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# Decreasing Hydraulic Retention Time Affects the Performance of Constructed Anaerobic Wetland for Acid Mine Drainage Remediation

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***Abstract*** – Acid mine drainage treatment through constructed wetlands offers several advantages over active systems, however the design and operation of these systems can be a real challenge for engineers and managers due to the various complex biological processes involved, which are sometimes not fully understood. In anaerobic wetlands, Hydraulic Retention Time (HRT) is one of the critical factors in system performance, as affects microbial activity and physicochemical processes. Very low HRT decrease the ability of Sulphate-Reducing Bacteria (SRB) to generate alkalinity and precipitate metals/metalloids in the form of sulphides, and the higher flow rates involved could lead to system aeration and pollutions flushing. This research evaluated the effect of varying HRT (5.4, 3.2 and 2.7 d) on AMD treatment efficiency in a small-scale anaerobic constructed wetland prototype. AMD was transported from the abandoned tailings at Mesapata, Ancash-Peru and stored in a 20L tank, then fed continuously to the wetland using a peristaltic pump. Water samples were collected at the inflow and outflow of the wetland (three times per month) for analysis of total metals/metalloids, acidity and sulphates. Daily pH and conductivity measurements were also taken. The results showed a high removal capacity of the wetland for Al, Fe, Cu, Zn, As, Cd and acidity under HRT of 5.4 d. However, at lower HRT the efficiencies decreased (acidity and Fe) and in some cases the efficiencies were negative (Al, Co, Ni, Cd). Conversely, As and Pb showed significant efficiencies despite increasing HRT. The results demonstrate the different effect of HRT on individual behaviour and metal/metalloid removal from microcosm wetlands, which should be taken into account by professionals when setting their AMD treatment targets.

***Keywords***: Anaerobic constructed wetland, acid mine drainage, heavy metal, hydraulic retention time

## 1. Introduction

Acid Mine Drainage (AMD) is an effluent generated by the chemical and biological oxidation of sulphide ($Fe_2S$) rich residues, produced especially by mining industry (e.g. tailings and abandoned pits) [1], [2]. Low pH and dangerous concentrations of sulphates, dissolved metals and metalloids endanger aquatic ecosystems, soil quality and public health. [3], [4], [5], [6]. To mitigate the impacts of AMD, wetlands emerge as a highly accepted sustainable alternative for application in rural areas, due to low chemical inflow and implementation costs, easy operation and maintenance, and the possibility of recycling organic waste [5]. Additionally, the sludge is less unstable, dense, and hazardous compared conventional systems. [3], [4]. As in natural systems, constructed wetlands treat water from biogeochemical cycles, with synergistic interactions between micro-organisms, plants and the mineral/organic substrate being the main remediation mechanisms [1]. In anaerobic constructed wetlands, the principal metal removal mechanism is by SRB that generate alkalinity and precipitate metals /metalloids to sulphide form. Adsorption/chelation on organic matter and phytoextraction/stabilization are less direct contributing mechanisms. In order to achieve the objectives of bioremediation, HRT plays a crucial role in determining the performance of the anaerobic system [7]. Low HTR decreases SRB activity, leading to less precipitation of metals/metalloids and washing out of organic material. Moreover, high treatment flows associated to very low retention time, alter the redox conditions and affect the solubility of metal species by altering the dissolved oxygen supply to the system [6], [7]. Conversely, excessive HRT could generate precipitation that short-circuits the system. Research into the behavior of metals under varying HRT is currently limited to the high Andean areas of Peru, where seasonal rainfall causes fluctuations in hydraulic and metal loads regimen, making the design, operation and maintenance of these systems challenging. The study evaluated the effectiveness of a small-scale anaerobic wetland prototype in removing heavy metals, acids and sulphates from the AMD of the Mesapata mine tailings in Ancash, Peru, over a 3-month period using three different HRT.

## 2. Materials and methods

### 2.1. Design of constructed anaerobic wetland

A Polyethylene plastic container (57x36x24cm) were used to implemented a small-scall constructed wetland. The first five centimetres of wetland media consisted of 3/8" round gravel covered with a small layer of straw and 10cm of organic matter (75% sheep manure and 25% compost), the porosity of the total substrate was 38%. In the organic media, 9 units of *Juncus articus* were transplanted from the surroundings of the Mesapata mine tailings (Catac-Ancash). To ensure anaerobic conditions, the water level was 2cm above the organic substrate surface.

### 2.2. Operational conditions

In a first step, to achieve complete adaptation and stabilisation of the wetland biological components, a constant DAM flow (2.0 ml/min) was supplied for 8 months using a peristaltic pump. Previously, AMD was carried from Mesapata mine tailings and stored in a 20l tank. In the second phase, 1.5, 2.5 and 3.5 ml/min, corresponding to HRT of 5.4, 3.2 and 2.7 d (1 month per flow rate), were evaluated successively for 84 days.

### 2.3. Wastewater sampling and analysis

Daily pH, temperature and electrical conductivity (CE) were recorded in the inflow and outflow using an Oakton PCTSTestr$^{TM}$50 Multiparameter. Moreover, water samples were collected weekly (HRT for each flow rate) and sent to a laboratory for analysis of acidity (titration), sulphates (turbidimetry) and total metals/metalloids (inductively coupled plasma mass spectrometry).

### 2.3. Data analysis

The removal efficiencies of metals/metalloids, acidity and sulphates were calculated as the percentage ratio of the difference in concentrations ($C_{outflow}$-$C_{inflow}$) and the inflow concentrations ($C_{inflow}$). Statistical differences of the efficiencies of the 3 flow rate groups were tested by Analysis of Variance (ANOVA) with Tukey's *post hoc* test ($p<0.05$) in R. Moreover, the physicochemical parameters of the effluents were compared with Maximum Permissible Limits (MPL) of Perú [8].

## 3. Results and discussion

Fig. 1 shows the pH and EC profile under the HRT evaluated. Collected AMD had an average pH of 3.38 ± 0.46 with with slight fluctuations due to the seasonality of rainfall in the AMD collection area. The pH outflow was different between between the 3 HRTs ($p<0.05$) with maximum values at 5.4 d (7.6±0.3) but decreasing at 3.2 d (5.43±0.80) and 2.7 d (3.82 ± (3.82 ± 0.20). However, percent pH increase capacity showed no difference between the first two HRT (98.39±14.52%, 88±34.72%, $p<0.05$), showing a high response capacity to the decrease in HRT despite the decrease in pH inflow. In anerobic wetlands, limestone is typically included as a support to raise pH and promote microbial activity and metal precipitation, results show that at high to moderate residence times only the incorporation of organic substrate under a supporting boulder generates alkalinity (bicarbonates) from sulphate reduction, consistent with the findings of Leon (2022) [9]. It also allows to reach the MPL for mining effluents for pH.

The EC of the inflow was high and presented remarkable temporal variations (Fig. 1-b), with an average of 1998.23±311.76 µS/cm. The EC of the treated water was significantly reduced at the highest HRT (1239.2±212.5 µS/cm, 40.88±6.13%), however, this capacity decreased at the lowest HRT. The conductivity depends on the dissolved ions, under high retention time precipitation of anions (sulphates) and cations (metals) can reduce the EC of the DAM, however, at the same time other elements such as Na, Ca, K, nitrates, chlorides and organic compounds present in the compost and manure can be enriched at lower HRT.

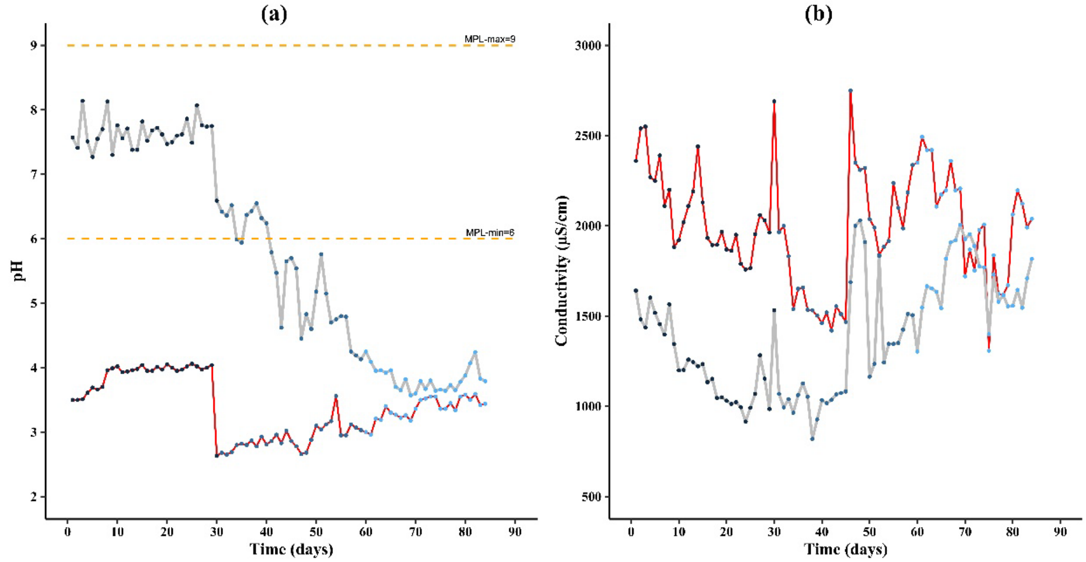

Fig. 1: (a) pH and (b) conductivity profile of wetland under three HTRs
Symbols: Red and grey lines represent water inflow and outflow respectively; yellow dashed lines represent maximum permissible limit of mining effluents in Peru. Black points: 5.4 d, blue points: 3.2 d and sky-blue points: 2.7 d

Fig. 2 shows the profile of acidity, sulphates and metals/metalloids under the three HRT. As with EC, temporal variations are observed over the period evaluated. The inflow was highly acidic (755.22± 248.98 mg/l) and present high concentrations of sulphates (1467.22±454.85 mg/l), Fe (92 - <200 mg/l), Mn (46.70-<50mg/l), Al (13.45±4. 32 mg/l), Zn (30.09±9.84 mg/l), As (0.36±0.33 mg/l) and Cd (0.11±0.05 mg/l), the last 3 elements exceeded the MPL of mining discharges and environmental liabilities effluents in Peru. The wetland demonstrated high removal efficiencies of Cr, Al, Fe, Cu, Zn, As, Cd and Pb, operated at a 5.4 d HRT (Table 1). Under adequate HTR, anaerobic conditions cause sulphide precipitation of these metals/metalloids (except Al), moreover bicarbonate produced in organic matter BSR oxidation and ammonium alkalinity character contribute to metal precipitation/coprecipitation [2].

As and Pb removal was maintained under all HRT, achieving the MPL throughout the experiment, suggesting that other mechanisms such as adsorption, chelation or phytoremediation may be important in the As-Pb removal at short retention times. As the HRT was decreased some metals started to show negative efficiencies, Al, Co and Ni at 3.2 d and Zn and Cd at 2.7 d, the less reducing and less alkaline conditions not only enhanced metal removal but also resulted in the remobilization of metals sequestered in the sediments. Mn showed negative efficiencies under all HRT. Mn sulphides present high water solubility under reducing conditions, in addition, precipitation as hydroxide requires a high pH (>9) [10]. Finally, in an anaerobic wetland it is to be expected that sulphate concentrations of AMD will decrease due to SRB activity; however, we found negatives sulphate removal efficiencies at 5.4 and 3.2 d of HRT. In the first months of operations, when mineralisation is in its first stage, the release of sulphates to water derived from organic matter is to be expected [11], intensified in high Andean areas where low temperatures limit microbial metabolism.

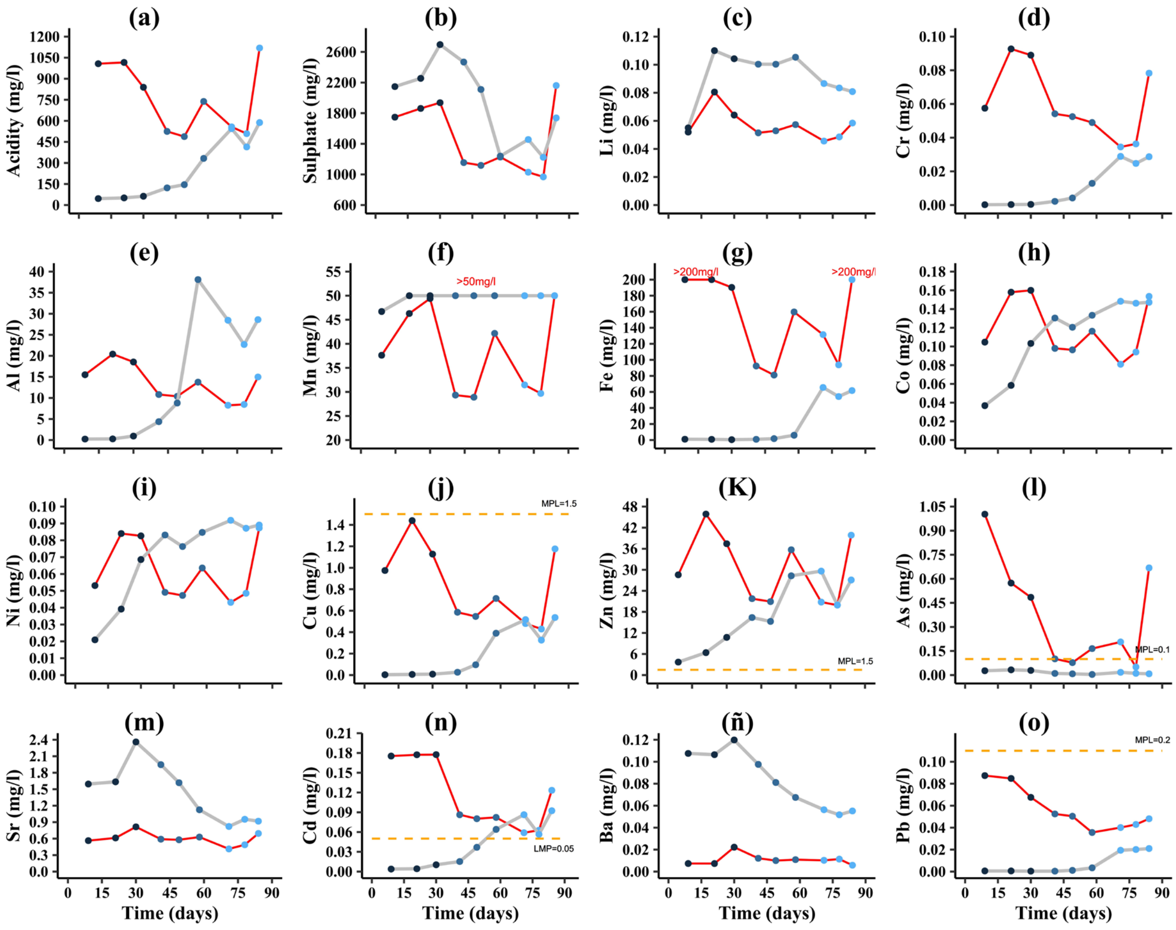

Fig. 2: (a) acidity, (b) sulphate, total of (c) lithium, (d) chromo, (e) aluminium, (f) manganese, (g) iron, (h) cobalt, (i) nickel, (j) copper, (k) zinc, (l) arsenic, (m) strontium, (n) cadmium, (ñ) barium and (o) lead profile of wetland under three HRTs. Symbols as Fig.1

Table. 1: Percentage removal efficiencies of acidity, sulphates, metals and metalloids under the three HRTs. Data are averages of three measurements. Different letters represent significant differences ($p<0.05$).

| **HRT (d)** | **Acidity (%)** | **Sulphate (%)** | **Li (%)** | **Cr (%)** | **Al (%)** | **Co (%)** | **Ni (%)** |
|---|---|---|---|---|---|---|---|
| 5.4 | $94.31 \pm 1.56^{a}$ | $-27.70 \pm 9.97^{a}$ | $-35.01 \pm 28.38^{a}$ | $99.63 \pm 0.07^{a}$ | $97.34 \pm 2.1^{a}$ | $54.44 \pm 16.45^{a}$ | $43.67 \pm 23.38^{a}$ |
| 3.2 | $67.29 \pm 11.1^{a}$ | $-67.80 \pm 31.79^{a}$ | $-89.47 \pm 26.16^{a}$ | $87.20 \pm 11.88^{a}$ | $-34.07 \pm 125.81^{ab}$ | $-24.24 \pm 9.253^{b}$ | $-54.65 \pm 18.94^{b}$ |
| 2.7 | $22.75 \pm 22.9^{b}$ | $-16.09 \pm 59.19^{a}$ | $-66.68 \pm 5.64^{a}$ | $37.18 \pm 23.99^{b}$ | $-167.85 \pm 76.73^{b}$ | $-44.79 \pm 44.54^{b}$ | $-64.78 \pm 56.87^{b}$ |
|  | **Cu (%)** | **Zn (%)** | **As (%)** | **Sr (%)** | **Cd (%)** | **Ba (%)** | **Pb (%)** |
| 5.4 | $99.50 \pm 0.22^{a}$ | $81.49 \pm 8.83^{a}$ | $95.22 \pm 1.82^{a}$ | $-179.87 \pm 11.8^{a}$ | $96.52 \pm 2.04^{a}$ | $-1054.39 \pm 532.7^{a}$ | $99.34 \pm 0.06^{a}$ |
| 3.2 | $74.47 \pm 26^{ab}$ | $24.14 \pm 3.13^{b}$ | $92.55 \pm 4.48^{a}$ | $-162.84 \pm 76.86^{a}$ | $52.84 \pm 30.13^{ab}$ | $-645.09 \pm 107.89^{a}$ | $95.84 \pm 4.72^{a}$ |
| 2.7 | $23.58 \pm 31.05^{b}$ | $-3.52 \pm 37.33^{b}$ | $89.83 \pm 10.1^{a}$ | $-75.45 \pm 37.47^{a}$ | $-3.79 \pm 37.63^{b}$ | $-551.05 \pm 261.72^{a}$ | $53.70 \pm 2.4^{b}$ |

## 4.Conclusion

Acid mine drainage is one of the main challenges faced by countries with a mining history such as Peru. In recent years, wetlands have emerged as economic alternatives with low operation and maintenance requirements for the treatment of small treatment flows. The present investigation demonstrated the effect of HRT on the performance of pollutant removal efficiency in microcosms. As expected, at longer HRT we found better efficiencies for most parameters, however, lower HRT decreases the metal reduction efficiency and even released metals from the substrate to the effluent. Due to the complexity of the processes and the different environmental variables involved in the treatment, it is necessary to continue with laboratory and field studies of these systems in order to apply them safely and effectively in the different scenarios of the Peruvian Andes.

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