The effect of substrate media on the removal of arsenic, boron and iron from an acidic wastewater in planted column reactors

K. Lizama Allende [a,*], T.D. Fletcher [a,b], G. Sun [c]

[a] Department of Civil Engineering, Building 60, Monash University, VIC 3800, Australia
[b] Melbourne School of Land and Environment, The University of Melbourne, VIC 3010, Australia
[c] School of Engineering and Physical Sciences, James Cook University, QLD 4811, Australia

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ABSTRACT

Acidic wastewaters, such as occur in acid mine drainage, typically contain heavy metals and metalloids that pose a serious threat to receiving waters, due to their high toxicity. In this study, vertical flow wetland columns, using a range of filter media, were investigated for their potential to provide an effective onsite treatment for acidic wastewaters with a pH value of 2.0 ± 0.1. The effectiveness of four types of wetland media: gravel, cocopeat, zeolite and limestone, was studied for the removal of arsenic, boron and iron, under an average hydraulic loading of $0.073\,m^3/m^2\,d$. On average, limestone wetland columns gave the highest removal percentage for arsenic (99%) and iron (98%), followed by zeolite columns (92% removal for arsenic and 86% for iron). Although gravel columns were able to remove 43% of dissolved arsenic (from average input of 3.0 ± 0.1 mg/L), they were not able to remove iron simultaneously. In contrast, wetland columns with cocopeat media only showed modest capacity for arsenic removal (9%), but greater capacity for removing iron (46%), and cocopeat was the only wetland media that demonstrated potential to remove boron. Overall, the results indicated that the most effective mechanism of arsenic removal in vertical flow wetlands is coprecipitation with iron, which can be enhanced by using alkaline wetland media to increase the pH of the wastewater. Combinations of media appear worthy of examination in order to optimise the efficacy and sustainability of heavy metal removal.

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1. Introduction

Acidic wastewaters, or runoff from natural arsenic-rich soil, often contain arsenic (As), boron (B) and metals that pose a serious pollution threat to waterways. Unfortunately, conventional treatment technologies for As removal such as adsorption, coagulation and membrane filtration have limitations [1], particularly related to costs, sludge generation and transportation [2,3]. Water contamination by boron poses similar problems; the presence of B in aquatic environment is causing increasing concern [4], in particular because its removal is not commonly achievable by conventional chemical treatment. Again, such conventional treatments are generally costly [5] and produce secondary waste (sludge).

During the past two decades constructed wetlands have been increasingly used, especially in rural regions, to treat domestic and agricultural effluents [6]. The growth of this technology is at least partly spurred by the rising cost of fossil fuel energies and concern about climate change, with wetlands offering a sustainable low-energy input alternative. Wetland technology has considerable potential, as it is considered efficient and cost-effective for the treatment of metal-containing waters, including those associated with mining activities [7]. While wetlands require large areas of space, their low energy use and typically low maintenance requirements make them a potentially ideal option for treating acidic wastewaters on remote sites.

To date, the ability of constructed wetlands to remove metals and metalloids from wastewaters has been generally recognised, but not sufficiently studied [8], especially concerning the removal of arsenic [9] and boron [10]. Current knowledge about metal removal in wetlands has been obtained primarily from studies on the treatment of acid mine drainage, which usually contains sulfate, iron (Fe) and manganese (Mn) as its main pollutants [11]. Most studies to date have been conducted on surface flow wetlands, with much fewer studies conducted in subsurface flow wetlands, where the contaminated waters pass through packed media, instead of flowing above it, thus allowing more extensive contact between the contaminants and media. It may thus be hypothesised that subsurface flow wetlands could offer greater and more reliable treatment performance than surface flow wetlands, as found by Buddhawong

* Corresponding author. Tel.: +61 3 9905 5332; fax: +61 3 9905 4944.
E-mail addresses: katherine.lizama@monash.edu (K. Lizama Allende),
tim.fletcher@unimelb.edu.au (T.D. Fletcher), guangzhi.sun@jcu.edu.au (G. Sun).

et al. [12]. However, subsurface flow wetlands may need regular maintenance or even reconstruction should the media bed become saturated with metals [13].

Despite the potential advantages of subsurface flow wetlands, the lack of information about their performance hinders their ready adoption. Firstly, experiments are needed to demonstrate which wetland medium, or combination of different media, are most suited to remove these pollutants. Although various media have been suggested for such purposes [14,15], experiments are rarely carried out to verify hypothesised suitability. In a preliminary lab-scale study, cocopeat, zeolite and limestone were found to have the ability to remove As, Fe and B [16] under neutral or slightly acidic environment; however, their ability to remove these pollutants under highly acidic condition, which is usually associated with contaminated waters on mining sites, was not studied.

Secondly, experiments are required to monitor the removal of As and other pollutants, under a range of loading rates and influent concentrations, to produce data that are relevant to the treatment of specific types of wastewaters. Such information could be used to tailor the design of such wetlands to the wastewater type. Although acidic conditions are generally associated with As and metals, the concentrations of the pollutants can vary significantly, depending on site conditions. Williams [17] presented hydrochemical data for As in 34 mining sites in 7 countries of South-east Asia, Africa and Latin America, and showed that the concentrations of As fluctuated between 0.005 and 72 mg/L, whereas the pH value ranged from 0.52 to 10.0. Acidic conditions primarily result from mining, hydrothermal and volcanic activities, or sulfide oxidation [18], although groundwater movement and surface runoff can also cause low pH and high As values in waters at, or close to mining sites. For example, the Azufre River in northern Chile (Lluta River Basin) has a pH value of around 1.8, and As, B and Fe concentrations of around 3, 30 and 100 mg/L, respectively [19]. Such water quality makes the river unsuitable for human use. As such, it is necessary to run experiments designed to rigorously test the performance of wetland systems for specific pollutant types and concentrations.

Thirdly, there is a need for studies which identify and quantify the environmental factors affecting As, B and metal removal in subsurface flow wetlands, as well as the links between the removal of different pollutants that result from chemical precipitation and co-precipitation. Two key factors that affect the removal of As in wetlands are: (1) pH and (2) the presence of Fe and S [9]. A previous study [16] provided some insights into the effect of pH and Fe in the removal of As. However, the study was incomplete. For example, the study did not quantify the removal of As under highly acidic conditions (e.g. pH < 2), which is likely to be the typical environment for mine drainage and many existing polluted rivers, such as the Azufre River in Chile [20]. Regarding the second factor, iron hydrochemistry controls As aqueous mobility in acid ferruginous mine waters when pH is below 4 [17]; the interaction between Fe and As in wetland environment can have a significant effect on the removal of both pollutants. This is a phenomenon that needs to be further studied because Fe and As are so commonly found together and optimising the treatment of one will typically require consideration of the other.

The aim of this study is therefore to investigate the use of vertical flow constructed wetlands to remove three target pollutants, As, Fe and B, from a synthetic acidic wastewater that simulates highly polluted river water (for example a river polluted by acid mine drainage). The efficiencies of four wetland media are studied: cocopeat, zeolite, limestone, and river gravel, with the aim of evaluating the pollutant removal efficiency of the different wetland media. A range of environmental factors, such as temperature, pH, Eh and $SO_4{}^{-2}$ levels, are monitored alongside the removal rates of the target pollutants, in order to explain the factors which must be taken into account when optimising subsurface wetlands for heavy metal removal in acidic waters. This study is part of a broader study that will, in future phases, consider aspects such as the influence of vegetation type on pollutant removal.

2. Materials and methods

2.1. The acidic wastewater

To simulate realistic, acidic polluted water, a case-study source water was chosen: the Azufre River, Northern Chile. This river begins at the foot of the Tacora volcano, on the upper part of the Lluta River catchment (150 km from Arica, the main city of the Arica and Parinacota Region). Due to its high concentrations of As and metals and its isolated location, the Azufre River represents a typical drainage from mining sites [20]. Representative synthetic wastewater was prepared using deionised water with the following reagents added per litre of water: 3 mL 1000 mg/L arsenic standard solution (arsenic acid As_2O_5 in H_2O), 3 mL 10,000 mg/L boron standard solution (boric acid H_3BO_3 in H_2O), 0.5 g $FeSO_4 \cdot 7H_2O$, and 0.425 mL H_2SO_4 (95–97% Merck ISO grade). As a result, the concentrations of the target pollutants in the synthetic feed were (average ± standard deviation): 3.08 ± 0.25 mg/L As, 32 ± 2.19 mg/L B, and 107.33 ± 6.53 mg/L Fe. The resulting pH value was 2.0 ± 0.1. Under this acidic condition, the metals were mostly dissolved, consistent with how they would be naturally found in the Azufre River.

2.2. The wetland system

Twenty subsurface vertical flow wetland columns were built using PVC pipes. Each column was 1 m tall and 100 mm in internal diameter, as illustrated in Fig. 1.

The wetland columns, placed in a greenhouse, were divided into four groups, each group employing gravel, cocopeat, zeolite and crushed limestone as the main substrate. Each group had five identical replicate columns that were operated as individual treatment units. The packed porosities of the media are 40%, 55%, 25% and 30% in gravel, cocopeat, zeolite, and crushed limestone columns, respectively. Each column had a 0.1 m deep drainage layer of 20–40 mm gravel at its base. The drainage layer was overlain with a single 0.7 m deep layer of the main substrate (gravel, cocopeat, zeolite or limestone), resulting in a total depth of 0.8 m (the main layer plus the drainage layer) (Fig. 1). In each column, a single plant of common reed (*Phragmites australis*) from the root-cuts of mature plants in a Melbourne wetland was planted. *Phragmites* was chosen primarily because of its documented tolerance to acidity (surviving well within pH range 2–8) [21]. Many other plants commonly used in wetlands have a narrow pH tolerance range, for example: pH range 4–10 for *Typha*, pH 5–7.5 for *Juncus*, and pH 4–9 for *Scirpus*. *Phragmites* is also widely used in constructed wetlands in the UK [22] and Europe, where subsurface flow wetlands are dominant, making it an ideal candidate as the 'standard' plant for use in the wetland media substrate. The *Phragmites* were given two months of establishment period to adapt to their new growth environment prior to commencement of the experiment.

During the experiments, the synthetic wastewater was stored in a 230 L continuously stirred feed tank. From the tank, two litres of synthetic wastewater were collected and dosed manually onto the top of each wetland column. The wastewater was freshly prepared each week before the first dosing, and it was kept to the next dosing day on the same week. The water passed by gravity through the wetland media during the dosing, as the outlet was non-restricted. Effluent from each column was collected underneath in an effluent collection tank. The manual dosing was carried out twice per week, giving a hydraulic loading rate of 4 L per week ($0.073 \, m^3/m^2 d$)
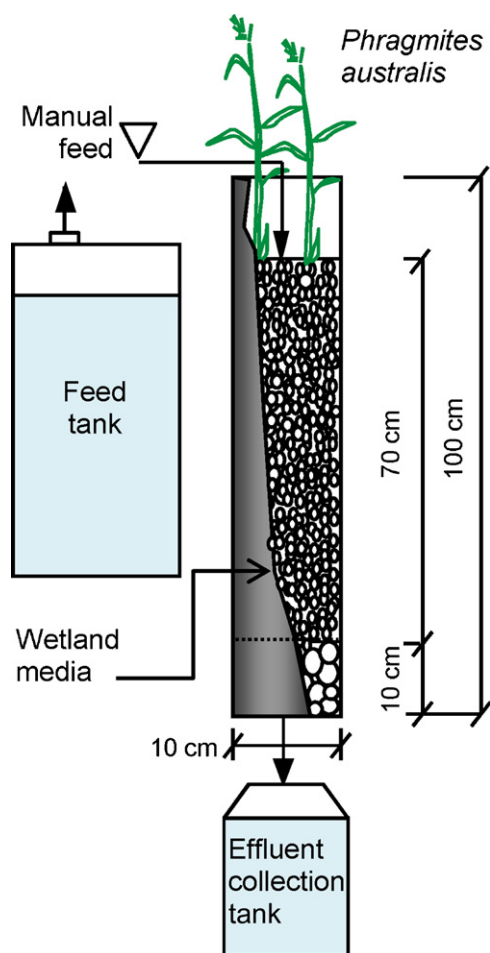
Fig. 1. A schematic diagram of the wetland column.

applied to each column. The dosing started in August 2010 and lasted for thirteen weeks.

2.3. Sampling and analysis

Water samples were collected from the inlet (feed tank) and outlet (effluent collection tank) of each column in week 1, 4, 7, 9, 11 and 13. Separate samples were taken for total and dissolved metal analysis, with analysis undertaken according to Standard Methods [23]. For the measurement of dissolved pollutants, the samples were filtered (through 0.45 μm cellulose acetate papers) and acidified (with nitric acid) immediately after sampling. The analyses of As, B and Fe concentrations were carried out for both unfiltered and filtered samples, to give total and dissolved values. The analyses of other parameters were only carried out for the unfiltered samples.

The concentrations of As, B and Fe were determined in a NATA (National Association of Testing Authorities, Australia, http://www.nata.asn.au/) accredited laboratory (with QC procedures based on Standard Methods [23]) by ICP-OES (and ICP-MS if the parameter analysed was below the OES detection limit). ICP-OES detection limits were 0.1 mg/L for As, 0.05 mg/L for B and 0.05 mg/L for Fe, whereas ICP-MS detection limits were 0.001 mg/L for As, 0.02 mg/L for B and 0.02 mg/L for Fe. In situ parameters were measured at Monash University. Dissolved oxygen (DO), pH and conductivity values were measured using three probes that were connected to a Sension 378 m. The probes were calibrated before measurement. An ORP Testr10 probe was used to measure redox potential (Eh). Sulfate (SO_4^{-2}) was measured using DR5000 UV/VIS spectrophotometer, based on Standard Methods [23]; total

suspended solids (TSS) were measured using the same equipment, based on a photometric method for sewage and industrial wastes [24].

The mineralogical composition of gravel, zeolite and limestone was analysed by X-ray diffraction (XRD). A Scintag diffractometer with a Cu K_α radiation source was used and the scans were performed continuously from $0°$ to $70°$ with a scan step size of $0.02°$.

2.4. Calculation and statistical analysis

2.4.1. Pollutant mass removal rates

For each target pollutant, its mean mass removal rate (in mg/m³d, where m³ represents the superficial volume of a column) and removal percentage (%) in each wetland group (gravel, cocopeat, zeolite and limestone) were calculated. The mass removal rate M_R was calculated as:

$$M_R = \frac{(Ct_{in} - Ct_{out}) \times Q}{V_{wetland}} \tag{1}$$

where Ct_{in} (mg/L) corresponds to the total concentration of As, B or Fe in the inflow; Ct_{out} is total concentration in the outflow; Q (L/d) is daily flow rate; and $V_{wetland}$ (m³) is the superficial volume of a single wetland column.

2.4.2. The effect of wetland media

To analyse the performance of the different wetland media, statistical tests were performed using PASW Statistics 18 and a significance level of $\alpha = 0.05$. Prior to this testing, Kolmogorov–Smirnov test was performed to check data normality. When data were not normal, they were log-transformed; in this case, p values are indicated as $p_{log-transformed}$.

The influence of different wetland media on the wastewater treatment results was statistically assessed by one way ANOVA to compare the mean concentrations of target pollutants in gravel, cocopeat, zeolite and limestone wetland columns, as well as the environmental parameters in the columns. When significant difference caused by the media was found ($p^A < 0.05$), multiple comparison post hoc tests were performed to distinguish which wetland media were significantly different: Tukey's test was applied when the assumption of homogeneity of variances was satisfied (as determined by Levene's test), or Games–Howell's test when this assumption was not satisfied (notation p^T and p^{GW}, respectively).

If the assumption of normality was not achieved, Kruskal–Wallis analysis was performed instead of ANOVA. When significant difference was found ($p^{KW} < 0.05$), Mann–Whitney post hoc test were performed to distinguish the mean differences which were significantly different ($p^{MW} < 0.05$).

2.4.3. Correlation between the removals of different pollutants

Because As can coprecipitate with Fe, and Fe precipitation is affected by pH, Spearman correlation factor ρ was calculated for each wetland group, to discover whether any significant relation can be found between: (1) the outflow concentrations of As and Fe (dissolved and total) and (2) the outflow concentrations of Fe (dissolved and total) and pH. Spearman ρ was used instead of Pearson's correlation due to the non-normal distribution of the data.

3. Results

3.1. Overall performance of the wetland system

Table 1 presents the mean influent and effluent concentration of As, B and Fe in each group of wetland columns during the experiments (five replicates multiplied by six data sets, giving thirty
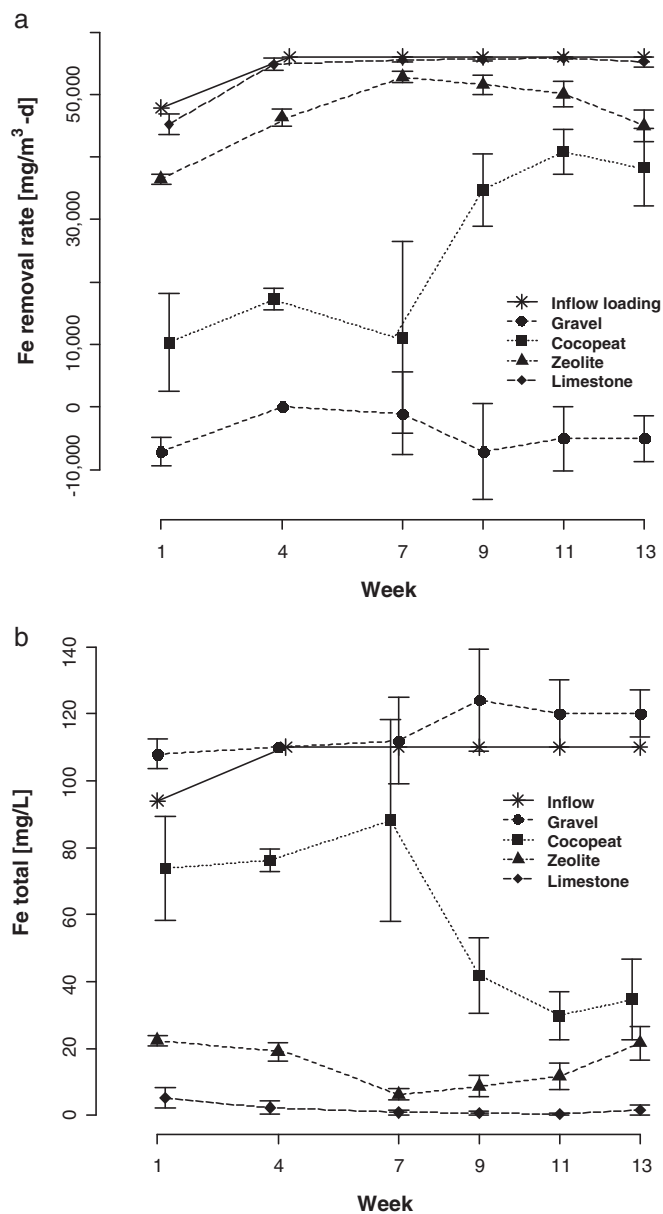
Table 1
Mean inflow and outflow concentrations – total and dissolved – of the target pollutants.

| | Mean inflow concentration (mg/L) [CV] | | Mean outflow concentration (mg/L) [CV] | | | | | | | |
| | | | G – gravel | | C – cocopeat | | Z – zeolite | | L – limestone | |
Pollutants	Dissolved	Total	Dissolved	Total	Dissolved	Total	Dissolved	Total	Dissolved	Total
As	3.0 [0.10]	3.1 [0.08]	1.7 [0.18]	1.7 [0.18]	2.7 [0.13]	2.8 [0.13]	0.250 [1.42]	0.258 [1.44]	0.010 [1.79]	0.021 [0.67]
B	32 [0.08]	32 [0.07]	31 [0.08]	31 [0.07]	29 [0.07]	30 [0.07]	31 [0.10]	31 [0.10]	31 [0.09]	31 [0.09]
Fe	105 [0.07]	107 [0.06]	113 [0.07]	116 [0.06]	56 [0.08]	57 [0.09]	14.8 [0.47]	15.0 [0.47]	0.11 [0.48]	1.85 [0.47]

CV, coefficient of variation = σ/μ.

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

| Parameter (unit) | Mean inflow value [CV] | Mean outflow value [CV] | | | |
	Value	Gravel	Cocopeat	Zeolite	Limestone
pH	2.0 [1.19]	2.0 [1.17]	1.8 [1.01]	2.6 [1.04]	6.7 [1.00]
DO (mg/L)	9.93 [0.19]	10.06 [0.21]	8.94 [0.23]	10.98 [0.60]	9.37 [0.18]
T (°C)	19.4 [0.22]	18.8 [0.24]	18.8 [0.21]	19.0 [0.21]	19.0 [0.19]
Eh (Mv)	453 [0.04]	502 [0.03]	501 [0.11]	498 [0.08]	198 [0.28]
TSS (mg/L)	5 [2.06]	26 [1.54]	8 [1.32]	1 [1.99]	26 [1.77]
Electrical conductivity (mS/cm)	4.98 [0.09]	4.37 [0.13]	7.04 [0.63]	2.10 [0.35]	2.40 [0.04]
SO$_4$ (mg/L)	907.23 [0.51]	938.59 [0.73]	953.66 [2.08]	1022.14 [2.12]	1142.72 [0.55]

For the pH values, CV was calculated using $-\log[\sigma]/-\log[\mu]$, where μ is the average of {H$^+$} and σ is the standard deviation of {H$^+$}.

values to obtain each mean value). In all wetland columns, and for the three target pollutants, the mean outflow concentrations were mostly lower than inflow concentrations (with the exception of Fe within the gravel wetlands), demonstrating that each wetland substrate type was capable of removing heavy metals from the acidic water. Pollutants were mainly in dissolved form in most effluents, with the exception of As and Fe in the effluents from the limestone wetland columns. Table 2 presents mean values of the environmental parameters being monitored, calculated similarly as the values in Table 1 (five replicates multiplied by six data sets, allowing thirty values to obtain each mean value). Table 2 shows that these values were affected differently by the types of media; while the DO values were only modestly affected, the pH was significantly affected by the media.

3.2. Removal of As

As shown in Table 1, limestone wetlands gave the lowest As outflow concentrations (dissolved and total) and thereby the highest removal efficiency. The efficiency of As removal was lower in zeolite and gravel columns. Wetland columns with cocopeat media were the least efficient for As removal. Fig. 2 gives the profile of As concentrations and removal rate over time. It can be observed that the As mass removal M_R in limestone wetlands followed the trend of the As loading throughout the experiment, whereas in zeolite wetlands the removal began to follow the trend of the As loading during the later part of the experiment. Gravel and cocopeat wetlands did not present a particular trend in removal over time. Both dissolved and total As concentration were significantly lower in the outflow than the inflow ($p^{KW} < 0.001$), confirming the

effectiveness of the wetland system as shown in Fig. 2. Furthermore, both dissolved and total As outflow concentration from each wetland substrate were significantly different to those in the inflow, and to each other (p^{MW} values shown in Table 3), indicating that each wetland substrate varied in its ability to remove As, with limestone the most effective, followed by zeolite, gravel and finally cocopeat.

3.3. Removal of Fe

Similarly to As removal, limestone wetlands gave the consistently lowest outflow concentration of total Fe. Zeolite and cocopeat wetlands, while achieving considerably lower removal than limestone, were far more effective than the gravel substrate, which generally resulted in a release of Fe (Fig. 3). The efficiency of Fe removal in cocopeat wetlands was found to improve with time, a trend that was similar to the removal of As in zeolite-based wetlands (Fig. 2). The type of substrate significantly affected the outflow concentration of dissolved and total Fe ($p^{KW} < 0.001$), with gravel being the only substrate to produce effluent concentrations which did not vary significantly from the influent concentrations (Table 4).

3.4. Removal of B

Boron removal rates appeared to be higher in all columns at the beginning of the experimental period, as indicated in Fig. 4. However, after 4 weeks of dosing, virtually no B was removed from the wastewater in gravel, limestone and zeolite columns. Cocopeat was thus the most effective substrate for boron removal. The type of substrate did affect the outflow concentration of dissolved and total

Table 3
Comparison of dissolved and total As concentration in the inflow of the wetland system and the outflow of each wetland group using Mann–Whitney post hoc tests. Bold type denotes significant difference.

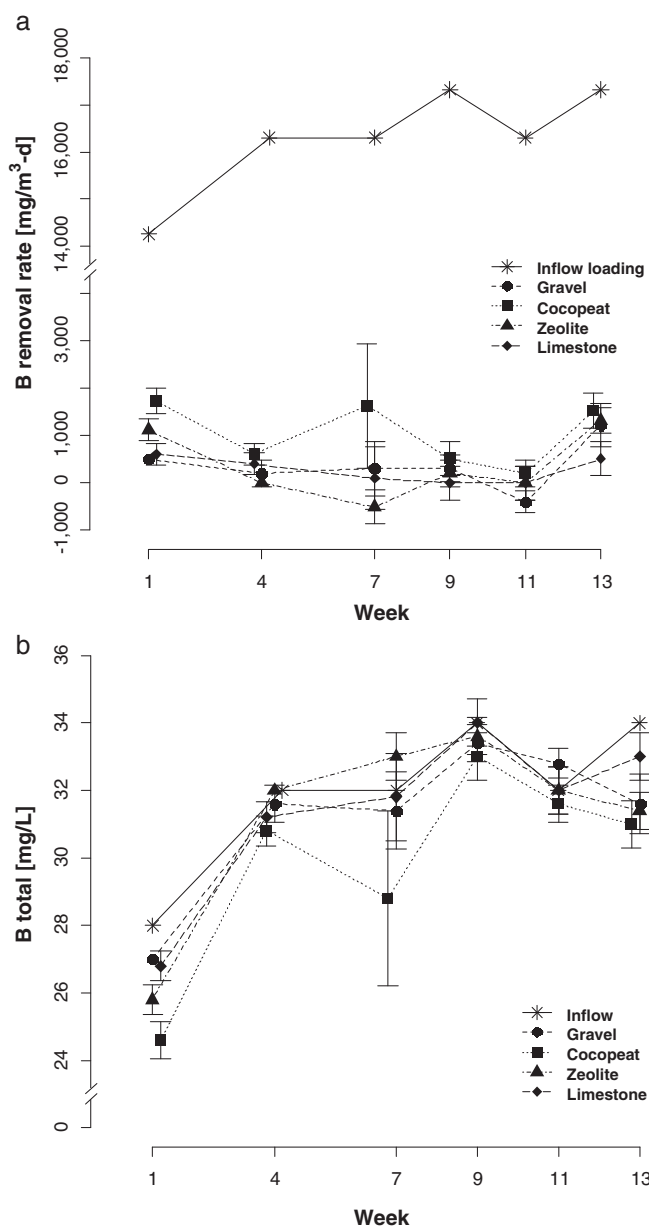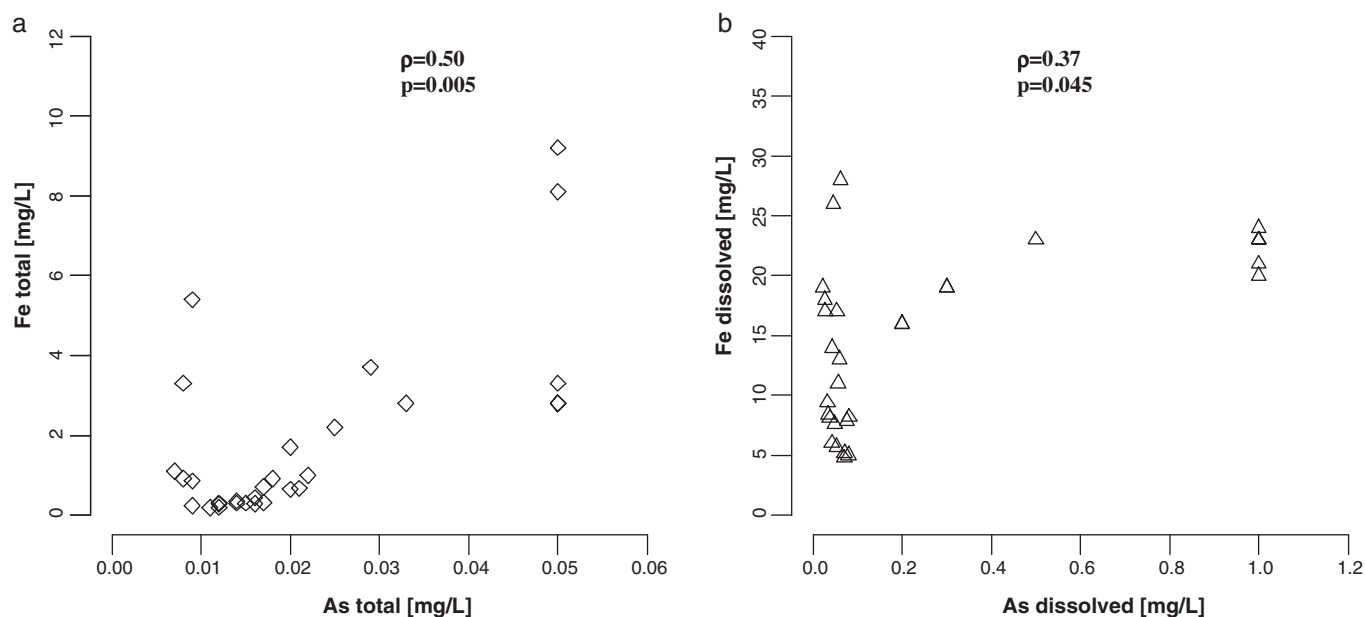| | Inflow | | Gravel | | Cocopeat | | Zeolite | |
	As dissolved (mg/L)	As total (mg/L)	As dissolved (mg/L)	As total (mg/L)	As dissolved (mg/L)	As total (mg/L)	As dissolved (mg/L)	As total (mg/L)
Gravel	**<0.001**	**<0.001**	–	–	–	–	–	–
Cocopeat	**0.029**	**0.023**	**<0.001**	**<0.001**	–	–	–	–
Zeolite	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	–	–
Limestone	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**

Fig. 2. Mean removal rate of total As (a), and mean inflow and outflow As total concentration in the four types of wetlands (b). Error bars indicate SD.

Table 4
Comparison of dissolved and total Fe concentration in the inflow of the wetland system and the outflow of each wetland group using Mann–Whitney post hoc tests. Bold type denotes significant difference.

	Inflow		Gravel		Cocopeat		Zeolite	
	Fe dissolved (mg/L)	Fe total (mg/L)	Fe dissolved (mg/L)	Fe total (mg/L)	Fe dissolved (mg/L)	Fe total (mg/L)	Fe dissolved (mg/L)	Fe total (mg/L)
Gravel	0.103	0.094	–	–	–	–	–	–
Cocopeat	**<0.001**	**<0.001**	**<0.001**	**<0.001**	–	–	–	–
Zeolite	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	–	–
Limestone	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**

Fig. 3. Mean removal rate of total Fe (a), and mean inflow and outflow Fe total concentration in the four types of wetlands (b). Error bars indicate SD.

Fig. 4. Mean removal rate of total B (a), and mean inflow and outflow B total concentration in the four types of wetlands (b). Error bars indicate SD.

B ($p^{KW} = 0.04$). However, cocopeat wetlands were the only wetland type that affected significantly the concentration of B when comparing to the inflow, as shown in Table 5.

3.5. Changes in environmental parameters

3.5.1. pH and Eh

The most significant change in pH occurred, predictably, in the limestone-based wetlands, increasing from 2.0 to 6.7 (Table 2).

Zeolite wetlands also caused an increase in pH, from 2.0 to 2.6. Kruskal–Wallis analysis ($p^{KW} < 0.001$) showed that the media significantly affected the pH values of effluent from the wetland columns. Gravel and cocopeat wetlands presented an average pH slightly lower than that of the inflow, but neither of them was significantly different to the inflow ($p^{MW} = 0.82$ for gravel, $p^{MW} = 0.33$ for cocopeat). A similar trend was observed for the redox

Table 5
Comparison of dissolved and total B concentration in the inflow of the wetland system and the outflow of each wetland group using Mann–Whitney post hoc tests. Bold type denotes significant difference.

	Inflow		Gravel		Cocopeat		Zeolite	
	B dissolved (mg/L)	B total (mg/L)	B dissolved (mg/L)	B total (mg/L)	B dissolved (mg/L)	B total (mg/L)	B dissolved (mg/L)	B total (mg/L)
Gravel	0.307	0.394	–	–	–	–	–	–
Cocopeat	**0.037**	0.058	0.054	**0.032**	–	–	–	–
Zeolite	0.584	0.523	0.270	0.751	**0.001**	**0.008**	–	–
Limestone	0.605	0.576	0.504	0.661	**0.012**	**0.016**	0.940	0.880

Fig. 5. Total As concentrations vs. Fe concentrations in the effluent from limestone wetlands (a), and dissolved As vs. Fe concentrations in the outflow from zeolite wetlands (b).

potential (Eh) of the effluent, as indicated by one-way ANOVA analysis result ($p^A < 0.001$); however in this case each media type (gravel, cocopeat, zeolite and limestone) was found to affect Eh significantly ($p^{GM} < 0.001$) as the wastewater passed through the columns, being gravel, cocopeat and zeolite Eh higher than the inflow, and limestone lower than the inflow (Table 2). Limestone Eh was also significantly lower to each other substrate ($p^{GM} < 0.001$). However, Eh in the gravel wetlands was not significantly different to that of cocopeat and zeolite. The zeolite and cocopeat media had similar Eh.

3.5.2. DO and sulfate

In contrast to pH and Eh, dissolved oxygen was not affected by the wetland media, with the mean DO values in the inflow and outflow of each column showing no significant difference ($p^A_{log-transformed} = 0.176$). Sulfate concentrations were significantly influenced only by the limestone media, with SO_4^{-2} concentrations in the outflow from these columns significantly higher from SO_4^{-2} concentrations in the inflow ($p^{MW} < 0.001$). Conversely, the outflow SO_4^{-2} levels from gravel, cocopeat and zeolite wetlands presented no significant difference with those in the inflow.

3.5.3. Electrical conductivity

The wetland media were found to significantly affect electrical conductivity values of the wastewater ($p^{KW} < 0.001$). In particular, conductivity in the outflow from gravel, zeolite and limestone wetlands were significantly lower than those in the inflow ($p = 0.032$ for gravel, $p^{MW} < 0.001$ for zeolite and limestone). Conversely, electrical conductivity was greater in the cocopeat media than in the inflow, although this difference was not statistically significant.

3.5.4. Total suspended solids (TSS)

Although there were significant differences in the TSS effluent levels between the media ($p^A_{log-transformed} = 0.001$), none of the outflow from any wetland substrate was significantly different to the inflow. Only zeolite wetlands decreased the TSS concentration (Table 2), although even in this case the decrease was not significant.

3.6. Correlation between As and Fe removal

Fig. 5 shows the plots of As outflow concentrations vs. Fe outflow concentrations in limestone and zeolite wetland columns. Removal of As and Fe were correlated as follows: (1) total As and Fe outflow concentrations from the limestone columns (Spearman $\rho = 0.5$, $p = 0.005$) and (2) dissolved As and Fe outflow concentrations from the zeolite columns (Spearman $\rho = 0.37$, $p = 0.045$).

No significant correlations were found between As and Fe concentrations (total and dissolved) in gravel and cocopeat columns.

3.7. Correlation between pH and the removal of Fe

The dissolved and total concentration of Fe from the outflow of limestone and zeolite wetlands decreased as the pH increased, as shown in Fig. 6 for limestone wetlands. Negative Spearman ρ values confirmed significant correlation between pH and Fe removal in both limestone (Spearman $\rho = -0.38$, $p = 0.037$; and Spearman $\rho = -0.59$, $p = 0.01$; for dissolved and total Fe concentration, respectively) and zeolite wetlands (Spearman $\rho = -0.47$, $p = 0.007$; and Spearman $\rho = -0.48$, $p = 0.008$; for dissolved and total Fe concentration, respectively). Conversely, the concentration of Fe was not significantly related to the pH levels in the outflow of gravel and cocopeat wetlands.

4. Discussion

4.1. The effect of wetland media on As, Fe and B removal

The results of this study show that the nature of wetland media is the main factor that determines the route and efficiency of the removal of As and Fe from acidic water. Among the four media, limestone gave the highest removal rates for As and Fe, followed by zeolite. Gravel has a moderate capacity to remove As but does not remove Fe. The ability of cocopeat to remove As and Fe is very limited, although the cocopeat columns enabled the removal of dissolved B at an average rate of 273 mg/m³d.
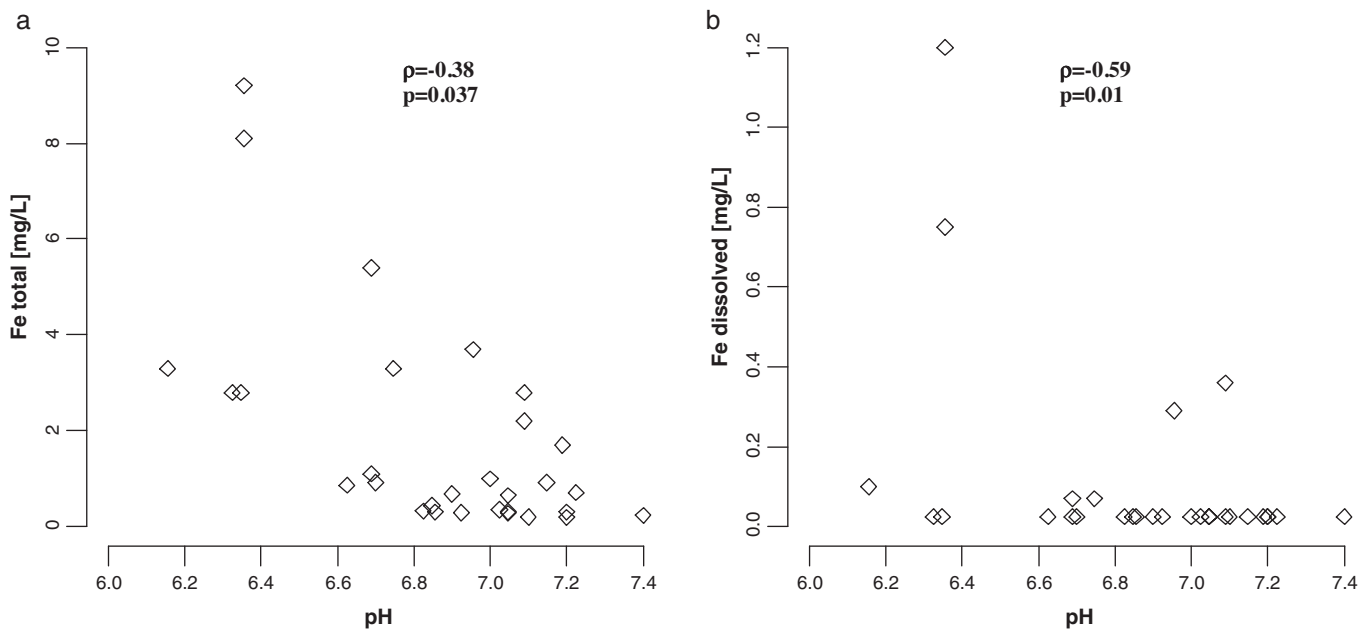
a

b

Fig. 6. Relationship between total Fe concentrations and pH values (a), and dissolved Fe vs. pH values (b), in the outflow from limestone wetlands.

4.1.1. Limestone columns

The good performance of limestone columns is attributed largely to their ability to increase pH. Iron in the effluents from the limestone wetlands is predominately in particulate form; as shown in Table 1, only 6% of the Fe is dissolved, giving a clear indication that Fe has precipitated in the limestone wetlands. The positive correlations between outflow As and Fe concentrations (Fig. 5), and negative correlations between total Fe and pH (Fig. 6), give further indication that Fe has precipitated as a result of higher pH, and Fe precipitation has caused simultaneous As coprecipitation.
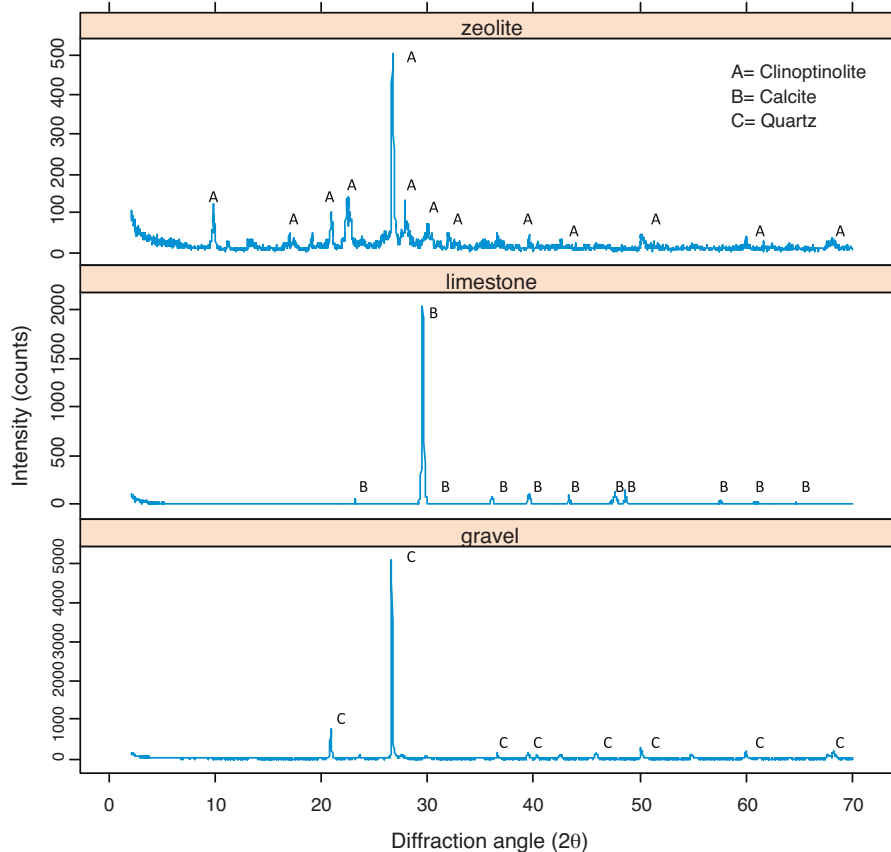
Fig. 7. X-ray diffraction (XRD) pattern of zeolite, limestone and gravel. The analysis shows that the main components of each are clinoptilolite, calcite and quartz, respectively. This information provides insights into the removal mechanisms in the corresponding wetland types.
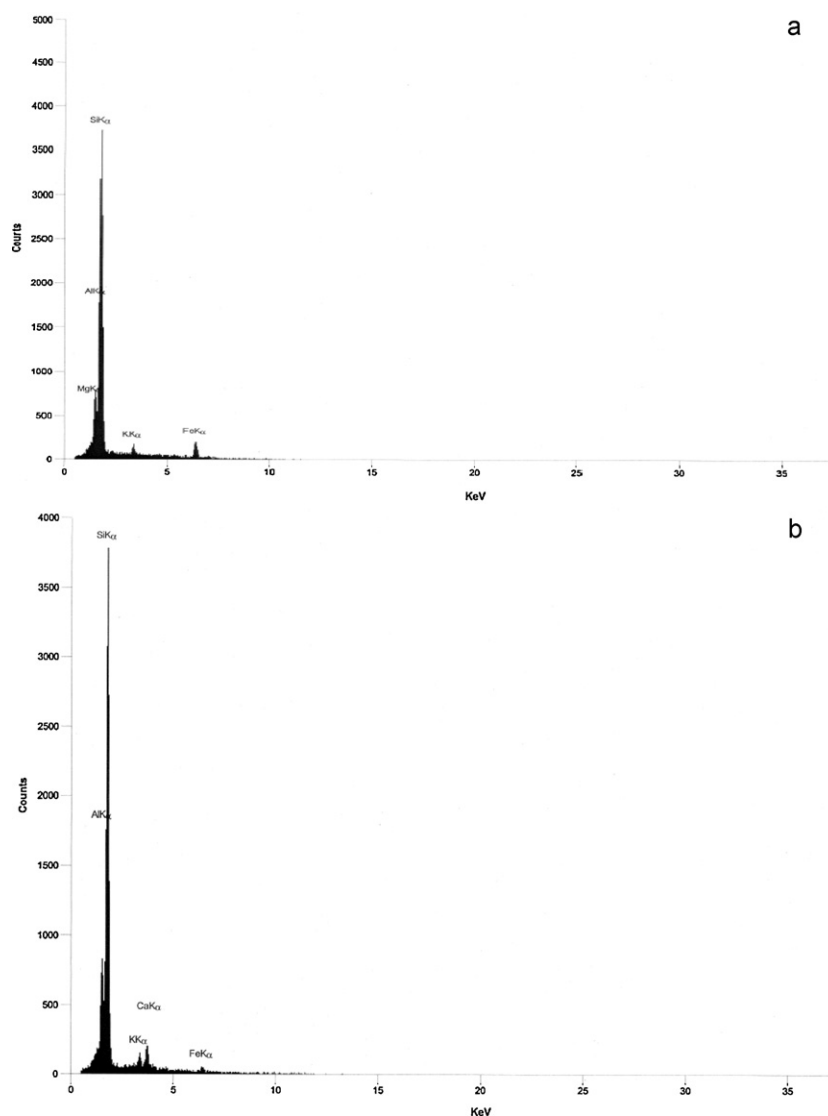
Fig. 8. Energy-dispersive spectroscopy (EDS) spectrum of gravel (a) and zeolite (b). This confirms the information provided by XRD analysis for each substrate, indicating that Si, Al, Mg, Fe and K are present in gravel, and that Si, Al, Ca, K and Fe are present in zeolite.

Other researchers have also tested the use of limestone as a supplementary substrate for As and metal removal in wetlands. Groudev et al. [25] reported the use of crushed limestone in a mixture with soil, silt, compost, cow manure and sand as the medium of four constructed wetlands designed to treat an acid mine drainage from an uranium deposit. Duncan [26] employed crushed limestone and wood pulp in three surface flow wetlands, to remove As, Cd and Zn. Ye et al. [15] suggested the use of crushed limestone to increase the removal of metals from acidic mine waste. These studies, together with the results from this study, all recommend the use of fine limestone chippings or grains in constructed wetlands, if As removal is a major objective.

In addition, limestone has previously been used as a sorbent for the removal of As (i.e. [27,28]). It should be noted that limestone is able to remove As from alkaline and no-Fe containing water, mainly due to the As-retention capacity of calcite $CaCO_3$ and goethite α-FeOOH, minerals occurring in limestone [27]. Limestone used in this study was identified by XRD as mainly in the form of calcite $CaCO_3$ (Fig. 7). Therefore, limestone cannot only remove As by coprecipitation with Fe due to its capability to raise pH, but also by sorption onto calcite. However, as mentioned above, coprecipitation with Fe appears to be the main removal mechanism in this study.

4.1.2. Cocopeat and gravel columns

In this study, cocopeat was chosen to demonstrate how organic matter in wetland matrices may affect As, Fe and B removal. Organic substrates, such as peat, have been reported to retain As [29,30], Fe [31,32], and B [33]. As shown in Table 1, cocopeat-based columns gave low As removal (9.7%), but higher Fe removal (46.7%). Although the sorption of As(V) onto organic matter has not been studied at pH level around 2, it has been found that the ability of humic acids to bind with As(V) improves when pH value increases from 4.6 to 8.4, with the maximum binding capacity occurring at pH 7 [34]. In this study, As(V) sorption onto humic acids appears to have been negatively affected by the presence of H^+ and Fe(III), suggesting a preference of cocopeat to bind with Fe, instead of As, at low pH (around 2.0).

Cocopeat was the only wetland medium showing modest ability to remove dissolved B; the removal of B in the cocopeat columns is likely to be a result of B binding with organic matter, as suggested by Sartaj and Fernandes [35]. However, the interaction between organic matter and B is complex; it has been found that organic matter can increase B removal in soil [36], but it can also inhibit the removal of B by occluding Fe/Al oxides present in soil [37]. Low pH generally presents an unfavourable condition for B removal, due

to the boron speciation. H_3BO_3, instead of $B(OH)_4{}^-$, predominates at low pH, making it more difficult for B to be removed by sorption, particularly onto organic matter, due to the lack of electrostatic attractions.

In contrast to the cocopeat columns, the gravel substrate gave higher As removal (45%) but no Fe removal. The leaching out of Fe after four weeks of operation is postulated to be a result of Fe adsorption reaching saturation, although further research will be needed to confirm this hypothesis. The mechanisms and sustainability of As removal within the gravel columns are unclear. The fact that there is no change of dissolved Fe concentration from inflow to outflow, as shown in Table 1, rules out the possibility of As coprecipitating with Fe. Binding to humic acids is also unlikely, due to the lack of organic matter in the gravel columns. X-ray diffraction analysis showed that the gravel is mainly quartz SiO_2 (Fig. 7). In addition, the energy-dispersive spectroscopy (EDS) spectrum showed that the main elements present in the gravel are Si, Al, Mg and Fe (Fig. 8a). Therefore, it is postulated that As may have been removed by sorption onto protonated alumina sites, as suggested by Clifford and Ghurye [38]. It is possible that the As may have also been exchanged by Si anions, as suggested by Arai et al., as silicate ions readily absorb onto mineral surfaces, and other oxyanions such as arsenate may replace the surface-absorbed Si anions [39].

4.1.3. Zeolite columns

Zeolite is well known for its very high cation exchange capacity. Boron is present primarily as a neutral species (H_3BO_3) at pH 2.6 (the mean pH value of the effluents from zeolite columns). As such, the ion-exchange capability of zeolite may not have been fully utilised. A higher pH, which transforms H_3BO_3 into $B(OH)_4{}^-$ form, would benefit ion exchange processes. In a batch experiment, it has been found that zeolite is less effective in removing B compared with another two media, fly ash and demineralised lignite, and the efficiency of zeolite improves at higher pH [40].

The capability of zeolite to remove arsenic has been reported [41], although most of the studies were on batch experiments (i.e. [42,43]). The zeolite-based wetlands showed impressive removal of As and Fe at low pH, despite the fact that low pH decreases metal removal by zeolite due to increased competition between cations and H^+ [44]. Zeolite employed in this study is mainly clinoptilolite $(NaKCa)_6(SiAl)_{36}O_{72}\cdot H_2O$ as indicated by the XRD analysis (Fig. 7). This was confirmed by the EDS spectrum as the presence of Si, Al, Ca, K (and Fe) was detected (Fig. 8b). Since the dissolved concentrations of As and Fe were positively correlated (Section 3.6), and pH and Fe concentration were negatively correlated (Section 3.7), a possible removal mechanism could be: H^+ and Fe cations are exchanged by other cations – such as Ca, Na, K – present on the zeolite surface, resulting in pH increases (Table 2) and the subsequent decreases in the concentration of Fe in solution (Fig. 3b). As this process progresses, As removal increases through time (Fig. 2b), being attracted by the Fe on the zeolite sites [45]. Another possible As removal mechanism is the exchange of aluminol or silanol hydroxyl groups and anionic species, in this case arsenate. These hydroxyl groups are developed at the edges of zeolite particles in the presence of water [46].

4.2. As removal routes

The removal of arsenic from contaminated water can follow several routes: (1) methylation or demethylation by interacting with biological organisms, (2) sorption, (3) oxidation or reduction (biotic or abiotic), (4) precipitation, and (5) coprecipitation, primarily with metals such as Fe [9]. Water chemistry (particularly pH) affects arsenic speciation [47] and the main route of As removal. The presence of iron in water can significantly affect sorption, precipitation and coprecipitation processes, as demonstrated in natural

environments where biogeochemical cycles of iron and arsenic tend to be coupled [48]. This study shows that in limestone and zeolite wetland columns As is primarily removed by coprecipitation with Fe, whereas in cocopeat and gravel columns the most likely As removal route is sorption onto organic matter or media surfaces.

The nature of the (co)precipitated As–Fe particles is unknown. As described by Wang et al. [49], more effective removal of As was expected due to the simultaneous formation of iron hydroxides (due to the raise in pH) and As removal, and therefore more surface was available for arsenic. Several researchers have investigated the As retention capacity of iron hydroxides by laboratory sorption experiments. These experiments do not, however, reflect the fact of the spontaneous formation of solid phases where coprecipitation is likely to occur [50], as in the case of limestone-based wetlands. In addition, calcium arsenates can also precipitate in oxidising environments and the presence of Ca and As. Geochemical modelling and the use of advanced techniques are required to further investigate the As speciation in the solid phase.

4.3. Other factors affecting the removal of As, Fe and B

4.3.1. Vegetation

The role of microorganisms and plants can affect the transformation of metals within wetlands, because it is unlikely that the metal removal process is completely abiotic [51]. The role of vegetation in the removal of metals can either be direct (by plant uptake) or indirect (by mediating other removal processes). For As removal, however, previous studies have found that plant uptake is not a major mechanism [8,12,15]. For Fe removal, plant uptake can play a more important role when Fe levels are up to 1 mg/L [52]. In this study the Fe levels were around 100 mg/L, meaning that Fe accumulation in plants may be not considered as an important sink for Fe. The situation is similar for B removal, as plants could play a more important role in its removal depending on the concentration: for example B concentrations above 10 mg/L were toxic to the duckweed *Lemna gibba*, but at B concentration below 2 mg/L the duckweed removed B efficiently [53]. The experimental data from this study do not explicitly test nor demonstrate the role of plants in the removal of any target pollutant, but the experiment showed that *P. australis* can tolerate low pH values; as such, the plants may grow in acidic waters and be used as wetland plants for the treatment of acidic wastewaters, such as coal and metal mine drainages, as reported by Mayes et al. [54]. If the accumulation by plants is considerable, harvesting may be considered as an option for long-term As removal [55], however As [55] and metals [13] are accumulated in roots more than in shoots, therefore harvesting of aboveground parts would not contribute to the removal of these pollutants. The presence of vegetation is key as a supply of organic matter, although this is often overlooked due to the short time span of most studies [7]. Therefore, studies of long time spans are required to confirm the role of vegetation in providing more sustainable As and metal removal, through the provision of: (1) organic matter as carbon source for bacteria and adsorption medium for metals, (2) surface area (roots) for attaching bacteria and iron plaque, (3) oxygen transfer into the rhizosphere and the substrate, stimulating the growth of metal-oxidising bacteria in the first case and facilitating coupled aerobic–anaerobic processes in the second case [9].

4.3.2. Sulfate and organic carbon

Apart from pH and Fe, other factors that can significantly affect the removal of As include the presence of sulfur (S) and organic carbon (OC), which potentially allow microbial transformations to immobilise As in wetland matrices [9]. In this study, because the columns were mostly aerobic (as shown by the DO values in Table 2), sulfate could not be reduced or retained in the columns,

and the formation of As/Fe sulfide minerals was unable to occur. Accordingly, no reduction in sulfate concentration was observed. Regarding the role of organic matter, the availability of organic carbon in cocopeat wetlands did not result in significant removal of As and Fe, compared with the efficiency achieved in the limestone columns, which removed Fe and As by precipitation and coprecipitation, respectively. As no bacterial seeding was carried out prior to the experiment, it was unlikely that sufficient microbial population was present in the columns, considering that without seeding microbial population cannot establish quickly in a constructed wetland [13]. Future research will investigate the role of microorganisms in the removal of As and Fe in wetland systems.

4.4. Long-term sustainability of the wetland media

As shown in Fig. 2, the removal of As in gravel wetlands tended to decrease over time, consistent with observations in other studies (e.g. [8,16]). This observation supports the hypothesis that gravel may not be appropriate to remove As and metals, mainly due to limited sorption capacity and inevitable clogging [13]. Two studies reported Fe release from gravel wetland matrices under reducing conditions [56,57]. In this study the wetland matrices did not present reducing conditions. The Fe adsorption ability of the gravel appears to be limited at low pH conditions, as pH is a main factor favouring Fe mobility in wetlands [57]. Therefore, gravel appears not to be an appropriate substrate to remove Fe under acidic conditions. Conversely, the decrease in the removal of As over time did not occur in zeolite and limestone wetlands, despite the high inflow concentrations of pollutants over time and their higher removal capacity compared to gravel and cocopeat wetlands. As is the case with the use of organic material, zeolite and calcitic materials as wetland media will require periodic maintenance as they become saturated [13]. In addition, as reported in Section 3.5, wetlands with gravel and limestone substrate produced effluents with higher TSS than the inflow. This may indicate that these substrates degrade due to the acidity of the inflow. Furthermore, the high removal efficiency of limestone reflected in precipitation of As and Fe (Section 4.1) may also be contributing to the increase TSS levels in the outflow. Further settling/filtration may be required if gravel or limestone are used to treat highly acidic water. Given that the lifespan of the media depends on the pollutants loading, it is recommended that breakthrough experiments particularly designed to saturate the wetland media are performed to find out the effective lifespan of the wetland system. This information is key in the design of constructed wetlands aimed at the removal of As and metals using alternative media.

4.5. Implications for target pollutants removal using constructed wetlands

The results demonstrate one route to effectively remove As and Fe from the acidic wastewater in vertical flow wetlands, i.e. the increase of pH to precipitate Fe and coprecipitate As; the use of limestone and zeolite as wetland media facilitated this removal route. Enhancing this route may also decrease phytotoxicity [58,59]. However, the long-term efficiency of limestone and zeolite wetland columns is unknown. In addition, results from the gravel wetland columns showed that coprecipitation was not the only route of As removal. To further understand As removal, the role of vegetation and microorganisms needs to be investigated in carefully designed experiments. This study suggests that organic substrates can be used to enhance the removal of B, but higher pH would be required. Overall, this study has generated useful new insights for media selection and As removal routes, but there is a

long way before wetland systems can be designed and built, with confidence, to remove As, B and Fe from wastewaters.

5. Conclusions

Vertical flow wetlands with limestone medium demonstrated high efficiency for the removal of As (99%) and Fe (98%) from acidic wastewater, when the average hydraulic loading on individual wetland columns was 0.073 m^3/m^2d and the As and Fe loadings were 0.23 and 7.8 g/m^2d, respectively.

The removal of Fe and As were correlated in wetland columns having limestone and zeolite as supporting media. The high efficiencies of the limestone columns were primarily due to their ability to raise the pH of the wastewater to stimulate Fe precipitation and As coprecipitation. Coprecipitation with Fe was shown to be the most effective route to remove As from the wastewater, but more studies are required to demonstrate the long-term efficiency and sustainability of As removal via coprecipitation.

On average, wetlands with zeolite medium removed 92% As and 86% Fe from the acidic wastewater. Conventional gravel wetland columns were able to remove 45% As, without simultaneous removal of Fe, indicating that, unlike in the limestone columns, coprecipitation with Fe was not the main route of As removal in the gravel columns.

Cocopeat was the only wetland medium that showed a reasonable ability to remove B, although on average the wetland columns with cocopeat medium only removed 9% As and 46% Fe from the wastewater.

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