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# Pilot-Scale Removal of Arsenic and Heavy Metals from Mining Wastewater Using Adsorption Combined with Constructed Wetland

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**Abstract:** This study was conducted to assess the removal of arsenic (As) and heavy metals from mining wastewater by the combination of adsorption, using modified iron-ore drainage sludge, and horizontal-subsurface-flow constructed wetland with common reed (*Phragmites australis*). The pilot-scale experiment with a constant flow rate of 5 $m^3$/day was operated for four months using real wastewater from a Pb–Zn mine in northern Vietnam. Atomic absorption spectroscopy was used for elemental analysis in wastewater and plant. X-ray diffraction (XRD), surface charge measurements (by a particle charge detector (PCD)), Fourier-transform infrared (FTIR), and surface area Brunauer–Emmet–Teller (BET) measurements were performed to determine the characteristics of the adsorbent. The results showed that the average removals of As, Mn, Cd, Zn, and Pb by the combined system with limestone substrate during four months were 80.3%, 96.9%, 79.6%, 52.9%, and 38.7%, respectively. The use of another constructed wetland substrate, laterite, demonstrated better removal efficiency of As than limestone. The concentrations of As and heavy metals in the effluent were lower than the limits established by the QCVN 40:2011/BTNMT for industrial wastewater, which indicated the feasibility of combining adsorption and constructed wetland for the treatment of mining wastewater.

**Keywords:** adsorbent; arsenic; constructed wetland; heavy metal; mining wastewater; removal

## 1. Introduction

Mining activities release large amounts of solid wastes and wastewater into the surrounding environment. Wastewater from mineral exploitation and processing is characterized by high concentrations of arsenic (As) and heavy metals (e.g., manganese (Mn), copper (Cu), lead (Pb), and zinc (Zn)) that may induce severe environmental problems and various risks to exposed humans and ecosystem [1–3]. A variety of treatment technologies have been extensively studied and applied, including adsorption, membrane filtration [4], coagulation [5], ion-exchange [6], electrocoagulation [7], and biological processes [8]. Naturally, any technology possesses both advantages and limitations, considering treatment effectiveness, installation, operational and maintenance cost, further treatment of secondary wastes, technical requirements, and time and space requirements [9,10].

Adsorption is considered a cost-effective method [11,12] when using adsorbents that require little processing or are industrial wastes or by-products [13]. The use of mining wastes as adsorbents is considered an environment-friendly technique with double benefits, as it allows to treat both solid wastes and contaminated water and to approach the ideal goal of waste-free production [14,15]. However, adsorption can be reversible, and the removal efficiency depends on the type of adsorbents and substances to be removed [16]. Therefore, the combination of adsorption with other technologies may be required for the effective treatment of wastewater contaminated with multiple heavy metals.

Constructed wetland (CW) planted with macrophytes has been widely applied for the treatment of municipal, industrial, and urban runoff wastewaters [17], considering their remediation effectiveness, simple operation [18,19], and benefits for ecosystem services [20]. *Phragmites australis* (common reed) has been commonly used in CW systems because of its cosmopolitan distribution, ease of growing, and ready adaptation to different environments [19,21]. In addition, this plant can accumulate heavy metals in its biomass [19] and is highly adaptable to many substrates, such as coke, gravel [22], blast furnace slag, ceramsite, vermiculite, gravel, paddy soil, red soil, turf [23], zeolite, limestone, and cocopeat [24].

Cho Don is the largest Pb–Zn mine in Vietnam. Commencing operation in the 18th century, it has released considerable amounts of wastewater contaminated with As and heavy metals (e.g., Pb and Mn) into the surrounding environment [25]. The remediation cost is of high importance in the selection of proper technologies for the removal of As and heavy metals from wastewater in this mine. Iron-ore sludge from a processing area near the Cho Don Pb–Zn mine was reported to be a promising adsorbent to remove As and heavy metals from water [26]. *P. australis* was observed to grow naturally along the main stream near Cho Don mine, and limestone was also found in the area. The use of the plant and these materials as adsorbent and substrate in the CW system may be an environment-friendly approach that reduces the transportation cost for wastewater treatment. In a laboratory experiment, the combination of an adsorbent modified from this iron-ore sludge and CW was reported to effectively remove As and heavy metals from synthetic solutions [27]. However, at pilot scale, the feasibility of this combined system has not been previously assessed using real wastewater.

The present study aimed to evaluate the potential of using an adsorbent and CW in removing As and heavy metals from the wastewater of Cho Don Pb–Zn mine.

## 2. Materials and Methods

### 2.1. Adsorbent, Plant, Substrate, and Mining Wastewater

This study used the same adsorbent as that introduced in previous research (SBC2-400-10S) [27]. This adsorbent (SBC2-400-10S) was of 2 mm diameter. The characteristics of this adsorbent are shown in Table 1. The obtained spectra by FTIR measurement of SBC2-400-10S showed peaks at 3610 $cm^{-1}$, which were probably from OH bending. In addition, the peaks at 1031 and 778 $cm^{-1}$ indicated the presence of Si–O–Si and Si–OH groups.

*P. australis*, more than 1 m high and approximately 1 mm in diameter, was collected along the main stream near the Cho Don Pb–Zn mine. The plants were cut to keep the belowground parts and 50 cm stems and washed well before transplanting in the CWs. *P. australis* was transplanted and grown in the CWs for a period of 3 months, before starting the operation of the combined system. Laterite and limestone were used as substrates in the CW system. The main minerals of laterite and limestone in the present study are shown in Table 1.

**Table 1.** Characteristics of adsorbent and substrates. BET: Brunauer–Emmet–Teller, PCD: Particle Charge Detector.

| Material Characteristics | | Adsorbent (SBC2-400-10S) | Substrates | |
|---|---|---|---|---|
| | | | Limestone | Laterite |
| Mineral composition (%) | Quartz | 43 * | - | 39 ** |
| | Muscovite | 13 * | - | - |
| | Illite | 13 * | - | 2 ** |
| | Kaolinite | 12 * | - | 36 ** |
| | Hematite | 7 * | - | 7 ** |
| | Goethite | 4 * | - | 15 ** |
| | Calcite | - | 14 | - |
| | Ankerite | - | 86 | - |
| BET ($m^2/g$) | | 39.5 | - | - |
| PCD ($mmol_{c\,(-)}\cdot kg^{-1}$) | | 88.7 | - | 52 ** |

* [27], ** [28].

Wastewater in the present study had these characteristics: pH 7.3, alkalinity 104 mg/L, electrical conductivity (EC) 776 µS/cm, total dissolved solids (TDS) 624 mg/L, total suspended solids (TSS) 42.8 mg/L, biological oxygen demand ($BOD_5$) 3.9 mg/L, and chemical oxygen demand (COD) 8.1 mg/L. The TSS, $BOD_5$, and COD values were lower than the maximum allowable limit (MAL) for wastewater for both category A (QCVN40:2011-BTNMT-A: water source for domestic water supply [29]) and category B (QCVN40:2011-BTNMT-B: water source not for domestic water supply [29]). The concentrations of Mn, Zn, Cd, Pb, and As in wastewater before entering the combined system during 4 months of investigation varied and were 2.56–3.75, 0.81–1.33, 0.33–0.63, 0.37–0.65, and 0.22–0.30 mg/L, respectively. The concentrations of Mn, Cd, Pb, and As exceeded the MAL for wastewater for both categories A and B [29]).

### 2.2. System Set-Up and Operation

The combined system was set up near the processing plant of Cho Don Pb–Zn mine, in northern Vietnam. Wastewater from the processing area that passed through two settling reservoirs was automatically pumped at a constant rate (5 $m^3$/day) into the treatment system, before discharging into a stream (Figure 1).

The treatment system consisted of eight modules with different functions: settling tank (module MD1), adsorbent tank (MD2), and CWs (MD3–8) (Figure 1 and Table 2). MD2 was designed to include two compartments with 0.71 $m^3$ of total working volume and 30 min of retention time. Water flowed from MD1 to the first compartment of MD2, before discharging into the second compartment. Approximately 138 kg of adsorbent (SBC2-400-10S) was added to the second compartment. The constructed wetlands, which received wastewater from MD2, included six modules (MD3–8). Figure 1b and Table 2 show the size parameters of these tanks. The grain size of the substrates (limestone and laterite) was set to be approximately 2–4 cm, the pore volume was 45 %, and the safety factor was 2%. Wastewater from MD6 was equally distributed into MD7 and MD8. Limestone was used as a substrate material for the growth of *P. australis* in MD3, MD4, MD5, MD6, and MD7, whereas laterite was used in MD8. The density of *P. australis* transplanted in CW was approximately 45 plants/$m^2$. In this study, hydraulic retention time (HRT) was set to be 46 h, according to previous laboratory experiments. The design of subsurface-flow CWs was calculated by the following equations:

Total surface area of CW (S) ($m^2$):

$$\begin{aligned} S &= S_{MD3} + S_{MD4} + \ldots + S_{MD8} \\ &= (4 \times 4.1) + (2 \times 2.05) = 20.5\ m^2 \end{aligned} \tag{1}$$

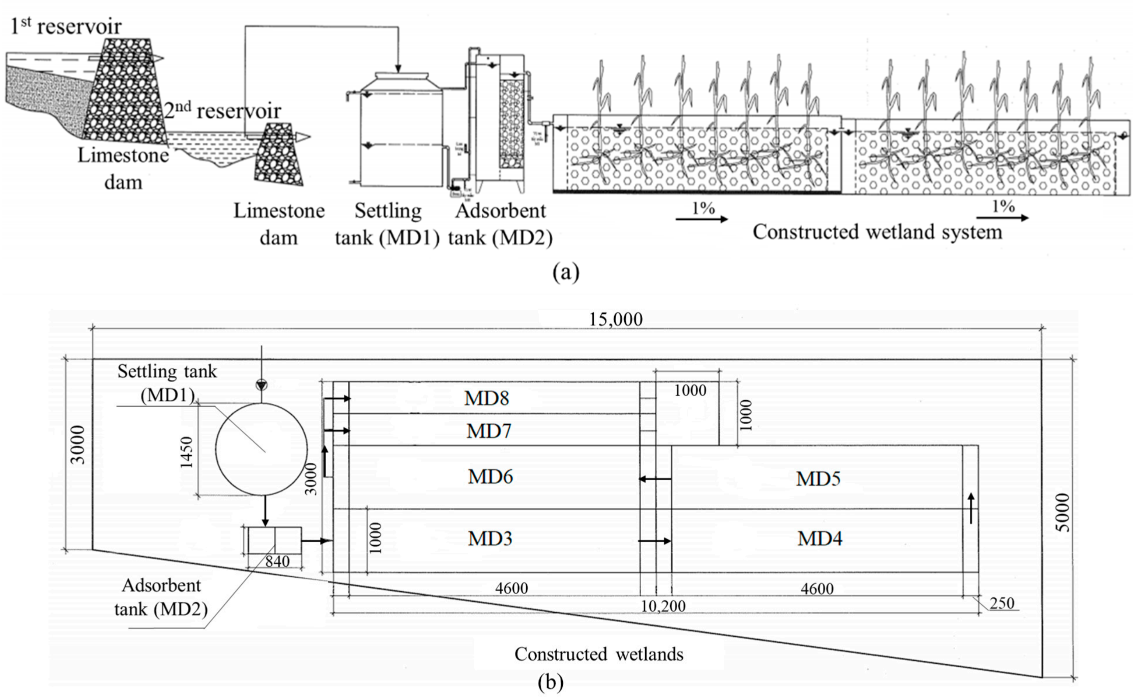


**Figure 1.** (**a**) Cross section, and (**b**) design parameters of the treatment system.

**Table 2.** Size parameters of modules of the treatment system. MD1: settling tank, MD2: adsorbent tank, MD3–MD8: constructed wetlands modules.

| Module | Filtration Materials (Substrates) | Dimension (Height (mm) × Width (mm) × Length) (mm)) | Working Volume ($m^3$) |
|---|---|---|---|
| MD1 | | 2000 × 1500 × 1500 | 4.5 |
| MD2 | SBC2-400-10S | 2000 × 420 × 840 | 0.71 |
| MD3–MD6 | Limestone | 1000 × 1000 × 4100 | 4.1 |
| MD7 | Limestone | 1000 × 500 × 4100 | 2.05 |
| MD8 | Laterite | 1000 × 500 × 4100 | 2.05 |

Total working volume of CW ($V_t$) ($m^3$):

$$V_t = V \times \varphi = \left(V_{MD3} + \ldots + V_{MD8}\right) \times 47\% = 9.64\ \text{m}^3 \tag{2}$$

Velocity of CW ($v_f$):

$$\begin{aligned} v_f &= Q \times \tfrac{1}{A_s} = 5 \times \tfrac{1}{1 \times 1 \times 47\%} \\ &= 10.6\ \text{m}^3/\text{m}^2 \cdot \text{day} \end{aligned} \tag{3}$$

Total surface loading of CW ($L_s$):

$$L_s = Q \times \frac{1}{S} = 5 \times \frac{1}{20.5} = 0.244\ \text{m}^3/\text{m}^2\text{day} \tag{4}$$

where $Q$ is the flow rate ($m^3$/day), $\varphi$ is the porosity of the substrate added with the safety factor (%), $A_s$ is the area of the cross section of CWs with $\varphi$ = 47%, 1 m high, and 1 m wide.

### 2.3. Sampling

Water samples before running into the treatment system and after flowing through each module (MD1–8) were collected on the first day, after 1, 2, and 3 weeks, and after 1, 1.5, 2, 2.5, 3, and 4 months of the combined system operation. In total, 90 samples were collected.

Adsorbent, *P. australis*, and substrate samples (0.8–1.0 kg of each) were collected before, and 4 months after the system operation. Each sample was collected by combining 3–5 aliquots of adsorbent, *P. australis*, or substrate. The number of collected adsorbent samples was six. From each module of CWs, one plant sample was collected. The number of collected plant samples was 12. In addition, six substrate samples from the CWs, including three limestone and three laterite samples, were also collected.

### 2.4. Analytical Methods

*P. australis* samples were separated into belowground (roots and rhizomes) and aboveground biomass (stems + leaves) parts and washed well with deionized water. The plant, adsorbent, and substrate samples were dried in an oven at 80 °C until the weight was constant and then ground into fine powder. In total, 100 mg of adsorbent was digested with an $HNO_3$/HF/HCl mixture (1:1:2, *v*/*v*). The plant samples were digested with 3 mL of $HNO_3$ and 0.6 mL $H_2O_2$ for each 100 mg aliquot. The concentrations of five target metals (i.e., Mn, Zn, Cd, Pb, and As) in the adsorbent and plant samples were determined by atomic absorption spectroscopy (AAS, Agilent 240FS with hydride generation accessory VGA77).

Surface charge, Fourier-transform infrared (FTIR), and surface area measurements were performed for the adsorbent. Surface charge was determined using a particle charge detector (PCD, Mütek 05). A FTIR Spectrometer (Nicolet iS5, Thermo Scientific) was used for the measurement of FTIR. Surface area was determined by Gemini VII 2390 surface area analyzer (Micromeritics). The Brunauer–Emmet–Teller (BET) method was used to calculate the specific surface area.

The mineral composition of the substrates (e.g., limestone and laterite) was determined using X-ray diffraction (XRD, D5005, Siemens) on powder samples. The XRD was equipped with a Cu (K$\alpha$1,2) target operated at 40 kV and 30 mA with a setting of $2\theta$ = (3–70)°, in steps of 0.02°.

All analyses were performed at the Key Laboratory of Geo-environment and Climate Change Response, Vietnam National University, Hanoi, Vietnam.

### 2.5. Calculation of Metal Removal and Accumulation

The removal efficiency (%) for the target metal was obtained using the following equation:

$$Removal\ efficiency\ (\%) = \frac{C_i - C_{effluent}}{C_i} \times 100\% \tag{5}$$

where $C_i$ is the concentration of each metal in wastewater before entering MD1, and $C_{effluent}$ is the concentration of each metal in wastewater after discharging from a target module (MD1, MD2, MD7, and MD8).

The amount of each metal removed from wastewater ($C_r$) by the adsorbent or CWs was calculated by the following equation:

$$C_r(\mathrm{mg}) = (C_{influent}(\mathrm{mg/L}) - C_{effluent}(\mathrm{mg/L}) \times T(\mathrm{days}) \times HLR(\mathrm{L/day}) \tag{6}$$

where $C_{influent}$ and $C_{effluent}$ are the concentrations of each metal in wastewater before and after entering each module (adsorbent tank or CW), respectively, T is the duration of treatment system operation, and HLR represents the hydraulic loading rate.

The amount of each metal adsorbed by the sorbent or accumulated in *P. australis* ($C_a$) was determined by the following equation:

$$C_a(\mathrm{mg}) = (C(\mathrm{mg/kg}) - C_o(\mathrm{mg/kg})) \times m\ (\mathrm{kg}) \tag{7}$$

where $C_o$ and $C$ are the concentrations of metal in the adsorbent or *P. australis* before and after the experiment, respectively, and m is the total mass of adsorbent or *P. australis* in the experiment.

## 3. Results

### *3.1. Removal of As and Heavy Metals from Mining Wastewater*

Figure 2 shows the concentrations of As and heavy metals in wastewater before entering the treatment system (initial wastewater—$C_i$) and in the effluent of different modules during 4 months of operation. A decreasing trend in the concentrations of As, Mn, Zn, Cd, and Pb in the effluent after running through different modules during 4 months of system operation was observed. The removal efficiencies of As and heavy metals by the adsorbent tank were higher than those by the settling tank and CWs (Table 3).

**Table 3.** Average removal efficiency (%) of As and heavy metals from wastewater in 4 months of operation.

| Moduls | As | Mn | Zn | Cd | Pb |
|---|---|---|---|---|---|
| MD1 | 9.56 | 2.64 | 27.2 | 13.7 | 28.1 |
| MD2 | 49.6 | 54.3 | 50.0 | 43.9 | 16.0 |
| MD3-7 | 30.7 | 42.6 | 2.87 | 35.7 | 22.7 |
| MD3-7 * | 75.1 | 98.8 | 30.2 | 83.7 | 42.8 |
| MD3-6 + MD8 | 34.7 | 32.1 | 2.39 | 31.9 | 18.3 |
| MD2 + MD3-7 | 80.3 | 96.9 | 52.9 | 79.6 | 38.7 |
| MD1 + MD2 + MD3-7 | 89.9 | 99.5 | 80.1 | 93.3 | 66.8 |

MD1: settling tank, MD2: adsorbent tank, MD3–7: constructed wetland with limestone substrate, MD8: constructed wetland with laterite substrate. * Removal efficiency calculated by using the concentration of metal in the influent before entering MD3.

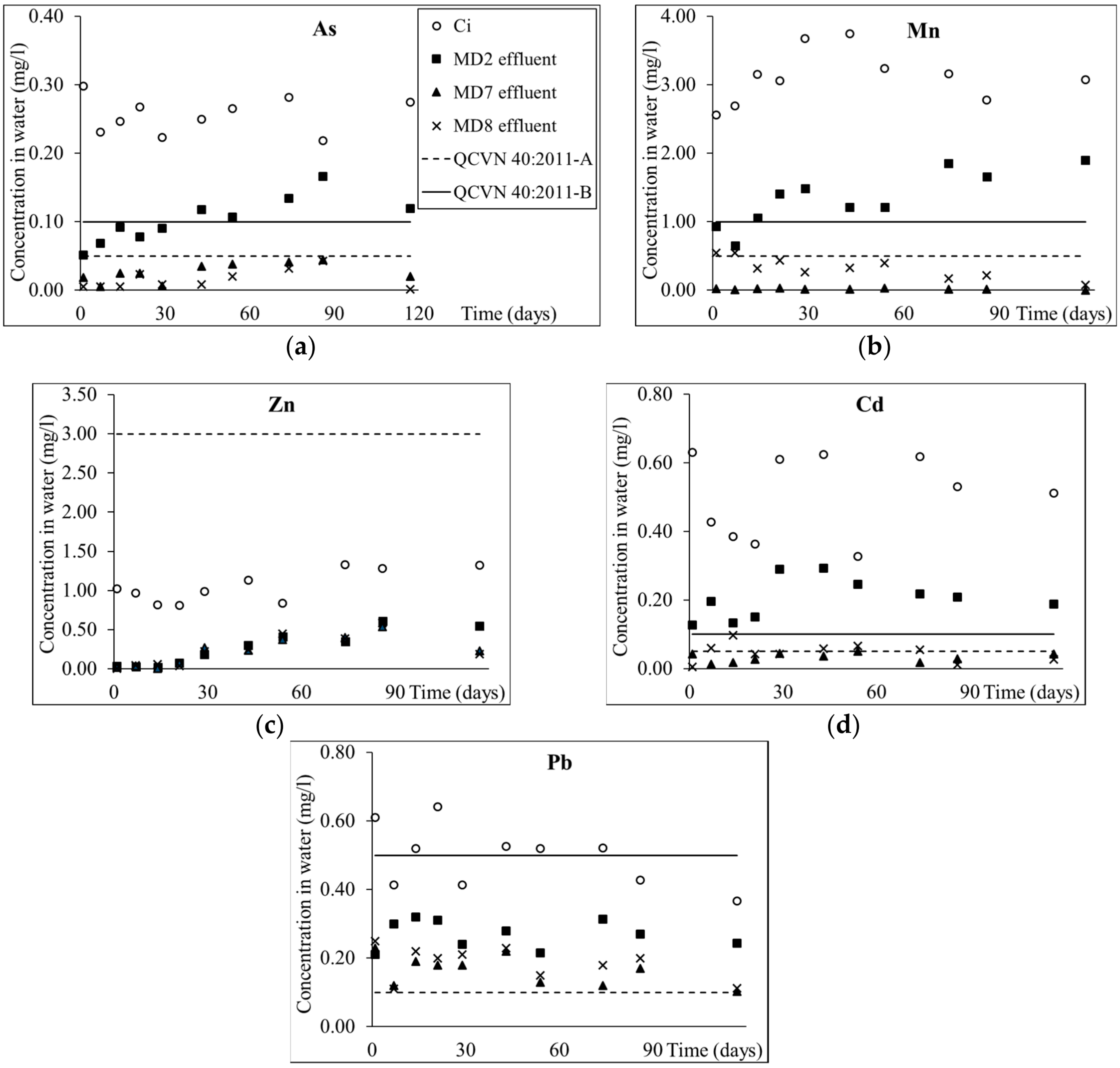
The concentrations of As in MD2 effluent (adsorbent tank) met the MAL for category B [29] during the first month and exceeded the MAL from the second month to the end of the experiment. However, the concentrations of As in the effluents of CWs (MD3–8) were lower than the MAL for category A [29]. The average removal efficiencies of As by MD1, MD2, MD3–7 (limestone substrate), and MD3–6 + MD8 were 9.56, 49.6, 30.7, and 34.7 %, respectively (Table 3). A decreasing trend of As removal by the adsorbent was observed from the beginning to the end of the experiment (Figure 2). The removal efficiency of As by CWs with laterite substrate (MD8) was higher than that with limestone (MD7) (Figure 2). High removal of As by laterite was possibly due to the additional adsorption of As by goethite minerals (39 %) in the laterite substrate in the present study [28]. Allende et al. [24] reported the higher removal efficiency of As by CW (99.9 %), possibly due to the longer retention time and the use of zeolite as a substrate.

The average concentration of Mn in the influent was 3.11 mg/L, which was approximately six- and three-fold higher than the MAL [29] for category A and B, respectively. During the first day of the experiment, the concentrations of Mn in MD2 effluent were lower than the MAL for category B, and after that, exceeded the MAL. However, Mn concentrations in the effluents of both MD7 and MD8 were lower than the MAL for category B [29], which demonstrated the efficiency of metal removal by the CWs. The removal efficiency of Mn by the adsorbent was gradually reduced during the experiment (Figure 2), implying the saturation of the active sites of the adsorbent and the attainment of equilibrium [30]. The average removal efficiencies of Mn by MD1, MD2, MD3–7, and MD3–6 + MD8 were 2.64, 54.3, 42.7, and 32.1 %, respectively (Table 3). The removal efficiency of Mn by the treatment system (settling tank, adsorbent tank, and CWs with limestone substrate) was 99.5 %.

The concentrations of Zn in the influent were lower than the MAL for category A [29] and were decreased rapidly by the adsorbent (MD2) (average of 50.0 % during 4 months) (Table 3, Figure 2). The concentrations of Cd in MD2 effluent were higher than the MAL for category B [29] and were continuously decreased by CWs, meeting the regulation category A (limestone substrate) and category B (laterite substrate) (Figure 2). The results of this study also showed a higher average removal of Cd by MD2 (44.0 %) than that by CWs (35.7 %) (Table 3).

Pb demonstrated lower removal efficiencies by the adsorbent and CWs than As, Mn, Zn, and Cd (Figure 2). The concentrations of Pb in the influent were slightly higher than the MAL for category B [29] and decreased, meeting the regulation for category B [29], in the effluent of MD7 and MD8. The average removal efficiency of Pb by the treatment system during 4 months of operation was 66.7 % (Table 3). The removal efficiency of Pb in this study was lower than those reported by Chen et al. [22] using coke and gravel substrates, possibly due to the CW designs and different substrates.

After 4 months of system operation, the average removal efficiency of As and heavy metals by the treatment system (settling tank, adsorbent tank, and CWs with limestone substrate) were in the following order: Mn (99.5 %) > Cd (93.3 %) > As (89.9 %) > Zn (80.1 %) > Pb (66.7 %). In addition, the results of this study demonstrated that CWs with laterite substrate showed higher removal efficiency of As than CWs with limestone, whereas the latter was more efficient for Mn, Pb, and Cd removal. This result indicates the significance of the selection of different substrates for the removal of targeted metals.



(**a**) (**b**) (**c**) (**d**) (**e**)

**Figure 2.** Concentrations of (**a**) As, (**b**) Mn, (**c**) Zn, (**d**) Cd, and (**e**) Pb in wastewater before entering the treatment system (Ci) and in the effluents from the adsorbent tank (MD2), constructed wetland with limestone substrate (MD3-MD7), and constructed wetland with laterite substrate (MD8).

The removal efficiencies of As, Mn, Zn, and Pb in the present study were lower than those reported by Ha and Anh [27] who used the same adsorbent (SBC2-400-10S) and horizontal-subsurface-flow CWs with limestone substrate and higher concentrations of these metals in the influent (Tables 3 and 4).

The difference may be due to the fact that the present study used the real wastewater released from a Pb-Zn mine, whereas the water in the previous study was prepared by the dilution of nitrate metal salts in a laboratory experiment. This result implies a variation of metal removal efficiencies when designing pilot and full-scale treatment systems on the basis of laboratory experiments.

The removal efficiencies of As and heavy metals by CWs using the data of the influent before entering the CWs (MD3) were calculated for comparison with previous studies. The removal efficiency of Zn by CWs in the present study (Table 3) was higher than that reported by Alessio et al. [31] using gravel substrates. However, Chen et al. [22], Ha and Anh [27], Yeh et al. [32], and Liu et al. [33] reported higher removal efficiency than those determined in this study. The removal efficiencies of Cd in this study were higher than those reported by Kumari and Tripathi [34] and Scholes et al. [35] and lower than those by Liu et al. [33]. The results of this study also demonstrated lower removal efficiencies of Pb compared to those reported in some studies, such as Chen et al. [22], Ha and Anh [27], Scholes et al. [35], Liu et al. [33], and those in Table 4. The type of wetland (i.e., surface-flow, horizontal-subsurface flow, and vertical-subsurface flow), substrates, retention time, hydraulic loading rate, and concentrations of metals in the influent may result in differences of metal removal efficiencies (Table 4).

### *3.2. Accumulation of As and Heavy Metals in the Adsorbent*

The concentrations of Mn, Zn, Pb, Cd, and As in the adsorbent before the experiment were 1460, 930, 245, 170, and 67 mg/kg, respectively; after 4 months of the experiment, they increased to 3930, 1870, 512, 420, and 289 mg/kg (Figure 3). The adsorption of metals by the adsorbent in this study can be explained by the results of specific surface area measurements (BET method), surface charge density measurements (by PCD), clay minerals presence (e.g., kaolinite and illite) [36], presence of high amounts of silica (Si–OH and Si–O–OH) [37,38], and OH bending [37,39]. In addition, the presence of hematite (7%) and goethite (4%) may result in the adsorption of As by the adsorbent (SBC2-400-10S) [40,41]. However, the adsorption capacities of SBC2-400-10S for heavy metals in this study were lower than those reported in previous batch experiments using activated carbon (Pb = 20.7 mg/g; Cd =17.8 mg/g; Zn = 19.9 mg/g) [42], montmorillonite (Pb = 31.1 mg/g; Cd = 30.7 mg/g) [43], and modified red mud (As = 1.08 mg/g) [44]. The lower adsorption capacities of SBC2-400-10S compared with those of other adsorbents were possibly due to the characteristics of the adsorbents, the concentrations of As and heavy metals, and the use of real mining wastewater in the present study.

The total amounts of Mn, Zn, Cd, Pb, and As adsorbed to SBC2-400-10S after 4 months were 341, 130, 34.5, 36.8, and 30.6 g, respectively. The amounts of Mn, Zn, Cd, Pb, and As removed by the adsorbent tank were 986, 292, 131, 53.5, and 74.2 g, respectively. The higher amounts of metals removed by the adsorbent tank compared with those adsorbed to SBC2-400-10S indicated the additional removal of heavy metals by other processes, such as co-precipitation or inner-sphere and outer-sphere complexation [45]. After reaching equilibrium, the adsorbents can be treated by desorption, recovering As and heavy metals [46] by using chemical substances [47,48], or be used in brick and cement production. However, further studies need to be performed to assess the possibility of metal leaching from the adsorbent.

**Table 4.** Constructed wetland designs, removal efficiencies, and concentrations of As and heavy metals in *P. australis*.

| Metals | Authors | Type of Wetland | Substrates | Length × width × depth (m) | Retention Time | Hydraulic Loading Rate | Operation Duration (Months) | Influent Concentration (mg/L) | Removal Efficiency (%) | Metal Content in *P. australis* (mg/kg-DW) | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | Belowground Biomass | Aboveground Biomass |
| As | This study | HSSF | Limestone | 1 × 1 × 4.1 + 1 × 0.5x4.1 | 2 d | 5 $m^3$/d | 4 | 0.1 | 75.1 | 21.9 | 17.8 |
| | | | Laterite | | | | | | 86.0 | | |
| | [24] | HSSF | Zeolite | 0.6 × 0.2 × 0.65 | 11 d | 30 mm/d | 5.5 | 2.6 | 99.9 | 0.00286 | 0.00234 |
| | [27] * | SF | Soil | 1.2 × 0.23 | 2 d | 0.05 $m^3$/day | 1 | 0.4 | 80.5 | - | - |
| | | HSSF | Limestone | 1.2 × 0.28 | | | | | 83.1 | | |
| | [49] | - | Sand | 1 × 0.6 | 10 d | - | - | 0.2 | - | 119.55 | 6.36 |
| | [50] | VSSF | Sand | 1 × 1 × 1.5 | 2–3w | 28 mm/d | 24 | | - | 1.65 | 0.58 |
| | [51] | HSSF | - | - | - | - | - | - | - | 4.95 | 0.18 |
| | [52] | - | Sediment | - | - | - | - | 37.6 | - | 1.2–2.4 | 0.1–0.6 |
| Mn | This study | HSSF | Limestone | 1 × 1 × 4.1 + 1 × 0.5 × 4.1 | 2 d | 5 $m^3$/day | 4 | 1.34 | 98.8 | 2200 | 506 |
| | [27] * | SF | Soil | 1.2 × 0.23 | 2 d | 0.05$m^3$/day | 1 | 4 | 91.2 | - | - |
| | | HSSF | Limestone | 1.2 × 0.28 | | | | | 94.1 | | |
| | [51] | HSSF | - | - | - | - | - | - | - | 266 | 175 |
| | [52] | - | Sediment | - | - | - | - | 2606 | - | 264.7–1178 | 193.3–361.9 |
| | [53] | VSSF | Goetextile | 12.5 × 30 × 0.6 | 2 d | 184 $m^3$/d | 10 | | - | 52 | 146 |
| | | HSSF | Gravel | 50 × 13 × 0.5 | 6.7 d | 22.5 $m^3$/d | | | | 58 | 60 |
| | [54] | - | Gravel | 30 × 3 × 0.6 | 15 d | 2000 l/d | 5 | 3.47 | - | 266 | 87.5 |
| Zn | This study | HSSF | Limestone | 1 × 1 × 4.1 + 1 × 0.5 × 4.1 | 2 d | 5 $m^3$/day | 4 | 0.26 | 30.2 | 188 | 144 |
| | [22] | - | Coke | 1.93 × 0.4 × 0.6 | 12.68 d | 300mL/min | 2 | 48.5 | 91.18 | - | 0.1016 |
| | | | Gravel | | 9.6 d | | | 5.268 | 61.57 | | 0.009 |
| | [27] | SF | Soil | 1.2 × 0.23 | 2 d | 0.05 $m^3$/day | 1 | 1.5 | 78.9 | - | - |
| | | HSSF | Limestone | 1.2 × 0.28 | | | | | 81.7 | | |
| | [31] | HSSF | Gravel | 12 × 2.5 × (1.5–2) | - | 8 $m^3$/d | 8 | 0.5 | 27 | 66.2 | 59.1 |
| | [32] | SF | Gravel and sand | 1.8 × 0.5 × 0.5 | 1.25 d | 16 cm/d | 4 | 0.366 | 92 | 160 | 60 |
| | [35] | SSP | Soil | 1 × 2 × 0.25 | | | 2 | 5 | 94.2 | 302.53 | 149.56 |
| | [55] | HSSF | - | - | - | - | - | - | - | 86 | 20.5 |
| | [52] | - | Sediment | - | - | - | - | 516 | - | 69.6–198 | 45.7–154.6 |
| | [53] | VSSF | Goetextile | 12.5 × 30 × 0.6 | 2 d | 184 $m^3$/d | - | - | - | 132 | 70 |
| | | HSSF | Gravel | 50 × 13 × 0.5 | 6.7 d | 22.5 $m^3$/d | 10 | - | - | 129 | 23 |
| | [54] | - | Gravel | 30 × 3 × 0.6 | 15 d | 2000 L/d | 5 | 0.12 | - | 46.3 | 16.6 |
| | [55] | - | - | - | - | - | - | - | - | 54.99–176.7 | 20.65–32.4 |

**Table 4.** *Cont.*

| Metals | Authors | Type of Wetland | Substrates | Length × width × depth (m) | Retention Time | Hydraulic Loading Rate | Operation Duration (Months) | Influent Concentration (mg/L) | Removal Efficiency (%) | Metal Content in *P. australis* (mg/kg-DW) | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | Belowground Biomass | Aboveground Biomass |
| Cd | This study | HSSF | Limestone | 1 × 1 × 4.1 + 1 × 0.5 × 4.1 | 2d | 5 m$^3$/day | 4 | 0.21 | 83.7 | 0.784 | 1.1 |
| | [33] | - | PVC | 0.5 × 0.5 × 0.3 | 16 d | - | 2 | 4.55 | 44.2 | - | 2.47 |
| | [34] | - | - | 360 m$^2$ | - | - | 4 | 1.73 | 72 | - | 0.007–0.04 |
| | [35] | SSP | Soil | 1 × 2 × 0.25 | | | 2 | 0.5 | 92.2 | 33.26 | 11.42 |
| | [50] | VSSF | Sand | 1 × 1 × 1.5 | 2–3 w | 28 mm/d | 24 | | - | 0.739 | <0.03 |
| | [51] | HSSF | - | - | - | - | - | - | - | 0.21 | 0.57–0.9 |
| | [52] | - | Sediment | - | - | - | - | 0.1 | - | 0.2–1.3 | <0.1 |
| | [53] | VSSF | Goetextile | 12.5 × 30 × 0.6 | 2 d | 184 m$^3$/d | - | - | - | 0.21 | 0.014 |
| | | HSSF | Gravel | 50 × 13 × 0.5 | 6.7 d | 22.5 m$^3$/d | 10 | | | 0.47 | 0.083 |
| | [54] | - | Gravel | 30 × 3 × 0.6 | 15 d | 2000 L/d | 5 | <0.01 | - | 0.25 | 0.05 |
| Pb | This study | HSSF | Limestone | 1 × 1 × 4.1 + 1 × 0.5x4.1 | 2 d | 5 m$^3$/day | 4 | 0.27 | 42.8 | 115 | 80.9 |
| | [22] | - | Coke | 1.93 × 0.4 × 0.6 | 12.68 d | 300 mL/min | - | 27.44 | 99.66 | - | 0.0763 |
| | | | Gravel | | 9.6 d | | | 49.89 | 99.53 | | 0.0736 |
| | [27] | SF | Soil | 1.2 × 0.23 | 2 d | 0.05 m$^3$/day | 1 | 0.6 | 73.5 | - | - |
| | | HSSF | Limestone | 1.2 × 0.28 | | | | | 81.1 | | |
| | [34] | - | - | 360 m$^2$ | - | - | 4 | 7.58 | 69 | - | 36-108 |
| | [35] | SSP | Soil | 1 × 2 × 0.25 | | | 2 | 2 | 96.4 | 152.88 | 54.3 |
| | [50] | VSSF | Sand | 1 × 1 × 1.5 | 2–3 w | 28 mm/d | 24 | - | - | 17.63 | 0.98 |
| | [51] | HSSF | - | - | - | - | - | - | - | 7.1 | 0.11 |
| | [52] | - | Sediment | - | - | - | - | 186 | - | 9.1–79.1 | 0.7–1.1 |
| | [53] | VSSF | Goetextile | 12.5 × 30 × 0.6 | 2 d | 184 m$^3$/d | - | - | - | 10 | 0.39 |
| | | HSSF | Gravel | 50 × 13 × 0.5 | 6.7 d | 22.5 m$^3$/d | 10 | | | 20 | 0.53 |
| | [54] | - | Gravel | 30 × 3 × 0.6 | 15 d | 2000 L/d | 5 | 0.06 | - | 12.2 | 0.1 |
| | [55] | - | - | - | - | - | - | - | - | 21.49–90.94 | 1.14–2.18 |

HSSF: horizontal subsurface flow, VSSF: vertical subsurface flow, SF: surface flow, SSP: subsurface flow, * Removal efficiency of constructed wetland combined with sorbent.

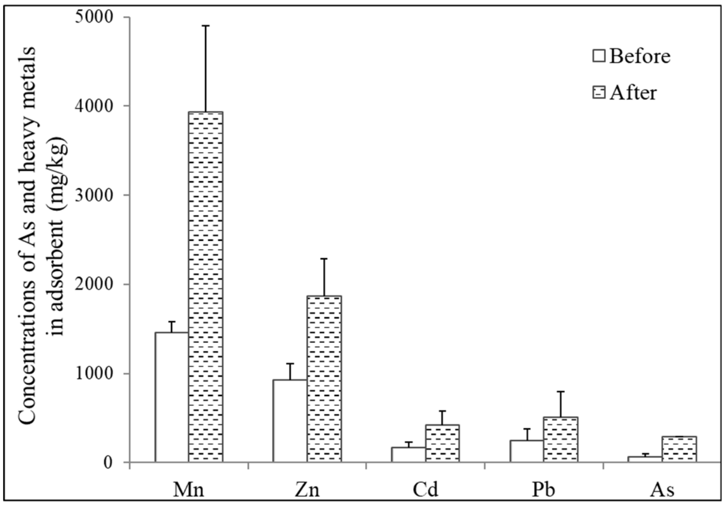


**Figure 3.** Concentrations of As and heavy metals in the adsorbent (mg/kg) after 4 months.

### *3.3. Plant Growth and Concentrations of As and Heavy Metals in P. australis*

The plants in CWs produced shoots after 1 month, and approximately 80% of the transplanted plants grew well. The system started after 3 months of transplanting, when the average height of *P. australis* was approximately 100 cm, and the average length of the new shoots was 25 cm. The plant showed continuous growth during the 4 months of the experiment.

The concentrations of Mn, Zn, Cd, Pb, and As in *P. australis* after 4 months of system operation were higher than those before the experiment (Figure 4). In addition, with the exception of Zn before the experiment, the concentrations of As and heavy metals in the belowground parts of the plant were higher than those in the aboveground biomass of *P. australis* (Figure 4). This is consistent with the results reported by Bonanno and Giudice [56] and Nga and Ha [57]. The concentrations of Mn, Zn, Cd, Pb, and As in the belowground parts were 194, 188, 0.78, 115, and 21.9 mg/kg-DW, respectively, while those in the aboveground biomass were 94.2, 144, 1.1, 80.9, and 17.8 mg/kg-DW. Higher concentrations of Mn and Zn than those of the other studied metals in the plant were possibly due to Mn and Zn being two essential elements for plant growth, whereas Zn, Pb, and As are known to be potentially toxic elements [58]. The concentrations of As, Mn, Zn, Cd, and Pb in both belowground and aboveground parts of the plant in this study were lower than those reported by Nga and Ha [57], reflecting the differences of metal concentrations between lab experiments and a field study, as well as the impacts of the initial concentrations and retention time.

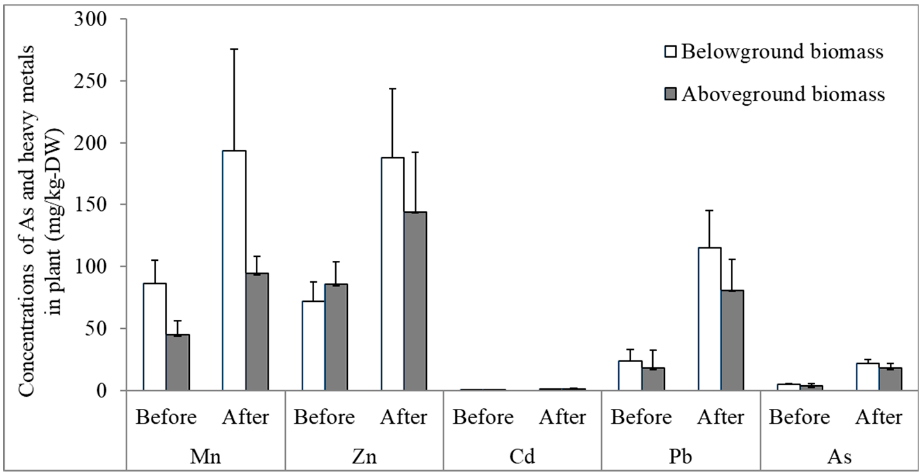


**Figure 4.** Accumulation of As and heavy metals in *Phragmites australis* (mg/kg-DW) after 4 months.

Table 4 shows the concentrations of As and heavy metals in *P. australis* in CWs. Alishir et al. [49] showed higher concentration of As in the belowground parts of the plant than that found in this study. However, As concentrations in both the belowground and aboveground parts of the plant in this study were higher than those in other studies [24,49–52] (Table 4). The concentrations of Mn in all parts of the plant in this study were higher than those in previous studies [51–54] (Table 4). We obtained higher concentrations of Zn in the plant than other studies [22,30,32,51,53–55]; however, Liu et al. [33] and Diego et al. [52] reported higher concentrations of Zn in the plant (Table 4). Schierup et al. [54] reported concentrations of Cd in the aboveground part of the plant within 4.4–13.5 mg/kg-DW; however, Cd concentrations in the plant in this study were higher than those in other researches [35,50–54] (Table 4). This study also demonstrated high concentrations of Pb in *P. australis* compared to previous studies, such as Chen et al. [22], Liu et al. [33], Vymazal et al. [51], Lesage et al. [53], and Phillips et al. [55] (Table 4); however, Pb concentration in this plant when receiving highway runoff reached 152.88 mg/kg-DW in the root [33] and 108 mg/kg-DW in the aboveground biomass [35] (Table 4).

The total amounts of Mn, Zn, Cd, Pb, and As removed from wastewater by the CWs with limestone substrate after 4 months were estimated to be 773, 43.1, 70.1, 101, and 44.8 g, respectively. The estimated biomass of *P. australis* in CWs was 5 kg/m$^2$ in dry weight (DW). Therefore, the amounts of Mn, Zn, Cd, Pb, and As accumulated in the whole plant were 18.0, 20.7, 0.116, 12.3, and 2.5 g, respectively. These values were much lower than those removed by the CWs. This result indicated that besides metal uptake and accumulation in *P. australis,* the processes of metal removal from CWs included adsorption to substrates, co-precipitation, filtration, and deposition in the rhizosphere [19,59]. These mechanisms of metal removal may involve the minerals present in the substrates of the CWs (Table 1) and the main sulfur minerals (e.g., sphalerite—ZnS, galena—PbS, and pyrite—$FeS_2$) of the Cho Don Pb–Zn mine [60], which released sulfates and Fe compounds through an oxidation process.

## 4. Conclusions

The 5 m$^3$/day pilot-scale constant flow rate of the combined system with modified iron mine drainage sludge and constructed wetlands showed efficient removal of As and heavy metals from contaminated wastewater in the largest Pb–Zn mine in Vietnam. The concentrations of As and heavy metals in the effluent during 4 months of the combined system operation were lower than the maximum allowable limit regulated by the QCVN 40:2011/BTNMT for industrial wastewater. The limestone substrate in CWs showed greater removal of Mn, Zn, Cd, and Zn than the laterite substrate, whereas the latter was more efficient for As removal. Further studies need to be conducted with the combined system using higher concentrations of metals in the influent and optimal conditions for metal removal before it can be applied at full scale.

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