

The removal of heavy metals by iron mine drainage sludge and *Phragmites australis*

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Abstract. This study was conducted to assess the removal of heavy metals from solutions by the combination of modified iron mine drainage sludge (sorbent column) and surface and subsurface flow constructed wetlands using the common reed (*Phragmites australis*) during 30 days of experiment. The results of this study demonstrated that the average removal rates of Zn, Pb, Mn, and As by sorbent column were 59.0, 55.1, 38.7, and 42.4%, respectively. The decreasing trend of removal rates of metals by sorbent column was obtained during the experiment. The average removal rates of Zn, Pb, Mn, and As by sorbent column-surface constructed wetland were 78.9, 73.5, 91.2, and 80.5%, respectively; those by sorbent column-subsurface flow constructed wetland were 81.7, 81.1, 94.1, and 83.1% which reflected that subsurface flow constructed wetland showed higher removal rate than the surface system. Concentrations of heavy metals in the outlet water were lower than the Vietnamese standard limits regulated for industrial wastewater. The results indicate the feasibility of integration of iron mine drainage sludge and constructed wetlands for wastewater treatment.

Keywords: constructed wetland, heavy metal, iron mine drainage sludge, *Phragmites australis*, removal

1. Introduction

Mining and smelting activities of metal ores have generated considerable amounts of waste materials to the surrounding environment [1]. Production of Cu, Pb, and Zn causes the greatest environmental degradation as the result of releasing large quantities of heavy metals such as Cu, Cd, Pb, and As [1]. A variety of chemical-physical technologies have been applied to deal with the removal of these metals from water, including precipitation [2], ion exchange [3], electrocoagulation [4], and biological processes [5]. Each treatment technology possesses both advantages and disadvantages. In low income countries, the remediation cost appears to be one of the most important criteria for choosing treatment technologies.

Several natural sorbents have been reported for wastewater treatment, including kaolinite [6], sludge [7,8], diatomite [9,10], and laterite [11,12]. Adsorption of heavy metals is considered an effective and low cost method which offers flexible design and operation, rapid removal, and small space [2,13]. However, adsorption can be reversible, energy consumption and removal efficiency depends on the type of adsorbents and substances to be removed [13]. Therefore, the combination with other treatment technologies may be required for effective removal of water contaminated with multiple heavy metals.

Phytoremediation have emerged as cost-effective, minimal energy consumption, and environment-friendly technologies for metal removal from solutions [14]. Aquatic plant species (e.g., *Lemna minor*



L., *Eichhornia crassipes*, *Polygonum amphibium* L.) have been widely used [15]. A number of studies and applications of constructed wetlands have been conducted for wastewater treatment for more than five decades [16]. It involves biotechnological process in which plants are important part of the treatment system [16]. Common reed (*Phragmites australis*) is one of the most widely distributed species in the world [17]. In addition, this plant species is well adapted with contaminated environments and is a potential candidate for phytoremediation of heavy metals [16,18]. Different substrate materials in constructed wetlands for *P. australis* growth have been reported such as zeolite and series of limestone and cocopeat [19], blast furnace slag, caramsite, vermiculite, gravel, paddy soil, red soil, and turf [20], coke and gravel [21].

This study was conducted to assess the removal rates of heavy metals from solutions by the combination of modified iron mine drainage sludge and constructed wetland using the *P. australis* in a pilot greenhouse scale experiment.

2. Materials and methods

2.1. Preparation of plant, sorbent, and inlet water for experiment

Iron mine drainage sludge from an iron processing mine in northern Vietnam was used for modification of sorbent in the experiment. Sorbent were prepared by addition of 10% sodium silicate solution with deionized water. The mixed samples were pressed using a machine to generate sorbent of 2-mm diameter and 1-2 cm length. Sorbent was then heated at 400 °C in 3 hours by an oven. The specific gravity of sodium silicate solution was 1.46 ± 0.01 g/ml; the contents of Na₂O and SiO₂ were 11.5% ~ 12.2%, and 27.5% ~ 29.5%, respectively. The percentage of quartz, muscovite, illite, kaolinite, hematite, talc, illite, goethite, and magnetite in the sorbent was 43, 13, 13, 12, 7, 7, 4, and 1%, respectively.

Phragmites australis was collected along a riverside of the Red River in Hanoi, Vietnam and washed with tap water. Plant was transplanted in two constructed tanks filled with soil and gravel/pebbles/sand for growth stabilization during 3 months by clean water and fertilized in a certain time. Plant density was one clumps of 3 stems per 15 cm x 15 cm. Average temperature was 22 °C and daily sunlight hours were approximately 12 hours.

Four metals (Pb, Zn, Mn, and As) were prepared as metal salts Mn(NO₃)₂·4H₂O, Zn(NO₃)₂·4H₂O, Pb(NO₃)₂, and Na₂HAsO₄ provided by Merck (Germany). The reagents were dissolved in Milli-Q water to obtain the desired contamination levels. Concentrations of Mn, Zn, Pb, and As in the inlet water in the experiment were 4.0, 1.5, 0.6, and 0.4 mg/L, respectively. Initial concentrations of heavy metals in water solutions were set the same as those in outlet wastewater of a processing ore area in the largest Pb-Zn mine in northern Vietnam after running through two settling reservoirs. The resulting solutions were adjusted to pH 7 with NaOH and HNO₃ using the Horiba D54 pH meter.

2.2. Experiment design

In the present experiment, pre-filtration column (sorbent column) and subsequent two types of constructed wetlands were set (Figure 1). After passing through sorbent column with constant water velocity of 100 L water per day, water was separated evenly into surface and subsurface constructed wetlands. Retention time of water in the sorbent column was approximately 30 minutes; that in constructed wetlands was 48 hours. The retention times were set based on optimal retention time for heavy metals removal at the previous laboratory experiments [22].

Sorbent column: modified iron mine drainage sludge of 1400 g was kept in a 1.8 L transparent acrylic tube.

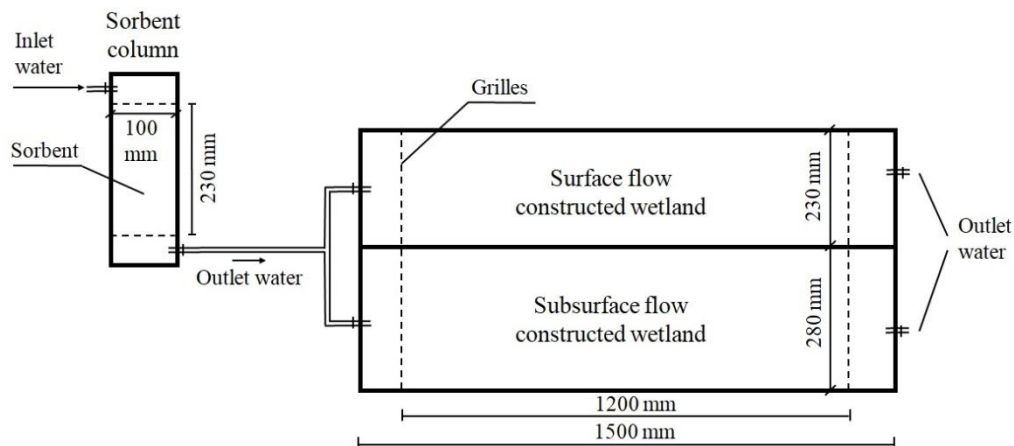


Figure 1. Experiment design of sorbent column and constructed wetland

Surface flow constructed wetland: Natural soil was used as a substrate. Porosity of substrate was 55% and safety factor was 2%. The height and length of constructed wetland system were designed to be 500 x 1500 mm, given the optimal conditions of anaerobic environment for bacteria activities and retention time of water in constructed wetland system. Design of surface flow constructed wetland was calculated by equations as follows:

$$V_{sfcw} = Q \times t = \frac{50}{24 \times 1000} \times 48 = 0.1 \text{ m}^3$$

$$V = \frac{V_{sfcw}}{\phi} = \frac{0.1}{57\%} = 0.175 \text{ m}^3$$

$$S = \frac{0.175}{0.5} = 0.35 \text{ m}^2$$

$$W = \frac{0.42}{1.5} = 0.23 \text{ m}$$

where V_{sfcw} is active volume (m^3), Q is water flow (m^3/hour), t is retention time (hour), V is constructed volume (m^3), ϕ is porosity of substrate added with safety factor (%), S is surface area of constructed wetland, and W is width of constructed wetland.

Subsurface flow CW: active volume, height and length of this system were set the same as that of the surface flow. Water ran in a horizontal pathway. Gravel of 2-4 cm grain size was used as a substrate. Pore volume of substrate was 45% and safety factor was 2%. Design of subsurface flow constructed wetland was calculated by equations as follows:

$$V_{sfcw} = Q \times t = \frac{50}{24 \times 1000} \times 48 = 0.1 \text{ m}^3$$

$$V = \frac{V_{sfcw}}{\phi} = \frac{0.1}{47\%} = 0.21 \text{ m}^3$$

$$S = \frac{0.21}{0.5} = 0.42 \text{ m}^2$$

$$W = \frac{0.42}{1.5} = 0.28 \text{ m}$$

Additional length of 150 mm was constructed between sorbent column and constructed wetlands for evenly and constantly allocating input water.

2.3. Sampling

Input and output water samples of sorbent column, surface and subsurface constructed wetland systems were collected before and at 1, 3, 5, 7, 10, 13, 16, 19, 22, 25, and 30 days of the experiment. Sorbent and plant samples were taken at the start and the end of the experiment.

2.4. Analytical methods

Eh and pH parameters were measured by HORIBA pH/COND METER D-54 equipment. Biological Oxygen Demand (BOD_5) was measured by Winkler titration and Chemical Oxygen Demand (COD)

was determined by dichromate reflux methods using potassium permanganate. The concentration of heavy metals in water was determined by Atomic Absorption Spectrometer (AAS; Agilent 240FS with hydride generation accessory VGA77) at VNU University of Science.

3. Result and Discussion

3.1. pH, BOD₅ and COD in water environment

pH of the water samples in the outlet of sorbent column, surface flow constructed wetland and subsurface flow constructed wetland varied within 7.03-7.85; 7.33-7.83 and 7.22-7.71, respectively. The results demonstrated that pH was stable during experiment. These pH values were within favourable ranges for *P. australis* growth [23, 24].

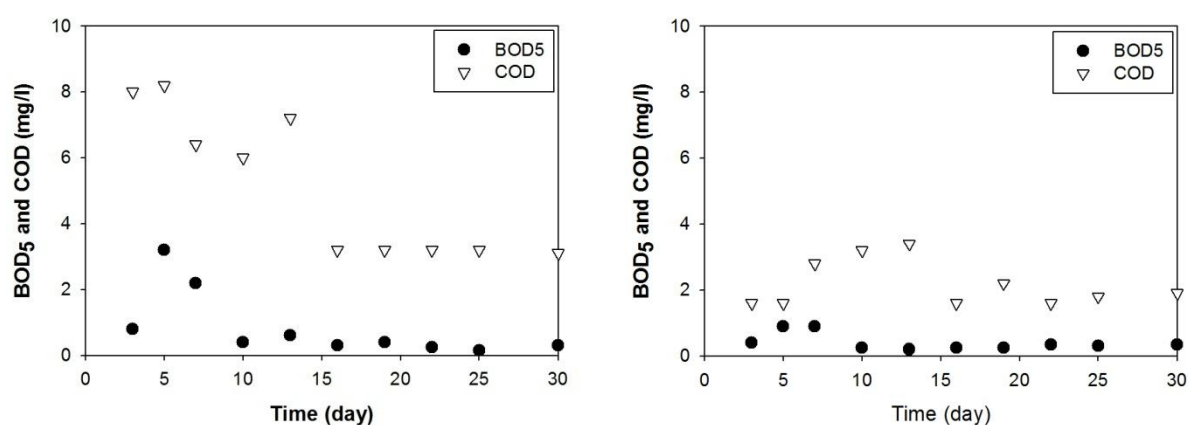


Figure 2. BOD₅ and COD in surface flow wetland (left) and subsurface flow wetland (right).

Biochemical oxygen demand (BOD₅) and chemical oxygen demand (COD) in outlet water of surface flow constructed wetland ranged within 0.2-3.2 and 3.1-8.2 (Figure 2). Those values of subsurface flow constructed wetland ranged within 0.2-0.9 and 1.6-3.2. Higher values of COD and BOD₅ of surface flow constructed wetland than those in the subsurface system were possibly due to higher amount of organic materials leaching from soil substrate. Variation of COD and BOD₅ values during the first 13 days of experiment may reflect the residue of organic fertilizer supply for plant growth before the experiment (Figure 2).

3.2. Concentration of heavy metals in water

The concentrations of heavy metals in outlet water of sorbent column and constructed wetlands decreased during the experiment in comparison with the inlet flow (Figure 3). The average removal rates of Zn, Pb, Mn, and As by sorbent column were 59.0, 55.1, 38.7, and 42.4%, respectively. The average removal rates of Zn, Pb, Mn, and As by sorbent column-surface flow constructed wetland were 78.9, 73.5, 91.2, and 80.5%, respectively; those by sorbent column-subsurface flow constructed wetland were 81.7, 81.1, 94.1, and 83.1%. These results demonstrated that the removal rates of heavy metals in subsurface flow constructed wetland were higher than those in the surface flow system. The removal rate of Pb by sorbent column was higher than that of As, Mn, and Zn. Subsurface and surface flow constructed wetlands demonstrated better removal of Mn than the other metals (Figures 3 and 4).

Concentration of Mn in outlet of sorbent column decreased dramatically during the first 10 days and remained almost constantly other days (Figure 3). Concentration of Mn in inlet of sorbent column was 4 mg/l which decreased to 0.92 mg/L on the first day and 2.78 mg/L on the 30th day of the experiment. Concentration of Mn in outlet of sorbent column exceeded the allowable limits on national technical regulation for industrial wastewater type A (QCVN40/2011-A: water source for domestic water supply) and type B (QCVN40/2011-B: water source not for domestic water supply) [25] (Figure 3). The removal rate of Mn was 77.1% on the first day, which decreased to 30.6% at the

last day of the experiment. Removal rates of Mn in sorbent column-surface flow constructed wetland and sorbent column-subsurface flow constructed wetland were 96.0 and 99.6%, respectively after 3 days, which decreased to 81.2 and 84.8% on the last day (Figure 4). Mn concentration in outlet water of constructed wetlands met the regulation QCVN40/2011-A during 19-25 days and QCVN40/2011-B [25] during the experiment. However, the decreasing trend of removal rate reflected treatment limit of Mn by the system which highlights the need for further setting of constructed wetlands for longer remediation.

Concentration of Zn was steadily decreased during 30 days of the experiment by sorbent column (Figure 3). The removal rate of Zn was 74.6% during the first day which decreased to 51.1% after 30 days of the experiment (Figure 4). However, the removal rates of constructed wetlands were relatively stable, indicating the long term remediation of Zn by these systems. Concentrations of Zn in both inlet and outlet water of 3 systems were lower than the allowable limit which was set to be 3 mg/L [25] (Figure 3). This fact required studies to assess the possibility of wastewater treatment with higher concentrations of Zn by constructed wetlands using *P. australis*.

Concentration of Pb in outflow of sorbent column gradually decreased during 30 days of the experiment (Figure 3). The removal rate of Pb was higher than that of other metals. The removal rate of Pb was 96.7% at the 1st day which decreased to 22.8% after 30 days of the experiment (Figure 4). The removal rate of Pb by sorbent column-surface flow constructed wetland and sorbent column-subsurface flow constructed wetland was 93.1 and 98.4%, respectively after 3 days which decreased to 54.7 and 64% after 30 days of the experiment. Concentrations of Pb in outlet water of sorbent column, sorbent column-surface flow constructed wetland and sorbent column-subsurface flow system at the 3rd day were 0.06, 0.03, and 0.01 mg/L, respectively which increased to 0.46, 0.27, and 0.22 mg/L after 30 days. Pb concentrations in outlet of 3 systems were lower than the regulation QCVN40/2011-B [25] which was set to be 0.5 mg/L (Figure 3). However, it is noted that concentrations of Pb in inlet water was slightly higher than values regulated at QCVN40/2011-B [25]. Pb concentrations in outlet water of constructed wetlands after 10 days of experiment met the QCVN40/2011-B limit [25].

Concentration of As in water decreased dramatically by sorbent column during 30 days of the experiment (Figure 3). Removal rates of As by surface and subsurface flow constructed wetlands were almost the same. The removal rates of As by sorbent column was 75% at the 1st day which decreased steadily (average 42.4 %) at the end of the experiment (Figure 4). Average of removal rates of As in sorbent column-surface flow and sorbent column-subsurface flow constructed wetlands were 80.5 and 83.1%, respectively. Concentrations of As in outlet water of sorbent column, sorbent column-surface flow constructed wetland and sorbent column-subsurface flow system varied within 0.10-0.28, 0.06-0.09, and 0.05-0.08 mg/l, respectively. Concentration of As in outlet of sorbent column exceeded the allowable limits regulated at QCVN40/2011-B [25]; however, those of sorbent column-constructed wetland were lower than the regulation QCVN40/2011-B during the experiment. Constant concentrations of As in outlet water indicated the stability of As removal by the systems; however, the near-allowable limit required longer contact duration of water with sorbent or constructed wetlands, higher volume of sorbent or larger scale of constructed wetlands.

Using the same sorbent as that in the present study, Chinh et al. [26] conducted the laboratory column experiment in which initial concentrations of Mn, Pb, Zn, and As in water solutions were 20, 20, 6, and 1 mg/L, respectively. The removal rates of Mn, Pb, Zn, and As during 25 days of the experiment were 27.9-97.6, 73.9-97.4, 51.0-53.0, and 96.4-98.2%, respectively [26]. In the present study, removal rates of Mn, Pb, Zn, and As by sorbent column varied within 30.0-77.1, 22.8-96.7, 51.1-74.6, and 31.2-75.0%, respectively. It is noted that concentrations of heavy metals in inlet water conducted by Chinh et al. [26] were higher than those in the present study; however, reverse trend of removal rates of Mn, Pb, and As was obtained. It is possibly due to different experimental conditions (e.g., temperature, sunlight) and initial metal concentrations. This is in agreement with the effects of temperature and metal concentrations on metal adsorption by sorbents [27, 28].

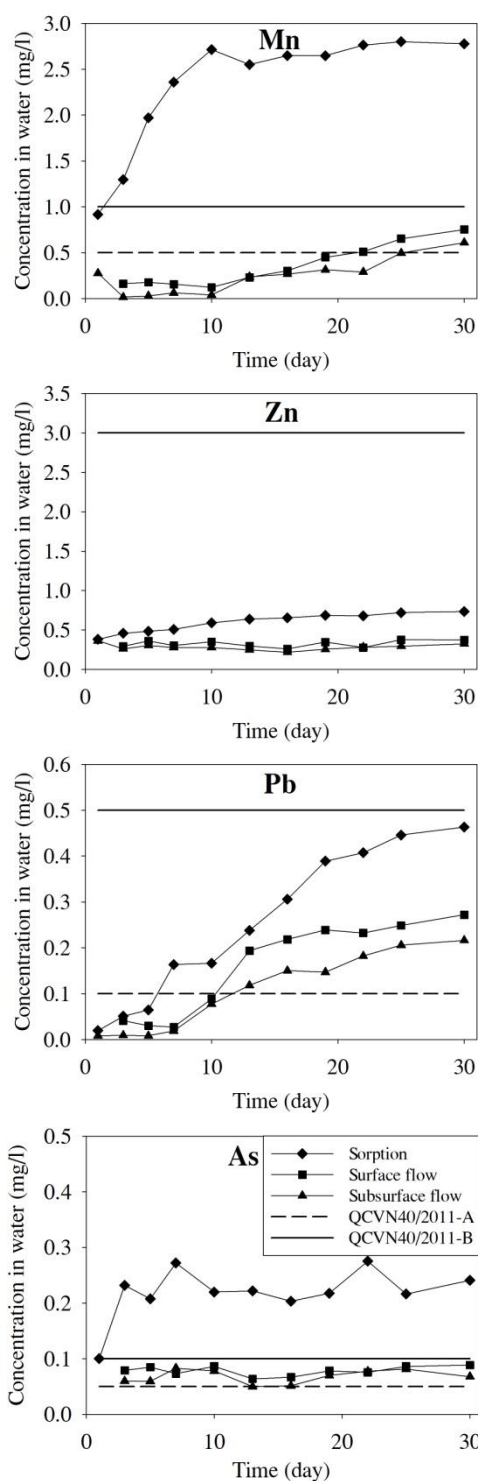


Figure 3. Concentrations of Mn, Zn, Pb, and As in outlet water from sorbent column, surface flow and subsurface flow constructed wetland systems.

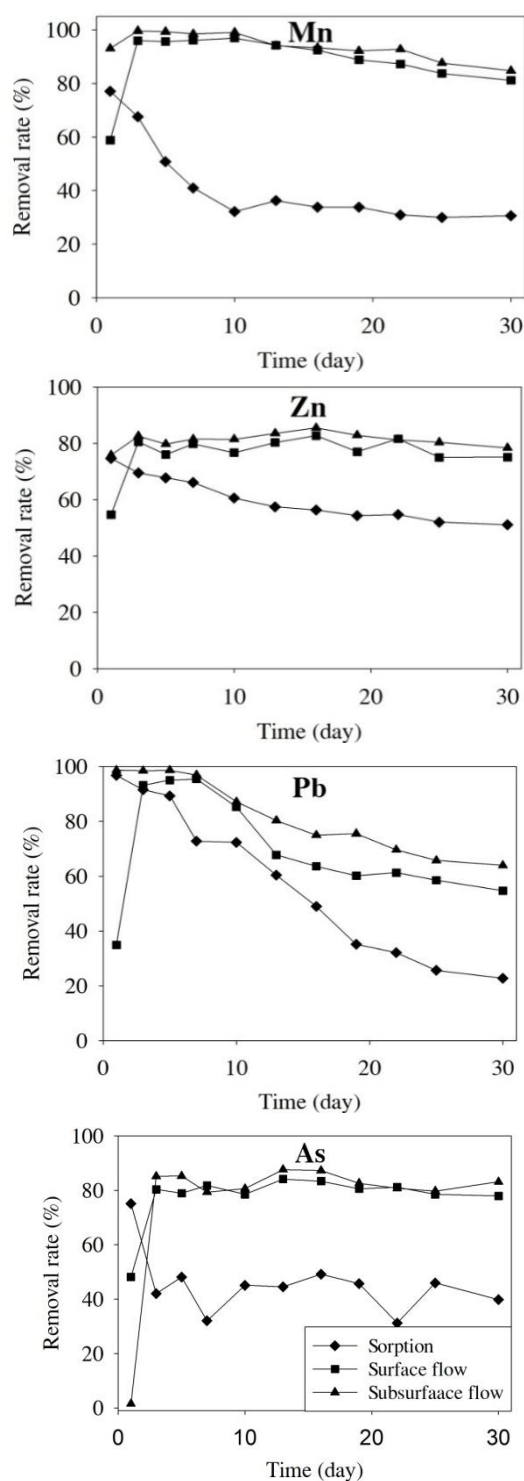


Figure 4. Removal rates of Mn, Zn, Pb, and As by sorbent column, surface flow and subsurface flow constructed wetland systems.

In sorbent column, heavy metals were possibly removed from water by both sorption and precipitation processes [26]. In constructed wetlands, heavy metals were removed or retained by both aerobic and anoxic/anaerobic processes [16]. Under anaerobic conditions, highly insoluble metal

sulphides are formed; under anoxic conditions, metals can also be removed from water due to formation of carbonates which are less stable than sulphides and co-precipitation to roots. Other amount of metal removal from constructed wetlands may be adsorbed to substrates and organic matters and could be retained by filtration and deposition in the rhizosphere [29]. *Phragmites australis* roots can also uptake and accumulate heavy metals in roots or aboveground part of the plant [16,22,30,31]. Highest concentrations of Mn, Zn, Pb, and As in the plant roots were 3920, 1020, 1350, and 183 mg/kg-DW, respectively; those in the stems were 465, 108, 227, and 74.0 mg/kg-DW; and those in the leaves were 716, 150, 157, and 88.3 mg/kg-DW [22]. Concentrations of Zn and Pb in the frond biomass of *P. australis* were reported to be 217 and 264 mg/m², respectively [16].

4. Conclusions

The integration of modified iron mine drainage sludge and surface flow or subsurface flow constructed wetlands showed potential of heavy metals treatment in the water. Concentrations of Mn, Zn, Pb, and As in the outlet of sorbent column-surface flow constructed wetland and sorbent column-subsurface flow constructed wetland were within Vietnamese regulation for industrial wastewater with the exception of Pb after 10 days of experiment. Sorbent column-subsurface flow constructed wetland demonstrated better heavy metals removal rate than sorbent column-surface flow system. Further studies need to be conducted for higher initial concentrations of inflow, longer experimental duration, and larger pilot scales of these integration systems before it can be applied in field conditions.

5. Acknowledgments

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6. References

- [1] Dudka S and Adriano D C 1997 Environmental impacts of metal ore mining and processing: a review *J. Environ. Qual.* **26** 590-602
- [2] Gunatilake S.K 2015 Methods of removing heavy metals from industrial wastewater *J. Multidiscip. Eng. Stu.* **1** 12-18
- [3] Gaikwad R W, Sapkal V S and Sapkal R S 2010 Ion exchange system design for removal of heavy metals from acid mine drainage wastewater *Acta Montan. Slovaca* **15** 298-304
- [4] Turdean G L and Popescu I C 2013 Electrochemical Method for Heavy Metals Detection by Inhibition of Acetylcholinesterase Immobilized on Pt-nanoparticles Modified Graphite Electrode *E3S Web of Conferences* vol 1 p 05007
- [5] Sonali R D and Jayant P K 2013 Biological methods for heavy metal removal - A review *International J. Eng. Sci. Innovative Technol.* **2**(5) 304-09
- [6] Adebawale K O, Unuabonah I E and Olu-Owolabi B I 2005 The effect of some operating variables on the adsorption of lead and cadmium ions on kaolinite clay *J. Hazard. Mater.* **134** 130-39
- [7] Hung D D and Minh N T 2011 Sorption of Zn(II) on Bao Loc modified- granular bauxite mine drainage sludge by column experiment *Vietnam J. Earth Sci.* **33** 591-98
- [8] Hülya G, Christian T, David M and Olaf S 2003 Adsorption of arsenate from water using neutralized red mud *J. Colloid Interface Sci.* **264** 327-34
- [9] Al-degs Y, Khraisheh M A M and Tutunji F 2001 Sorption of lead ions on diatomite and manganese oxides modified diatomite *Water Res.* **15** 3724-28
- [10] Li E, Zeng X and Fan Y 2009 Removal of chromium ion (III) from aqueous solution by manganese oxide and microemulsion modified diatomite *Desalination* **238**(1-3) 158-65
- [11] Thao N H P, Ha N T H, Thuy P T, Khai N M, Nga T T H 2016 Study the environmental pollution treatment ability of laterite *VNU J. Science* **32**(1S), 321-26
- [12] Yu X, Zhu L, Guo B and He S 2008 Adsorption of mercury on laterite from Guizhou Province,

- China *J. Environ. Sci.* **20** 1328-34
- [13] Fu F and Wang Q 2011 Removal of heavy metal ions from wastewaters: A review *J. Environ. Manage.* **92** 407-18
- [14] Ha N T H, Sakakibara M and Sano S 2011 Accumulation of Indium and other heavy metals by *Eleocharis acicularis*: An option for phytoremediation and phytomining *Bioresour. Technol.* **102** 2228-34
- [15] Wang Q, Cui Y and Dong Y 2002 Phytoremediation of polluted waters: potentials and prospects of wetland plants *Biotechnol. Acta* **22**(1-2) 199-208
- [16] Vymazal J and Brezinova T 2016 Accumulation of heavy metals in aboveground biomass of *Phragmites australis* in horizontal flow constructed wetlands for wastewater treatment: a review *Chem. Eng. J.* **290** 232-42
- [17] Hocking P J, Finlayson C M and Chick A J 1983 The biology of Australian weeds. 12. *Phragmites australis* (Cav.) Trin. ex Steudel *J. The Australian Institute of Agricultural Science* **49** 123-32
- [18] Jiang X and Wang C 2008 Zinc distribution and zinc-binding forms in *Phragmites australis* under zinc pollution *J. Plant Physiol.* **1165**(7) 697-704
- [19] Allende L K, McCarthy D T and Fletcher T D 2014 The influence of media type on removal of arsenic, iron and boron from acidic wastewater in horizontal flow wetland microcosms planted with *Phragmites australis* *Chem. Eng. J.* **246** 217-28
- [20] Zhu W L, Cui L H, Ouyang Y, Long C F and Tang X D 2011 Kinetic adsorption of ammonium nitrogen by substrate materials for constructed wetlands *Pedosphere* **21**(4) 454-63
- [21] Chen M Z, Tang Y Y, Li X P and Yu Z X 2009 Study on the heavy metals removal efficiencies of constructed wetlands with Different Substrates *J. Water Resource Prot.* **1** 1-57
- [22] Nga T T H and Ha N T H 2016 Simultaneous removal of some heavy metals and arsenic from aqueous solutions by *Phragmites australis* Vietnam *J. Sci. Technol.* **54**(2A) 259-64
- [23] Chabreck R H 1972 *Vegetation, water and soil characteristics of the Louisiana coastal region Bulletin 664* (Louisiana State University, Louisiana Agricultural Experiment Station. Baton Rouge, LA) p 72
- [24] USDA NRCS 2012 The PLANTS database [Online] Available. <http://plants.usda.gov>
- [25] QCVN40:2011-BTNMT National Technical Regulation on Industrial Wastewater Quality
- [26] Chinh L S, Nhuan M T, Hai N X, Hai N T, Thang D N, Giang N T, Quy T D and Ha N T H 2016 The potential of modified iron mine drainage sludge for treatment of water contaminated with heavy metals *VNU J. Sci.* **32**(1S) 38-44
- [27] Johnson B B 1990 Effect of pH, temperature, and concentration on the adsorption of cadmium on goethite *Environ. Sci. Technol.* **24** 112-18
- [28] Dzombak D A and Morel F M M J 1986 *Colloid Interface Sci.* **112** 588-98
- [29] Marchand L, Mench M, Jacob D L and Otte M L 2010 Metal and metalloid removal in constructed wetlands, with emphasis on the importance of plants and standardized measurements: a review *Environ. Pollut.* **158** 3447-61
- [30] Afrous A, Manshouri M, Liaghat A, Pazira E and Sedghi H 2011 Mercury and arsenic accumulation by three species of aquatic plants in Dezful, Iran, *Afr. J. Agric. Res.* **6**(24) 5391-97
- [31] Vaiekonyt R, Kiviat E, Nsenga F and Ostfeld A 2014 An exploration of common reed (*Phragmites australis*) bioenergy potential in North America *Mires. and Peat* **13**(12) 1-9