Enhancing the removal of arsenic, boron and heavy metals in subsurface flow constructed wetlands using different supporting media

K. Lizama Allende, T. D. Fletcher and G. Sun

ABSTRACT

The presence of arsenic and heavy metals in drinking water sources poses a serious health risk due to chronic toxicological effects. Constructed wetlands have the potential to remove arsenic and heavy metals, but little is known about pollutant removal efficiency and reliability of wetlands for this task. This lab-scale study investigated the use of vertical subsurface flow constructed wetlands for removing arsenic, boron, copper, zinc, iron and manganese from synthetic wastewater. Gravel, limestone, zeolite and cocopeat were employed as wetland media. Conventional gravel media only showed limited capability in removing arsenic, iron, copper and zinc; and it showed virtually no capability in removing manganese and boron. In contrast, alternative wetland media: cocopeat, zeolite and limestone, demonstrated significant efficiencies — in terms of percentage removal and mass rate per m³ of wetland volume — for removing arsenic, iron, manganese, copper and zinc; their ability to remove boron, in terms of mass removal rate, was also higher than that of the gravel media. The overall results demonstrated the potential of using vertical flow wetlands to remove arsenic and metals from contaminated water, having cocopeat, zeolite or limestone as supporting media.

Key words | arsenic removal, boron removal, heavy metal removal, subsurface flow constructed wetlands, supporting media

INTRODUCTION

Arsenic is well known for its chronic toxicity, particularly when exposure occurs over prolonged periods. Arsenic pollution in natural waters has been reported in different countries, such as Bangladesh, USA, China, India and Chile. About 100 million people are currently drinking water with As concentrations up to 100 times 10 μg/L which is the World Health Organisation guideline (Mohan & Pittman 2011). In Chile, the Loa River has As and boron (B) concentrations around 1,400 and 21,000 μg/L, respectively (Romero et al. 2005). This river is a major waterway in Antofagasta Region and the main source of drinking and irrigation for several populated areas (Landrum et al. 2009). The presence of As and B in the Loa River is due to the El Tatio Geyser Field geothermal field, which forms the headwaters of the Salado River — a tributary to the Loa River — and these headwaters have As concentrations around 33,700 μg/L (Landrum et al. 2009).

In addition, metals/metalloids such as boron, iron (Fe), manganese (Mn), copper (Cu) and zinc (Zn) can also limit the use and reuse of water resources, either by natural or anthropogenic pollution. Boron contamination in the water environment is causing increasing concern (Xu & Jiang 2011).

In many cases, treatment of contaminated water is limited due to isolated location of the water streams and the elevated investment and operation costs of conventional technologies.

Constructed wetlands are known to be effective in removing several trace metals from contaminated water (Kadlec & Wallace 2000). A number of studies have been carried out to investigate their metal removal efficiency (Kleinmann & Girts 1997; Richards 1992; Sobolewski 1999; Sjöblom 2003). Most of these studies have focused on acid mine drainage treatment, primarily to remove sulfate, Fe and Mn (Wallace 2006) by surface flow wetlands. Little is known about subsurface flow wetlands, and few literature reports are available on the performance of wetlands for the removal of As and B. Furthermore, the mechanisms of As removal have not been elaborated (Singhankant et al. 2009).
The use of alternative media in constructed wetlands has been suggested by different researchers, with the aim of improving removal performance. For example, Sarafraz et al. (2003) showed that the use of zeolite in a horizontal subsurface constructed wetland enhanced Zn sorption, and proposed zeolite as an alternative to sand and gravel. Nevertheless, little research in this area has been conducted. This study investigated the performance of four different supporting media: gravel, cocopeat, zeolite and limestone in the removal of six target pollutants: As, B, Fe, Mn, Cu and Zn using vertical subsurface flow constructed wetlands.

MATERIALS AND METHODS

The wetland system

The lab-scale wetlands consisted of twelve subsurface vertical flow wetland columns that were built using stormwater PVC pipes. Each column had 1 m height and 100 mm internal diameter and was installed in a greenhouse. The wetland columns were divided into four groups, namely group G – employing gravel as main substrate, Z – zeolite as main substrate, C – cocopeat as main substrate, and L – crushed limestone as main substrate; each group had three replicate columns. Each column had a drainage layer of 20–40 mm cream pebbles at the base which was 0.1 m deep. The drainage layer was topped with a layer of main substrates (G, Z, C or L) that was 0.7 m deep. In each wetland column, common reed (Phragmites australis) was planted. The Phragmites were given two months to adapt to their new growth environment prior to the experiment.

Operation of the wetland system

Synthetic wastewater was prepared to simulate the concentration of the target pollutants in polluted surface waters in Chile. The synthetic wastewater was prepared using tap water, with the following reagents added per litre of water: 1 mL 1,000 mg/L arsenic standard solution (As$_2$O$_5$ in H$_2$O), 0.025 mL 10,000 mg/L boron standard solution (H$_3$BO$_3$ in H$_2$O), 125 mg FeSO$_4$·7H$_2$O, 7.2 mg MnCl$_2$·4H$_2$O, 3.9 mg CuSO$_4$·7H$_2$O, 4.4 mg ZnSO$_4$·7H$_2$O, and 0.7 mg Na$_2$S$_2$O$_3$·5H$_2$O. The total concentration of the metals were (average ± standard deviation): 0.89 ± 0.05 mg/L As, 24.0 ± 0.0 mg/L B, 1.43 ± 0.40 mg/L Cu, 21.0 ± 1.4 mg/L Fe, 2.38 ± 0.82 mg/L Mn and 1.25 ± 0.44 mg/L Zn. An agitated feed tank stored the wastewater during the experiment. From it, 2 L of synthetic wastewater were taken and dosed manually in each wetland, three times per week in the first month and twice per week in the second month.

Sampling and analysis

After each dosing, two types of water samples from each wetland column and from the feed tank were collected and acidified with nitric acid (HNO$_3$) to pH <2 for total and dissolved metals analysis. For the latter, the samples were filtered through 0.45 μm cellulose acetate filters. Weekly composite samples were prepared adding an equal volume of each corresponding daily sample for every week. Metal concentrations in these composite samples for weeks 1, 3, 5 and 7 were determined by ICP-MS in a NATA accredited laboratory (4 values per column plus the inflow). In-situ parameters were also monitored after each dosing (20 values per column plus the inflow). Dissolved oxygen (DO) was measured using 51,970 probe, whilst for pH and conductivity 51,910 and 51,975 probes were used, respectively. All these probes were connected to a Sension 378 meter. An ORP Testr10 probe was used to measure redox potential (Eh). Sulfate (SO$_4$) was measured using DR5000 UV/VIS spectrophotometer based on an adapted standard method (APHA/AWWA/WEF 2005). Alkalinity was quantified using a HACH alkalinity test kit, low range and high range tests.

RESULTS

Overall performance

Table 1 presents the average performance of the system during the operation period, for each group of wetland columns. As shown in Table 1, the concentration of all the target pollutants in the outflow from the gravel wetland columns was higher than that from other columns, demonstrating that the three types of alternative wetland substrate had greater removal pollutant removal efficiencies than the traditional gravel substrate. Furthermore, gravel appeared to have limited capability to remove As, Fe, Cu and Zn; and almost null capability to remove B and Mn.

The changes in the monitored parameters are presented in Table 2.

The removal of As and Fe

Cocopeat, zeolite and limestone wetlands presented high As removal rates (average above 98%) for the entire
experimental period, whereas for gravel wetlands the rates decreased over time, both as percentage and as daily mass removed per volume. In addition, the removal of As in terms of mass was almost the same for the alternative wetland media, and it only decreased when the inflow concentration decreased (Figure 1(a)). The removal of Fe presented a very similar trend: cocopeat, zeolite and limestone wetlands removal was around 99%, but gravel wetlands removal decreased with time (Figure 1(b)). Boron was removed by cocopeat, zeolite, limestone and gravel wetlands at the beginning of the experiment, but then it was leached out by cocopeat and gravel wetlands (Figure 2(a)). In addition, gravel wetlands barely removed Mn. As shown in Figure 2(b); cocopeat, zeolite and limestone wetlands removed around 94% total Mn on average, whereas gravel wetlands even presented negative removal.

The removal of Cu and Zn

High removal rates were observed in cocopeat, zeolite and limestone wetlands for these metals, regardless of fluctuations in inflow concentration (Figure 3(a) and 3(b)). In contrast, decreasing removal rates over time were observed in gravel wetlands, despite the fact that the daily mass removal rate increased when the inflow concentration increased.

### Table 1 | Mean inflow and outflow concentrations of the target pollutants

<table>
<thead>
<tr>
<th>Mean inflow concentration (mg/L) [CV]</th>
<th>Mean outflow concentration (mg/L) [CV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dissolved</td>
<td>Total</td>
</tr>
<tr>
<td>As</td>
<td>0.001 [0.952]</td>
</tr>
<tr>
<td>B</td>
<td>23.5 [0.04]</td>
</tr>
<tr>
<td>Cu</td>
<td>0.047 [0.699]</td>
</tr>
<tr>
<td>Fe</td>
<td>UD</td>
</tr>
<tr>
<td>Mn</td>
<td>2.275 [0.33]</td>
</tr>
<tr>
<td>Zn</td>
<td>0.723 [0.473]</td>
</tr>
</tbody>
</table>

CV – coefficient of variation = $\sigma/\mu$, UD: undetectable, where $\sigma$ is the average of $(H^+)$ and $\mu$ is the standard deviation of $(H^+)$. For samples under the detection limit (0.001 mg/L for As and 0.02 mg/L for Fe), half of that value was considered for the calculations.

### Table 2 | Mean inflow and outflow levels of monitored water quality parameters

<table>
<thead>
<tr>
<th>Parameter value in the inflow [CV*]</th>
<th>Mean value in the outflow (CV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unit</td>
<td>Inflow value</td>
</tr>
<tr>
<td>SO4</td>
<td>mg/L</td>
</tr>
<tr>
<td>pH</td>
<td>–</td>
</tr>
<tr>
<td>DO</td>
<td>mg/L</td>
</tr>
<tr>
<td>T</td>
<td>ºC</td>
</tr>
<tr>
<td>Alkalinity</td>
<td>mg/L CaCO3</td>
</tr>
<tr>
<td>Eh</td>
<td>mV</td>
</tr>
<tr>
<td>Conductivity</td>
<td>μS/cm</td>
</tr>
</tbody>
</table>

For the pH values, the CV was calculated using $\text{CV} = \frac{\log(\sigma) - \log(\mu)}{\log(\mu)}$, where $\sigma$ is the average of $(H^+)$ and $\mu$ is the standard deviation of $(H^+)$. For samples under the detection limit (0.001 mg/L for As and 0.02 mg/L for Fe), half of that value was considered for the calculations.
DISCUSSION

The difference in the removal rates suggests that the removal of the target pollutants in vertical flow wetlands was primarily affected by the type of substrate. Gravel presented limited removal of As, whereas all the alternative media exhibited excess capability to remove As (average removal percentage over 98%). This supports Singhankant et al.’s (2009) study, who reported that the efficiency of As removal decreased over time in their sand/gravel constructed wetlands. This limitation was also observed in the performance of the gravel wetlands to remove the other five target pollutants. Furthermore, the use of sand/gravel media in subsurface flow wetlands is not recommended for the removal of metals due to limited sorption capacity and inability to form new storage sediments without clogging the wetland matrix (Kadlec & Wallace 2009). As such, the results suggest that gravel is unsuited to be employed as wetland media for the removal of As – and metals-rich wastewater. On the other hand, the lack of similar studies prevents comparison of the performance of cocopeat, zeolite and limestone as alternative media. However, these materials have been
employed to some extent to remove various of the target pollutants. The exception is cocopeat (chosen as an alternative to peat) which apparently has not been studied for metals removal.

The removal of heavy metals can be achieved via different processes depending on whether they are dissolved or particulated. The principle process that removes heavy metals in natural and constructed wetlands is sedimentation; however, other processes such as precipitation must occur first since sedimentation only removes particulated metals (Sheoran & Sheoran 2006). Looking at the speciation of As, Fe and Cu in the inflow, the three of them were mostly particulated (Table 1). Therefore, physical processes such as filtration and sedimentation would be enough to remove them. According to Table 1, As and Fe in the outflow from gravel wetlands were also mainly particulated. Moreover, given the correlation between total As and Fe outflow concentration ($R^2 = 0.98$) and As and Fe removal rate ($R^2 = 0.97$), it can be asserted that Fe oxides trapped As by coprecipitation/sorption. Similar findings were reported by Buddhawong et al. (2005), who concluded that As binding with the Fe content of the gravel media was responsible for As removal. The sorption of metals on oxides is widely known (Stumm & Morgan 1996). Different authors attribute this property as an important source of metal removal in constructed wetlands if Fe/Mn oxides are present (Sjöblom 2003). Arsenate sorption onto most metals (hydr)oxides (Inskeep et al. 2002), but specially onto Fe and Mn oxyhydroxides has been reported by a number of researchers (Kneebone et al. 2002; Pastén et al. 2006). Thus, Fe oxides containing As were filtered in gravel wetlands, but given the medium gravel size (7 mm), filtration capability was limited.

In contrast, the total concentration of Cu was always lower in the outflow from gravel wetlands than in the inflow, but the dissolved concentration was on average higher in the outflow than in the inflow (Table 1). In addition, Zn was mainly particulated in the outflow from gravel wetlands, whereas it was mostly dissolved in the inflow (Table 1). However, the dissolved concentration of Zn was lower in the outflow than in the inflow. Therefore, gravel wetlands filtered total As, Fe, Cu and Zn; released dissolved Cu, and removed dissolved Zn, but due to their limited removal capacity the total concentration of Zn increased consistently in the outflow. Both Cu and Zn can be removed by Fe oxides (Kröpfelová et al. 2009), but because conflicting information exists regarding competitive sorption of Cu and Zn on Fe oxides (Violante et al. 2005; Covelo et al. 2007), their effect on Cu and Zn removal is not clear. In cocopeat, zeolite and limestone wetlands, dissolved Cu and Zn were removed; whereas dissolved As and Fe were not (Table 1). This shows that these wetlands were able not only to retain particulated metals, but also to remove/release dissolved metals. Different authors have proposed that the main mechanism for mobilisation of As sorbed on Fe oxides is reductive dissolution (Mukherjee et al. 2009). Since mostly aerobic conditions were found (Table 2), further experimental evidence is required to understand the As and Fe retention/mobilisation mechanisms.

Boron was mostly dissolved in the inflow (98%) and the outflow from gravel (97%), cocopeat, zeolite and limestone wetlands (99%), whereas Mn was mostly dissolved in the inflow (99%) and the outflow from gravel (99%), cocopeat (97%) and limestone wetlands (91%); but not in the outflow from zeolite wetlands (43%) (Table 1). This may indicate that the main B removal process is sorption, mainly when it is present as borate $\text{B(OH)}_4$. In addition, the presence of organic matter contributes to the adsorption of B in soils (Sartaj & Fernandes 2005). The good performance of cocopeat wetlands only at the beginning of the experimental period can be explained by a limited sorption capacity of this substrate, as reported by Sartaj et al. (1999) for a peat filter. In addition, the adsorption of boron on soils depends on the pH of the solution (Kot 2009); so the lower the pH, the lower the adsorption. Low pH could explain the low removal rates in gravel wetlands, whilst high pH could explain the highest removal rates in zeolite and limestone wetlands (Table 2).

The speciation of metals is the main factor that determines their bioavailability. Dissolved metals represent the most bioavailable form, especially when the metal is present as ionic or weakly complexed species (Cooper et al. 1996). Most metal removal studies only report total concentrations, however the dissolved fraction should be reported since some guidelines (such as US EPA National Water Quality Criteria (US EPA 2009)) do consider it. Dissolved As(V), as a highly reactive metalloid, may have different routes, As(III) being the most toxic species. Due to the complexity of the wetland environment and the reactivity of the pollutants with media, vegetation and microorganisms, different solid and soluble species can be found in the wetland system. They may be modelled using an aqueous geochemical program, and identified in the solid phase using advanced techniques such as X-ray diffraction. Future stages of this investigation will consider the use of these tools to provide knowledge in the performance of constructed wetlands.
Further research is currently being undertaken to remove As efficiently in subsurface constructed wetlands, particularly aiming to understand the removal mechanisms. Apparently, plant uptake plays a minor role in As removal (García et al. 2010). Future work will investigate the role of vegetation and microorganisms in the removal of the target pollutants.

CONCLUSIONS

This experimental study showed that cocopeat, zeolite and limestone can be used as the main media in vertical flow wetlands, to enhance the removal of As, B, Fe, Mn, Cu and Zn. In addition to providing filtration capability to remove particulated pollutants, these alternative substrates were able to provide different factors, such as organic matter (cocopeat), ion exchange sites (zeolite) and alkalinity (crushed limestone), which all contributed to the removal of the target pollutants of this study. In comparison, gravel wetlands only showed limited ability to remove As, Fe, Cu and Zn, and virtually no capability to remove B and Mn.

ACKNOWLEDGEMENTS

The authors would like to thank the Chilean Government (Becas Chile) for sponsoring Katherine Lizama A.’s Ph.D. studies. Trevor Tovey from Unimin Australia Limited is thanked for providing limestone.

REFERENCES


Cooper, P. F., Job, G. D., Green, M. B. & Shutes, R. B. E. 1996 Reed Beds and Constructed Wetlands for Wastewater Treatment. WRc Publications, Medmenham, Marlow, UK.


Kadlec, R. H. & Wallace, S. D. 2009 Treatment Wetlands. CRC, Boca Raton, FL, USA.


Richards, Moorhead, and Laing Ltd. 1992 Constructed Wetlands to Ameliorate Metal-rich Mine Waters. National Rivers Authority, R&D Note 102, Bristol, UK.


Sartaj, M., Fernandes, L. & Castonguay, N. 1999 Treatment of leachate from a landfill receiving industrial, commercial, institutional, and construction/demolition wastes in an engineered wetland. In: Constructed Wetlands for the


