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Fate and Transfer of Heavy Metals in Constructed Wetland Mesocosms Subjected Different Hydraulic Regime

Alya A. Mohammed[1], Ahmed S. Al Chalabi[1*], Angham O. Sahei[1]

[1] Department of Environmental and Pollution Technical Engineering, Basrah Engineering Technical College, Southern Technical University, Al Basra, Iraq

* Corresponding author's e-mail: ahmed.sadiq@stu.edu.iq

ABSTRACT

A constructed wetland may consume different levels of pollution in different types of wastewater. The focus of this study was the removal of heavy metals (Pb, Cr, and Cd) by plants and their fate in constructed wetland mesocosms. With hydraulic regime manipulation, heavy metals were retained in the ferric dewatered sludge either by adsorption to the carboxylate groups and iron oxy-hydroxide under anaerobic conditions or by co-precipitation with iron oxy-hydroxide under aerobic conditions. Under anaerobic conditions, most heavy metals accumulate in the bottom layer and decrease when moving to the top one. In turn, under aerobic conditions, most of the heavy metals accumulate in the bottom and top layers. Plants play a minor role in heavy metal removal. About 16% of total heavy metals added to the ferric dewatered treatment sludge were taken up by plants. Roots accumulated roughly 64% of the total lead take up by plants, 66% of the chromium, and 63% of the cadmium, respectively, and passed 36%, 34%, and 37% of the aboveground tissues for harvesting. As a conclusion of this study, when constructed wetland is used, the role of hydraulic regime, substance used, and vegetation should not be ignored in the process of wastewater purification in constructed wetland.

Keywords: constricted wetland, ferric dewatered sludge, heavy metals, hydraulic regime, plants.

INTRODUCTION

Unlike other toxic pollutants, heavy metals (HMs) are not degradable. Therefore, HMs show the tendency to accumulate in our environment. In the long term, part of HMs could reach human beings through the food change, and thus can cause serious health damage. Different methods have been developed to remove HMs from the surrounding area. Constructed wetlands are inexpensive, use little energy, and are simple to operate, and have been used to retain HMs from various types of wastewater in ecosystems (Dong et al., 2016). In constructed wetlands, HMs are concentrated within a convenient area, which may depend on the hydrology of the system.

Redox potential, dissolved oxygen (DO), and pH in the wetland system are the crucial factors known to influence the mobility of HMs (Vymazal et al., 2010). During the passage of wastewater through the filtration media, HMs can be removed by biodegradation, as well as physicochemical processes in different aerobic, anoxic, and anaerobic zones in a constructed wetland.

The majority of the published literature focuses on the performance of horizontal flow systems for HMs removal by adsorption. The filtration media can remove HMs by adsorption and binding processes. The positive charge of HMs can be attracted by the negative charge of filtration media. Depending on the media, adsorption could be physisorption, which is a physical processes with weak bindings, or chemisorption, which is a chemical processes with strong bindings (Marchand et al., 2010). Under anoxic and anaerobic conditions, the vital processes dealing with HMs accumulation/mobilization are the creation of hydrogen sulfide by sulfate reduction bacteria and the hydrolysis of Fe/Mn (Vymazal et al., 2010).However, taking into consideration that intermittent loading in vertical flow can dominate the aerobic condition for a long time, the removal of HMs could occur by precipitation or co-precipitation of Fe/Mn hydrous oxides (Mohammed and Babatunde, 2017). The effective surface for adsorption can be available in vertical flow constricted wetland beds, especially at the great depth of these beds. On the other hand, this great depth could enhance anaerobic conditions, which are favorable for precipitation. This precipitation is considered long-term HMs removal in constructed wetlands (Stefanakis et al., 2014). On the other hand, vegetation, one of the essential constructed wetland components (Dong, et al., 2016), is capable of absorbing HMs from wastewater in the dissolved form by the roots and then taking it up to other parts of plants (Stefanakis, et al., 2014).

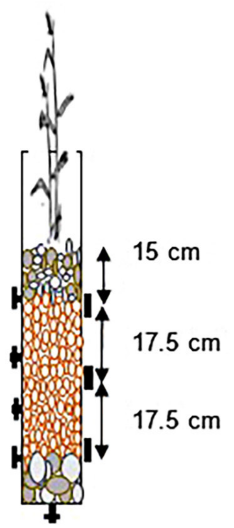
The direct contribution of plants is not significant to the uptake of HMs (up to 5%) compared with the total amount of HMs removed in constructed wetland systems (Stefanakis et al., 2014). However, there is an indirect role of plants in HMs removal and could be considered more important in other processes such as complexation with organics on the plants' roots, providing an attractive area for attached bacteria, and releasing oxygen (even very limited) in the root zone [Stefanakis et al., 2014; Vymazal and Brezinova, 2016; Mohammed, 2017]. In addition, roots can enhance the conductivity of the water as they grow through the soil, and after the roots' death, they make spaces in the soil (Thani et al., 2019). The major purpose of this study was to evaluate the hydraulic regime of constructed wetlands on HMs removal from synthetic wastewater. As a result, 1) the fate of metals was monitored at different depths in constructed wetlands mesocosms; 2) the efficiency of plants in wetland mesocosms for removing metals was investigated; and 3) the extent to which each part of plants takes up these heavy metals was determined.

EXPERIMENTAL WORKS

System configuration

The experiments were conducted for 220 days (started on May 10, 2015) and consisted of two columns used to study the removal of HMs. The down flow was operated in vertical flow constricted wetland. The two columns were operated under different conditions to achieve different hydraulic regimes where, peristaltic pumps were used to generate a cycle of wet/dry period. Each cycle gave a 3.83h wet and a 0.17h dry period in column A, while in column B a 1.00h wet and 3.00h dry period were used. The system was set up outdoors using two perspex columns with a 10 cm diameter and a height of 110 cm. Three holes (on each column) were used for ferric dewatered sludge to be taken at different depth as shown in Figure 1a. The media were taken from this hole every month. Each column was filled with ferric dewatered sludge (FDS) and two layers of gravel. A layer of 7± 2 mm gravel for a depth of 15 cm placed at the top and 22± 3 mm of round gravel served as a drainage layer (giving the system an

a)



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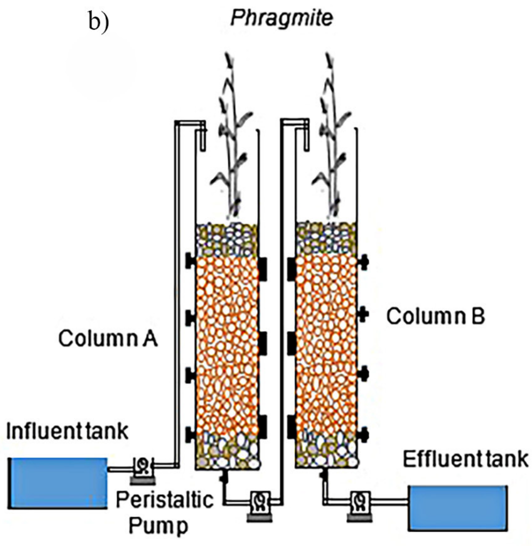

Figure 1. (a) Schematic of single constructed wetland, (b) schematic description of the constructed wetlands

average porosity of 0.43) as shown in Figure 1b. The FDS consisted of Fe (193.85 mg/g), and iron oxalate (162 mg/g) while the specific surface area was 132 m^2/g; hence, this medium had high affinity and strong bonding for HMs (Mohammed, 2017). *Phragmites australis* was planted in the main layer of each column.

To simulate wastewater, $CdSO_4 \cdot H_2O$ salt, $Cr(SO_4)_2 \cdot 12H_2O$ salt, and $PbCl_2$ salt, respectively for cadmium(Cd), chromium (Cr), and lead (Pb) were used to synthesise wastewater in the laboratory. The initial concentrations of HMs were (0.230 mg/l – 0.630 mg/l), (0.240 mg/l – 0.650 mg/l) and (0.240 mg/l – 0.810 mg/l) for Pb, Cr, and Cd, respectively. HANNA HI 991301 probe was used to Measure pH, DO and redox potential.

Heavy metals analysis

In ferric dewatered sludge

First, 500 mg of FDS was dried in an oven for two days at 70°C. The sample was then digested with 4.5 ml of HNO_3 and 1.5 ml of HCl in a microwave (Milestone Ethos 1600). After digestion, the sample was filtered using 0.45 µm, in order to obtain a clear sample and then analyzed for Pb, Cr, and Cd using ICP/OES.

In phragmites australis plants

After two months' growth where lush vegetation was observed, three samples of Phragmites australis plants were selected randomly from each column, dried in an oven for two days at 70°C, and then analyzed for HMs. The HMs concentrations in the plant were determined by using a microwave oven. Dry powder of Phragmites australis (400 mg) was mineralized in 5 ml of 69% v/v nitric acid, 5 ml of deionized water, and 2 mL of 30% v/v H_2O_2. Deionized water was used to finalize the volume (25 ml). Then, the sample was analyzed for Pb, Cr, and Cd by using ICP/OES after filtered with 0.45 µm.

Statistical analysis

The results were statistically analyzed using one-way analysis of variance (ANOVA) and the t-test. For all tests, alpha was set at 0.05. Statistical analyses of HM concentrations along the FDS and in plants were used. The differences between HM concentrations in the filtration beds were statistically evaluated through the one-way ANOVA for vertical (top, mid, and bottom layers) on one hand and for plants (roots, stems, and leaves) on the other hand.

RESULT AND DISCUSSION

Heavy metals in ferric dewatered sludge

Depending on the hydraulic regime of column A, there are aerobic, anoxic, and anaerobic conditions along this column where average DO concentrations were between 1.77 and 0.41 mg/l as shown in Table 1. All HMs have the same removal fate in this column, where the concentrations of HMs in FDS increase from the top layer to the bottom one in this column, as shown in Figure 2a. In the first layer (15 cm depth), the dominant condition was aerobic condition, which promoted the formation of iron oxides and hydroxides, resulting in HMs removal by adsorption and co-precipitation (Marchand et al., 2010). However, the presence of a sufficient amount of SO_4 could impede co-precipitate. This amount of SO_4 in this study was from the sulfate salts in the prepared synthetic wastewater and from FDS (Mohammed et al., 2016).

As shown in Table 1, the dominant conditions in the second and third layers (32 cm and 50 cm) were anoxic and anaerobic. The main process for the removal of HMs in these conditions could be by adsorption to the carboxylate groups in the humic substances or to the iron oxy-hydroxide in FDS as reported in (Mohammed et al., 2016). The adsorption process could be more pronounced when redox potentials are between 100 mV and-100 mV (Marchand et al., 2010). The average values of redox potentials in this study were 134 mV, 60 mV, and -152 mV, respectively, from top to bottom layers. Moreover, the hydraulic regime provided a high contact time between wastewater and FDS (3 hours and 50 minutes) and the use of FDS as the main media could enhance HMs adsorption; the pH value was considered the main factor affecting HMs adsorption, the pH average values for all layers were between 7.5 and 7.8. It was found that the maximum adsorption capacity of HMs to

Table 1. Physical properties in column A

Depth (cm)	DO (mg/l)	pH	ORP (mV)
15	1.77±0.45	7.812±0.23	134.13
32	0.86±0.07	7.65±0.21	-60.75
50	0.41±0.05	7.87±0.23	-152.25

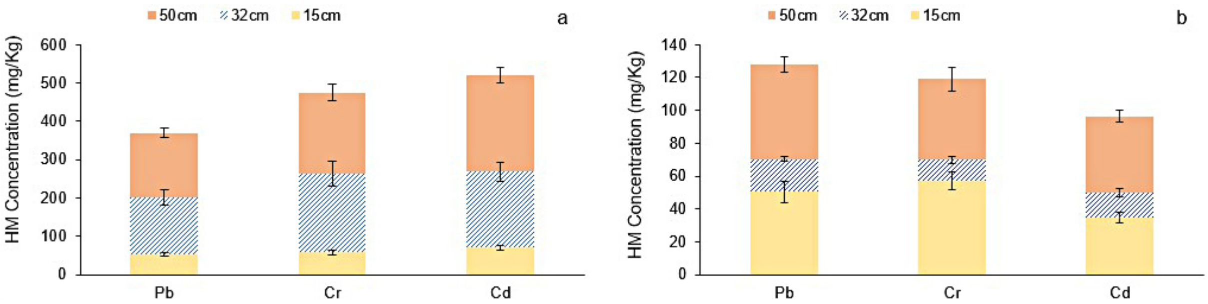

Figure 2. Heavy metals accumulate in ferric dewatered sludge: (a) in column A, (b) in column B

the FDS using the Langmuir isotherm model at pH 7 was 20 mg/Kg, 130 mg/Kg and 30 mg/Kg for Pb, Cr and Cd, respectively (Mohammed, 2017).

The rest of the HMs, which could not be removed in column A, were introduced to column B. The aerobic condition was the dominant condition for all layers in column B, as shown in Table 2, where the average DO concentrations decreased from 5.2 mg/l at the top layer to 1.7 mg/l at the bottom one, the aerobic condition was the dominant condition for all layers in column B. This is due to the hydraulic regime that is used in this stage, as there is 3 hours for aeration of this column and 1 hour for filling. HMs are concentrated in the top and bottom areas. It seems that HMs had a similar profile in those layers as precipitation and co-precipitation were the dominant processes for HMs removal in this column. Ferrous iron is oxidized to ferric iron and becomes a metal adsorbing form at a redox potential of +120 mV. The average values of redox potentials in column B were between +230 mV and +144 mV (Table 2). Iron in aeration environment tends to oxidize and hydrolyze as a result HMs could co-precipitate with iron oxy-hydroxide (Marchand et al., 2010). Moreover, the pH of wastewater tends to drop when the iron oxy-hydroxide process occurs (Kosolapov et al. 2004). There was a decrease in pH value from 7.1 to 6.9 when wastewater flowed from the top layer to the mid layer, which confirms the oxy-hydroxide process.

At pH 6.9 (as in mid layer) HMs tend to be in dissolved form and the removal of HMs could be by adsorption to the FDS. The solubility of HMs extremely depend on pH value (Laaraj et al., 2022), Cr can precipitate at pH> 6 (Coelho et al. 2014), Cd also undergo precipitate at pH> 8 (Chen et al. 2015), while Pb precipitation could occur at pH > 7.2 (Ercan and Aydın, 2013). It seems that the removal of HMs in this layer was by taken up by plants, as HMs tend to be in dissolved form.

The precipitation as HMs hydroxide or co-precipitation with iron oxy-hydroxide caused the clogging problem (from 14/08/2015 to 28/08/2015) in this column. The precipitate of HMs could procedure a film-like covering on the FDS surface (Knowles et al. 2011). The clogging phenomena were caused wastewater ponding on the surface of this column and this could be because of chemical precipitation of HMs that occurs in the first layer.

Table 2. Physical properties in column B

Depth (cm)	DO (mg/l)	pH	ORP (mV)
15	5.23±0.67	7.14±0.26	230.25
32	2.98±0.53	6.98±0.17	144.5
50	1.76±0.17	7.02±0.21	150.75

Plants uptake of heavy metals

Although HMs concentrations were found in plants after HMs were added to the soil media, live plants have been noted to play a minor role in HMs removal. The bioavailability of HMs enhances plant uptake (Ugya and Meguellati, 2022). The result of HMs accumulating in leaves, stems, and roots is shown in Figure 3 for both columns A and B. The figure shows the same trend of HMs removal for different hydraulic regimes where the accumulation of HMs in roots was greater than their accumulation in aboveground biomass. The study by (Vymazal et al., 2009) shows the same result. They found that the belowground/aboveground HMs concentration ratio ranged between 0.9 and 69.5. The ratio between HMs concertation in belowground biomass and HMs concertation in aboveground biomass in this study was 5.88 mg/kg in column A and 4.48 mg/kg in column B. The roots' capacity to accumulate each metal, rather than pass it to the shoots, depends on plant density, plant species and the

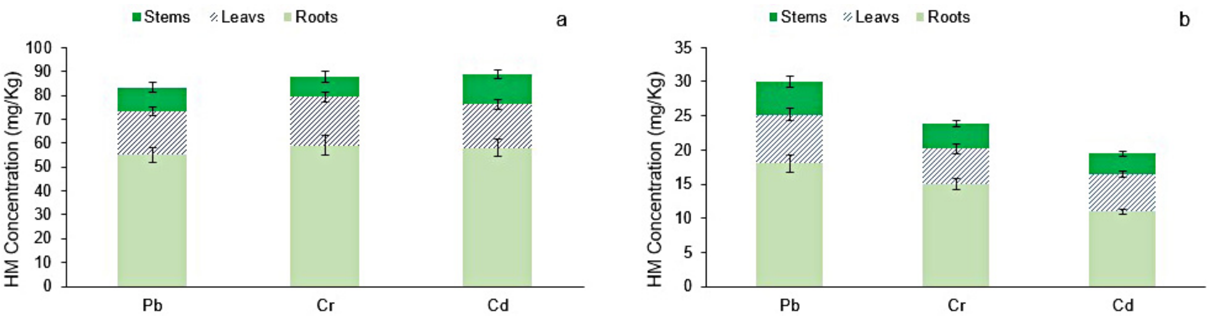

Figure 3. Heavy metal uptake by plants: (a) in column A, (b) in column B

HMs concentration supplied (Zuidervaart, 1996). It was suggested that HMs speciation in incoming wastewater, metal fractionation in soil media, and the ability of the plants to transfer HMs to aboveground parts play a key role in influencing the HMs accumulation in aboveground tissues of plants (Vymazal and Brezinova, 2016). In addition, it seems that HM concentrations vary substantially between leaves and stems, with concentrations often being higher in leaves. In aboveground biomass, the highest concentrations were recorded for Cr in leaves, followed by Pb and Cd in column A, and Pb in leaves, followed by Cd and Cr in column B. Moreover, it was observed that about 36% of total uptake by plants of Pb, 34% of Cr and 37% of Cd for both columns were found in the aboveground tissues. The total HMs concentration in aboveground tissues was 87.7 mg/kg in column A and 29.4 mg/kg in column B, and these concentrations were available for harvesting.

Statistical analysis

The results in FDS from the statistical analysis when t-test and ANOVA were used showed that the differences were very high in column A for all layers. In column B, at the depths of 15 cm and 50 cm, the results showed a significant difference for the HMs, with a highly significant difference ($p < 0.05$) compared with the depth of 32 cm. On the other hand, a comparison between the HMs concentrations in column A and HMs concentrations in column B were used and the results showed a high significant difference in column A compared with column B. This may be because of the high concentration of HMs in column A. Moreover, the results for the plant showed that there were significant differences for HMs concentrations in the roots of plants with a highly significant difference ($p < 0.05$) compared to leaves and stems, and the differences were very high in column A.

CONCLUSIONS

While the wetland media (FDS) was very effective in removing HMs from wastewater, the hydraulic regime plays an important role in controlling DO supply to the media. The removal of HMs under aerobic conditions seems to be by co-precipitation or precipitation with iron oxy-hydroxide, which caused the clogging problem. The retention of HMs in this condition was bottom layer > top layer > mid layer. Under anaerobic conditions, the removal of HMs was through adsorption to the carboxylate groups and iron oxy-hydroxide where there is enough contact time. The retention of HMs through column A increased from the bottom layer to the top layer. The formation of iron oxy-hydroxide seemed to be the best mechanism of HMs retention. Plants, on the other hand (even in low portions); play a role in HMs removal in both belowground biomass and aboveground biomass parts. However, the accumulation of HMs in roots was greater than their accumulation in aboveground biomass. Consequently, this study demonstrates the accumulation of HMs in different layers of constructed wetland using ferric dewatered sludge as substrate and the role of plants in HMs removal at different hydraulic regimes.

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