



Communication

Arsenic Removal Using Horizontal Subsurface Flow Constructed Wetlands: A Sustainable Alternative for Arsenic-Rich Acidic Waters

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Abstract: Constructed wetlands (CW) have been widely used to treat different types of water, including acid mine drainage (AMD). However, little is known about their performance in the removal of As from AMD. In this study, a laboratory-scale horizontal subsurface flow (HSSF) CW system was tested to evaluate its capacity to treat highly acidic, As-rich contaminated water resembling AMD. Vegetated and non-vegetated cells, having limestone or zeolite as the main supporting media, were built and operated to evaluate the effect of the media type and the presence of *Phragmites australis* on the removal of arsenic, iron (Fe), lead (Pb), and zinc (Zn), and on the neutralization capacity. The four types of cells were highly effective in the removal of As and Pb (removal > 99%), and Fe (removal > 98%), whereas Zn removal rates depended on the cell type. Limestone cells raised the pH from ~1.9 to ~7.5, while zeolite cells raised it to ~4. These results suggest that the media type has a key role in the neutralization capacity, and that the presence of vegetation affected mainly the removal of Zn. Knowledge from this study will contribute to guiding the implementation of HSSF CW for treating As-rich AMD.

Keywords: constructed wetland; horizontal subsurface flow; acid mine drainage; arsenic removal; supporting media

1. Introduction

The presence of As in water sources is a worldwide threat due to its toxicity and carcinogenic effects [1]. Despite the number of available technologies, further research is required to develop more efficient As removal technologies, since they all have drawbacks [2].

Constructed wetlands, as natural water treatment systems, have low investment and operation costs [3]. As such, they offer a sustainable alternative for water treatment. The main application of constructed wetlands (CW) has been the treatment of different wastewaters, however they also have high potential to treat metal-contaminated water [4]. In fact, the main use of CW for this purpose has been in acid mine drainage (AMD) treatment. In these waters, As may be present in a wide range of



(b)

Figure 1. (a) Diagram of the cells. (b) Photograph of the wetland system.

2.2. Synthetic Water

Synthetic acidic water representative of the Azufre River, Northern Chile [13], was prepared using tap water and chemicals (Table 1). Water was prepared every week and stored in a continuously stirred 2000 L PVC tank.

Table 1. Main characteristics of the synthetic water. Number of measurements = 13.

Parameter	Unit	Average \pm SD
pH	-	1.9 \pm 0.1
T	$^{\circ}$ C	21.8 \pm 1.5
TDS	g/L	4.15 \pm 0.26
Hardness	mg/L CaCO ₃	1554 \pm 179
ORP	mV	6472 \pm 23
SO ₄	mg/L	2092 \pm 509
As	mg/L	2.03 \pm 0.19
Fe	mg/L	61.54 \pm 7.79
Pb	mg/L	0.89 \pm 0.10
Zn	mg/L	11.92 \pm 1.30
Mn	mg/L	10.9 \pm 0.46
Al	mg/L	58 \pm 4.2

2.3. Operation, Sampling, and Analysis

The system was operated under a hydraulic loading rate (HLR) of 20 mm/day, which is in the range of those used in HSSF CW removing As [14]. A peristaltic pump was used to continuously dose each cell during 14 weeks between October and December (i.e., fall to spring in the southern hemisphere). Water samples from the outlet of each cell and from the feeding tank were collected every two weeks. Arsenic and metals were analyzed by ICP OES Perkin Elmer Optima 7300 V. Total dissolved solids (TDS) and pH were measured using a Corning Check Mate 90 conductivimeter and a pH electrode connected to a Hanna HI 2550 meter, respectively. Hardness was measured using the 2340C EDTA Titrimetric method [15].

2.4. Water Losses

Water losses due to evaporation or evapotranspiration (ET) were estimated by quantifying the difference in water volume entering and exiting each cell at each sampling event. In this way, these measurements were used to correct As and metal concentrations, and pH in the outflow [8].

2.5. Geochemical Modeling

Finally, geochemical modeling using PHREEQC [16] was performed to evaluate the effect of water losses and pH on the precipitation of solid phases that may be involved in the removal of As, Fe, Pb, and Zn. The saturation indexes (SI) of solid phases were obtained at 20 °C, 25 °C, and 30 °C for each type of cell: LV, LNV, ZV, and ZNV. For each type of cell, the corresponding water loss and pH (average values) were used to simulate chemical equilibria under three different temperatures: 19.8%, 21.8%, 22.7%, and 21.3%; and 7.58, 7.6, 4.2, and 4.48; respectively.

3. Results and Discussion

3.1. Neutralization Capacity of the System

The cell type had a strong effect on the pH values in the outflow (Figure 2). Limestone cells were able to raise pH values up to 7.5–8, remaining rather constant through time; whereas, zeolite cells could only raise them to ~6 at the beginning of the experiment, then they decreased quickly and remained stable around 4. The fact that the pH values were mainly stable for both media types towards the end of the experiment (despite the lower neutralization capacity of zeolite) indicates that longer experimental periods may be required to fully quantify their neutralization capacity.

These results are consistent with a previous study using similar media in HSSF [10]. However, in the present study, limestone cells achieved higher pH values in the outflow despite the lower pH values in the inflow, compared to the previous study. This suggests that the limestone neutralization capacity was sufficient to maintain alkaline values during the whole experimental period. This capacity also triggered As and metal removal, which is discussed as follows.

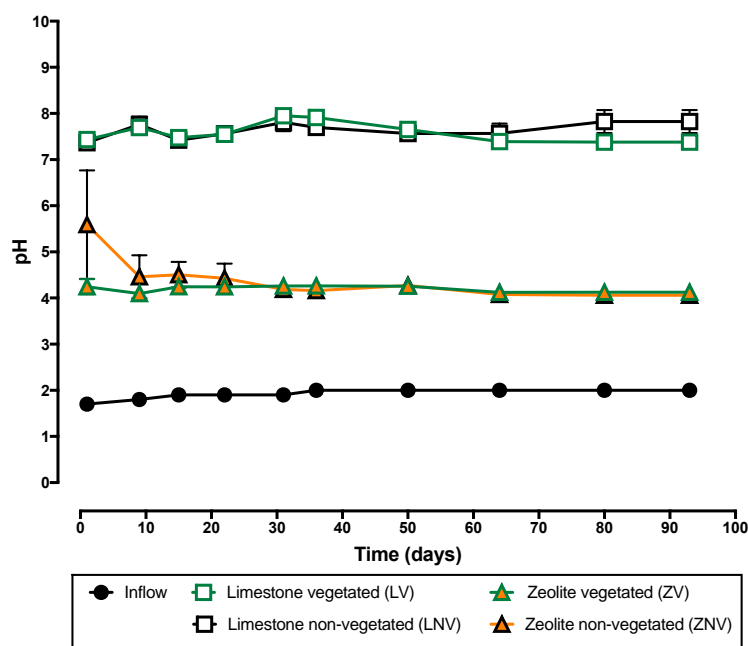
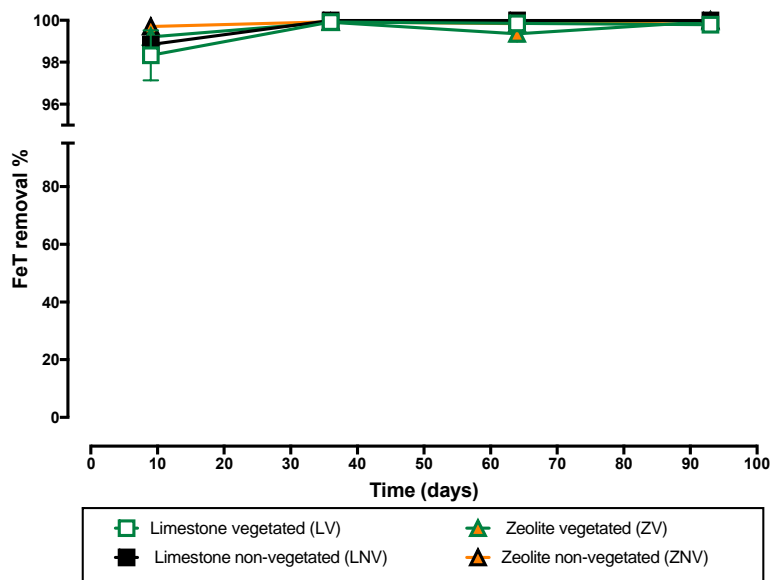


Figure 2. pH profile in the inflow and outflow of the wetland system. Data corresponds to average values, and error bars indicate minimum and maximum values.

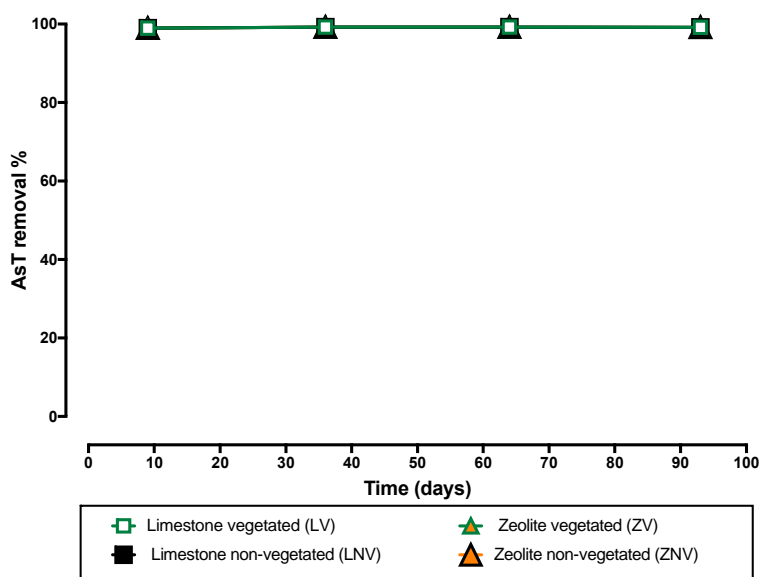
3.2. Iron and Arsenic Removal

Iron removal was also similar between cell types, with a removal greater than 98% after 9 days of operation (Figure 3). These results suggest that saturation of the media was not reached during the experimental period. The behavior of Fe removal over time was similar between vegetated and non-vegetated cells, suggesting that this removal was independent of the presence of plants. In addition, both zeolite and limestone cells showed high Fe removal capacity. Similarly, the system was

highly effective in the removal of arsenic, since it was not detected in the outflow from any zeolite or limestone cell (limit of detection LD = 0.036 mg/L). The removal of Fe is correlated with the removal of As in both types of cells, which can be explained by the removal processes that occur inside the supporting media.



(a)



(b)

Figure 3. Iron (a) and arsenic (b) removal in the zeolite and limestone cells (vegetated and non-vegetated). Data corresponds to average values, and error bars indicate minimum and maximum values for each cell type. When measurements were reported below the limit of detection, half of the corresponding value was considered as the actual concentration.

In the case of limestone cells, an increase in pH up to 8 was observed (Figure 2), which suggests a direct influence of pH on the removal of Fe, and in an indirect way, on the removal of As. The

neutralization of the pH in this system under oxidizing conditions can favor the formation of Fe minerals, such as ferric (Fe (III))-oxyhydroxides, that precipitate more efficiently at higher pH values (4–9). The presence of these minerals favors As removal from the aqueous phase by processes of surface sorption, due to their high affinity for As. Fe (III)-oxyhydroxides have a higher number of sorption sites, particularly in amorphous Fe (III)-oxyhydroxides [17,18]. Arsenic is highly affine to Fe oxides and oxyhydroxides, and its removal may be a consequence of adsorption processes inside the limestone cells. Despite the relevance that sorption processes can have in the removal of As, it is not possible to rule out coprecipitation processes and precipitation of ferric arsenate (FeAsO_4) during the system operation. In the same way, it cannot be ruled out that both removal processes (sorption and coprecipitation) occur simultaneously inside the limestone cells.

On the contrary, in zeolite cells the pH increase was lower than that in limestone cells, reaching average values of 4.2 for ZV and 4.48 for ZNV (Figure 2). Under these conditions in oxic environments, precipitation of Fe (III)-oxyhydroxides, and adsorption and coprecipitation processes of Fe and As, can also occur. Adsorption may occur on preformed Fe (III)-oxyhydroxides, and coprecipitation will occur as a simultaneous removal process. Interestingly, it has been observed that As (V) is absorbed more efficiently by Fe (III)-oxyhydroxides between pH 4–7, with an optimal yield at values close to 4, which would explain the high removal rates observed in zeolite cells [19–22]. In turn, the pH-dependent adsorption process is more evident in amorphous Fe (III)-oxyhydroxides [20,22]. Therefore, the pH values reached in the zeolite cells allow an optimal removal of As (V) by adsorption processes. In addition, several studies have shown that zeolite has a high binding affinity for arsenic and can remove high dissolved concentrations of this metalloid [23,24], but very little is known about its performance for this purpose under highly acidic conditions [12]. The capacity of zeolite to sorb As has been widely reported, also showing high removal efficiencies for different metals [25]. Similarly, in the zeolite cells arsenic removal may be the consequence of multiple simultaneous sorption and coprecipitation processes, including sorption on zeolite, sorption on Fe (III)-oxyhydroxide, or coprecipitation of Fe and As during Fe (III)-oxyhydroxides formation.

Our results are consistent with previous studies in SSF CW reporting that arsenic can be efficiently removed in these systems. Singhakant et al. [26] reported that As was found primarily in the residual fractions retained primarily in the pores of the supporting media (sand and gravel), being co-removed with Fe and Mn. Similarly, Singhakant et al. [27] found that the primary mechanism of As removal in CW was the retention in the pores of bed materials (50–57% of total fraction), independent of the presence of plants (vetiver grasses). Complementarily, our previous works have shown high removal of Fe and As from acidic water in vertical [28] and horizontal flow wetland cells [10]. Results from this work are more promising since the acidic water was more representative of the Azufre River, and as such it had other pollutants apart from As and Fe (Table 1) which were not considered in our previous studies. Those pollutants included Pb and Zn.

3.3. Lead and Zinc Removal

Similarly to the case of As, Pb was not detected in the outflow of any cell ($\text{LD} = 0.018 \text{ mg/L}$). On the other hand, Zn removal was affected by the medium type, since limestone cells were more effective than the zeolite ones (Figure 4).

Limestone beds have been used for Zn removal from mine waters, since limestone can trigger Zn removal by precipitation of smithsonite ZnCO_3 [29]. In addition, some differences could be observed in the case of Zn between vegetated and control cells, since removal efficiencies were higher in vegetated cells for both media types (Figure 4). These results are similar to those reported by Sarafraz et al. [30], who reported that vegetated HSSF cells having zeolite as part of the media were more effective in the removal of Zn than the non-vegetated ones. They also reported that Pb was not detected in the outflow regardless of the presence of vegetation. In fact, they recommended the use of zeolite as alternative wetland media based on their results.

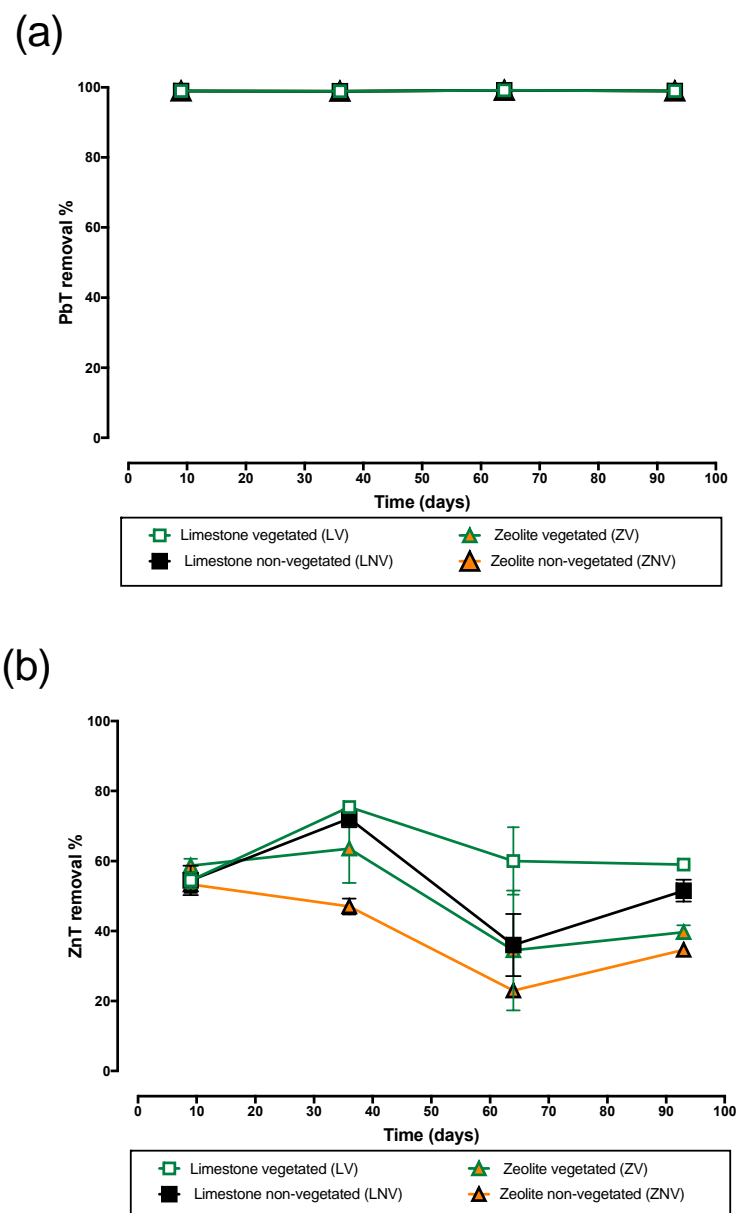


Figure 4. Lead (a) and zinc (b) removal in the zeolite and limestone cells (vegetated and non-vegetated). Data corresponds to average values, and error bars indicate minimum and maximum values for each cell type. When measurements were reported below the limit of detection, half of the corresponding value was considered as the actual concentration.

In wetlands, Pb can precipitate with sulfide, sulfate, and carbonate forming insoluble compounds, or be sorbed onto organic or inorganic substrates, such as Fe oxyhydroxides [31]. Fe oxyhydroxides can also sorb other metals including Zn, and this process is known to be important in constructed wetlands aiming for metal removal [32,33]. In addition, similar to the case of As, metals may coprecipitate when Fe precipitates as oxyhydroxides [4]. However, the elevated Zn concentrations in the inflow compared to those of Pb may be affecting Zn removal, in addition to the presence of other metals that may compete for sorption sites (Table 1). As mentioned previously, in this study the inflow water was a realistic representation of the Azufre River, thus this synthetic water had other pollutants (apart from As and Fe, Table 1) than those present in the synthetic water used in our previous studies. As such, these results are more representative of AMD treatment, and thus they provide valuable information to be considered for a potential pilot-scale application.

3.4. Water Losses and Geochemical Modeling

Water losses were similar between cells regardless of the medium type and the presence of vegetation. Average values were $19.8 \pm 7\%$, $21.8 \pm 7\%$, $22.7 \pm 9.4\%$, and $21.3 \pm 9.2\%$ for LV, LNV, ZV, and ZNV cells, respectively. Given the high effectivity of the system and thus low level of pollutants in the outflow from all cells, the concentration effect was not noticeable. Water losses in CW due to ET must be considered to evaluate removal capacity, and mitigation strategies must be assessed.

To investigate the role of chemical precipitation triggered by pH adjustment on the removal of the pollutants, we simulated the precipitation of mineral phases, also considering the pollutants concentration due to water losses. In limestone cells, saturation indexes indicated that several Fe phases (Fe_2O_3 hematite and FeOOH goethite, for example) and Pb phases ($\text{Pb}(\text{OH})_2$ and larnakite PbO , PbSO_4) may precipitate (Table S1, Supplementary Material). Similar results were obtained regarding formation of Fe phases in zeolite cells, but Pb phases were subsaturated (Table S2, Supplementary Material). In both cases, these trends were independent of the simulated temperatures (Table S3–S6, Supplementary Material). In addition, As and Zn phases were subsaturated in all cells for each simulated temperature (data not shown).

These results are consistent with the elevated Fe removal rates in all cells. However, they do not reflect As, Pb, or Zn removal. This is probably due to the fact that these simulations only considered pH adjustment and did not consider limestone dissolution, zeolite sorption capacity, As/Pb/Zn sorption onto Fe oxyhydroxides, or coprecipitation. This indicates that these processes have an important role in treatment performance. As such, further modeling efforts considering these processes should be made.

3.5. Role of Vegetation

Important differences between vegetated and non-vegetated cells could not be observed during the experimental period for As, Fe, and Pb due to the high removal efficiencies. It is well known that the role of vegetation in As removal in CW is mainly indirect [11]. One of these roles is provision of organic matter, which is often overlooked due to the short time span of most studies [4]. As such, longer experimental periods are required to observe these effects. In this study, we observed that vegetated zeolite cells presented lower pH than non-vegetated ones at the beginning of the experiment, whereas vegetated limestone cells presented lower pH than non-vegetated ones towards the end of the experiment (Figure 1). The pH of the rhizosphere is generally acidic due to various processes that include organic acids release and cation–anion exchange [34], and thus the presence of plants may affect outflow pH. This parameter is key in metal removal in wetlands since it affects metal speciation and availability, sorption capacities, and precipitation and dissolution reactions.

Another important role of vegetation is oxygen transfer through roots, which facilitates the co-existence of aerobic and anaerobic zones, and the formation of iron oxides, hydroxides, and oxyhydroxides such as the iron-plaques [4,11]. The capacity of iron plaque to adsorb metals is well known [4], and this may explain the higher Zn removal in vegetated cells for both media types. In addition, Zn plant uptake can also occur, and it has been widely documented for various wetland plants, including *P. australis* [35,36]. Similar to the case of As, metal accumulation in plant tissues plays a minor role in metals removal in CW [37]. Despite this, some researchers indicated that the presence of vegetation increased metal retention, whereas others suggested that their presence decreased it [38]. This will depend mainly on the metal type, the predominant removal mechanisms, the environmental conditions, and the operation and design parameters. As such, more research is required to elucidate the role of wetland vegetation in metal removal, especially under acidic conditions.

4. Conclusions

Horizontal subsurface flow constructed wetlands with limestone and zeolite as the main supporting media were highly effective in treating highly acidic water resembling AMD. The removal rates were $> 99\%$ for As and Pb, $> 98\%$ for Fe, and fluctuated between 23% and 75% for Zn depending

on the cell type. Limestone wetlands could be more appropriate than zeolite wetlands given the higher pH in the effluent (7.5 versus 4 approximately) and the higher Zn removal rates (60% versus 50% on average). Vegetated cells showed higher Zn removal rates than non-vegetated cells for both media types, suggesting that the presence of *P. australis* had a direct role in Zn removal.

This is the first study showing the effectiveness of HSSF CW to treat highly acidic, As-rich and metals-rich water. As such, HSSF CW may offer a sustainable option for treating these types of contaminated water. Future studies, including the quantification of As and metals accumulation in media and vegetation, the use of advanced techniques to analyze solid phases, and geochemical modeling, are required to elucidate the main removal mechanisms and guide CW design for As and metals removal.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4441/10/10/1447/s1>. Table S1: Saturation index values for relevant phases in the limestone cells for T = 20 °C, Table S2: Saturation index values for relevant phases in the zeolite cells for T = 20 °C, Table S3: Saturation index values for relevant phases in the limestone cells for T = 25 °C, Table S4: Saturation index values for relevant phases in the zeolite cells for T = 25 °C, Table S5: Saturation index values for relevant phases in the limestone cells for T = 30 °C, Table S6: Saturation index values for relevant phases in the zeolite cells for T = 30 °C.

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