Table 1). The lower rate of heavy metals and As accumulation in shoots compared with roots may reflect the poorer capacity of *P. australis* for translocating these elements.

The concentrations of Zn, Cd, and Pb in the plant stems and leaves in the present study were lower than those in *P. australis* reported to be 217, 37, and 264 mg kg–1 dry wt., respectively [11]. However, high accumulation of Mn and As in the plant shoots was obtained in comparison with that in other studies [12, 13]. In addition, the concentrations of heavy metals and As in this study were lower than those in other aquatic macrophytes including *Eleocharis acicularis* [9,14], *Eichhornia crassipes* [15], and *Lemna minor* L. [16].

3.3. Potential of *P. australis* for phytoremediation

A suitable plant for phytoremediation would have a high capacity to accumulate heavy metals and metalloids and a high biomass and rapid growth [8]. In addition, plants able to concentrate metals within the whole plant at concentrations 100 times higher than that in the growing solution (Bioconcentration factor - BCF) should be considered good accumulators [14].

However, the high bioconcentration factor (BCF) for Mn, Zn, Cd, Pb, and As were obtained to be 112, 111, 130, 253, and 187, respectively. *P. australis* can be adapted well with the high concentrations of metals in water. In addition, this plant species has high biomass of more than 200 t/ha [17]. These characteristics together with the data of metal accumulation in plant presented in this study indicate that *P. australis* might be a good candidate species for phytoremediation of water contaminated with multiple heavy metals.

4. CONCLUSIONS

P. australis, which is easily cultivated and controlled and is well adapted to contaminated environments, high biomass and rapid growth, its accumulation and high simultaneous removal efficiency of Mn, Zn, Cd, Pb, and As is a potential candidate for phytoremediation of wastewater from Pb-Zn mine.

Acknowledgements: This research was supported by the National Science and Technology Program for Sustainable Development of Vietnam' Northwest Region (KHCN-TB.02C/13-18).

REFERENCES

1. Dudka S. and Adriano D.C.–Environmental impacts of metal ore mining and processing: a review, J. Environ. Qual. **26** (1997) 590–602.
2. Ha N. T. H., Sakakibara M., Sano S. and Nhuan M. T. – Uptake of metals and metalloids by plants growing in a lead–zinc mine area, Northern Vietnam, J. Hazard. Mater. **186** (2011) 1384–1391.

3. Pahlsson A. M. B.–Toxicity of heavy metals (Zn, Cu, Cd, Pb) to vascular plants, Water Air Soil Pollut. **47** (1989) 287–319.
4. Kamal M., Ghaly A.E., Mahmoud N. and Cote R.–Phytoaccumulation of heavy metals by aquatic plants, J. Environ. Int. **29** (2004) 1029–1039.
5. Kabata-Pendias A. and Pendias H.–Trace Elements in Soils and Plants, CRC Press, Florida, USA, 1986, pp.56.
6. IGS (Institute of Geological Science, Vietnam Academy of Science and Technology)– Integrated Investigation, Mining Potential Evaluation of some Important Natural Resources (Pb-Zn, Au) in Government-Permitted Exploitation Mines for Socioeconomic Development of Bac-Kan Province: Investigation Report (In Vietnamese), Hanoi, Vietnam, 2000.
7. Wang, Q., Cui, Y. and Dong, Y.–Phytoremediation of polluted waters: potentials and prospects of wetland plants, Acta Biotechnol. **22** (1–2) (2002) 199–208.
8. Garbisu C. and Alkorta I.– Phytoextraction: a cost-effective plant based technology for the removal of metals from the environment, Bioresour. Technol. **77** (3) (2001) 229–236.
9. Sakakibara M., Ohmori Y., Ha N.T.H., Sano S. and Sera K.–Phytoremediation of heavy metal-contaminated water and sediment by aquatic macrophyte *Eleocharis acicularis*, Clean-soil, air, water **39** (8) (2011) 735-741.
10. Jiang X. and Wanga C.–Zinc distribution and zinc-binding forms in *Phragmitesaustralis* under zinc pollution, J Plant Physiol**165** (7) (2008) 697–704.
11. Vymazal J. and Březinová T.–Accumulation of heavy metals in aboveground biomass of *Phragmitesaustralis* in horizontal flow constructed wetlands for wastewater treatment: A review, Chem. Eng. J. **290** (2016) 232–242.
12. Afrous A., ManshouriM., LiaghatA., PaziraE. and SedghiH.–Mercury and arsenic accumulation by three species of aquatic plants in Dezful, Iran,Afr. J. Agric. Res. **6** (24) (2011) 5391-5397.
13. VaičekonytėR., KiviatE., NsengaF. andOstfeldA. –An exploration of common reed (*Phragmitesaustralis*) bioenergy potential in North America, Mires and Peat **13** (12) (2014) 1–9.
14. Ha N.T.H., Sakakibara M. and Sano S.–Accumulation of Indium and other heavy metals by *Eleocharisacicularis*: An option for phytoremediation and phytomining, Bioresour. Technol. **102** (2011) 2228–2234.
15. Muramoto S. and Oki Y.– Removal of some heavy metals from polluted water by water hyacinth (*Eichhornia crassipes*), Bull. Environ. Contam. Toxicol. **30** (1983) 170–177.
16. Zayed A., Gowthaman S. and Terry N.–Phytoremediation of trace elements by wetland plants: 1. Duckweed, J. Environ. Qual. **27**(3) (1998) 715–721.
17. Brix H., Sorrel B.K. and Lorenzen B.–Are *Phragmites* dominated wetlands a net source or net sink of greenhouse gases?, Aquat. Bot. **69** (2001) 313–324.