Constructed Wetlands for Treatment of Alkaline Bauxite Residue Leachate: Ten Years of Monitoring a Single Cell System and Optimising Designs for a Multi-Cell Approach

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Abstract

Limited data are available for long term constructed wetland (CW) use for alkaline leachates. This paper summarises monitoring from a single cell CW operating for 10 years to treat bauxite residue leachate, successfully dropping pH from 11.5 to 7.14 (±0.14). Lessons from the single cell informed the construction of two new multi-celled systems with differing substrate mixes: one with 8% organic matter content, the other 12%. The new systems came online in 2024 with the first 6 months monitoring showing pH reductions from ≈11.2 to 7.41 (8% OM) and 7.14 (12% OM) alongside trace element (Al, As and V) reduction.

Keywords: Bauxite residue leachate, alkaline leachate, constructed wetlands

Introduction

Mining and processing of minerals for metal production has generated in excess of 100 billion tonnes of waste and tailings globally: with annual quantities projected to increase as demand for metals rises (Hund *et al.* 2020; Valenta *et al.* 2023). The alumina industry accounts for >4.6 billion tonnes of bauxite residue (BR), with >170 million tonnes generated annually (International Aluminium Institute 2022; Qin *et al.* 2023). Due to the use of sodium hydroxide (NaOH) to extract Aluminium (Al), leachates formed from BR are inherently alkaline (pH 9-13.2) and contain elevated concentrations of Al, arsenic (As), vanadium (V) and sodium (Na) (Burke *et al.* 2013; Higgins *et al.* 2017).

Long term management of leachates from BR and other mine waste storage facilities poses a challenge to operators and regulators, as leachates may form for decades post closure (Di Carlo *et al.* 2019; Mayes *et al.* 2008). Each facility must be assessed to ensure the post-closure plan is appropriate for site specific parameters (leachate chemistry, space constraints, climatic conditions, other treatments/remediation works to waste piles) and may include active or passive treatment technologies. Increasingly, passive approaches, such as constructed wetlands (CWs), are preferred due to lower long term operational costs, but equivalent treatment performance efficiencies (Hedin 2020).

Relative to acidic and neutral drainages, CW treatment of alkaline leachates has received less attention, and consequently there are a lack of long term datasets available (Vymazal *et al.* 2021). Treatment of BR leachate (average influent pH 11.5) to achieve a discharge of pH<9 using a passive CW has been demonstrated over a 7.5 year timespan, with a single cell CW achieving an effluent of pH of 7.1 (Hudson *et al.* 2023b). However, monitoring the efficacy of CW operation and associated substrate saturation for longer periods is necessary to determine their ongoing operation and potential lifespans. Additionally, further design optimisations, such as increased organic matter in the substrate to aid both pH reduction (Buckley *et al.* 2016) and retention of trace elements of increasing interest such as V, have been demonstrated at lab scale (Hudson *et al.* 2024). However, further investigations are necessary to determine whether these findings are scalable.

This paper presents the findings of two ongoing CW pilot studies treating BR leachate at an operating alumina refinery: a single cell CW which has been operational for 10 years, and the initial 6 months monitoring of 2 new multicell systems (3 cells each) built using different substrate OM contents.

Methods

Site Description-Single Cell:

The single cell pilot, which has been operating for 10 years, is 4 m × 11 m constructed at a bauxite residue disposal area (BRDA) at Aughinish Alumina, Ireland. The substrate was a transplanted local soil (pH = 6.7, EC = 188μS cm^{-1}, CEC 38 cmol kg^{-1}, and 2.8% organic C content), planted with *Phragmites australis*, *Typha latifolia* and *Sparangium erectum* supplied locally (FH Wetland Systems Ltd). Vegetation was acclimatised over 6 months with fresh water.

The CW inflow is controlled by a PLC mixing system and three 1000L tanks: a leachate tank, a mixing tank and a dosing tank. Alkaline leachate and deionised water were mixed until the target pH of ~11.5 was reached. Leachate is then pumped to the dosing tank, where it was discharged to the CW at a summer (May-September) rate of 45-55L h^{-1} or winter rate (October-April) of 10-30L h^{-1}. Varied rates are due to increased winter precipitation.

Site Description- Multi-cell systems:

Two parallel multi-cell systems were constructed at a separate location on the same BRDA facility. Each system contains three cells of approximately 8m × 4m each, with a spillway between each cell. The feed system loading the cells is the same as the single cell, feeding both systems at the same rate and target pH, currently averaging 11.2.

The substrate in one system consists of 8% OM and the other system contains 12% OM. Both systems were planted with *P. australis*, *T. laitifolia* and *S. erectum*. A PLC system of the same configuration also feeds the two multicell systems.

Monitoring and Sampling-Single Cell:

Inflow and outflow pH was measured from May 2015 using a field probe, with monthly averages reported over the 10-year operating period. Additional samples of water and sediments were taken throughout the operational period for elemental analysis, with samples filtered through 0.45μm filters and determined by ICP-MS. Detailed analyses (pH EC, trace elements, microbial community) of the sediments after 4 and 5 years of operation are available separately (Hudson *et al.* 2023a; O'Connor and Courtney 2020). Monitoring of inflow and outflow for pH, conductivity and trace elements on a bi-weekly basis has been conducted since June 2024.

Monitoring and Sampling-Multi-Celled Systems:

Loading of the new multi-cell systems began in April 2024, where monitoring of the pH and EC of the inflow and outflows were taken daily. Additional water samples were collected from the inflow and outflow of each cell and system on a bi-monthly basis since June 2024 (6-month period) for elemental analysis to assess pH, conductivity and trace element removal rates.

Results

Single Cell

Average monthly outflow pH (7.14±0.18, Fig. 1) was consistently far lower than the upper pH9 discharge limit. Removal of Al (96%), As (85%) and V (71%) has been sustained over the 10-year operating period while Na concentrations also decreased by an average 22% and was mostly found in soluble forms in the substrate (up to 60% of total). Na removal efficiency has decreased as time has passed, with removal decreasing from significant reductions of 31% after year 1 and 13% in year 5, to negligible removal of Na and release (-8% ±22) in the past 6 months monitoring. Monitoring from June 2024-Dec 2024 showed Al, As and V concentrations in the effluent were significantly reduced compared to the influent, decreasing by 99, 90 and 73% respectively (Fig. 2), with no significant difference between the influent and effluent Na concentrations.

Multi-celled Systems:

Over the 6-month sampling period, the 12% OM system has shown greater pH reduction in the final outflow (pH=7.1±0.14) when compared with the 8% OM system (pH=7.41±0.17). Both systems effectively reduced pH below the pH 9 threshold within the first cell (Fig. 3).

Removal rates of Al and V at the outflows were 99.9% and 99.2% in both substrate systems. Arsenic concentrations were below the limit of detection in all samples of the inflows and outflows across the sampling period. Initial measurements show the V and Al are removed to below the limit of detection

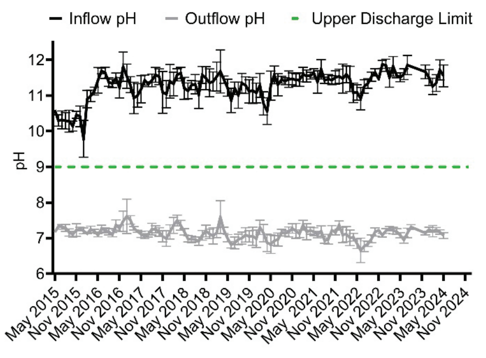

Figure 1 *Monthly average of inflow and outflow pH values from May 2015, with the upper discharge limit of pH 9 marked. Error bars denote standard deviation.*

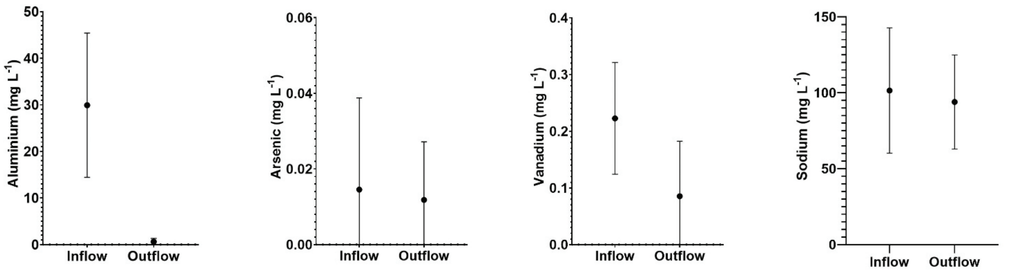

Figure 2 *Average inflow and outflow concentrations of Al, As, V and Na of the single cell system over a 6-month operating period from June to December 2024. Error bars denote standard deviation.*

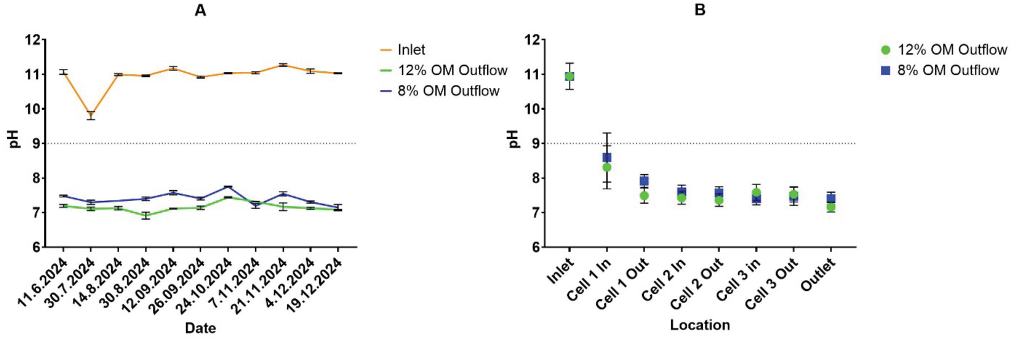

Figure 3 *A) Average pH over 6-month period at inflow and outflow points of the multi-celled systems whose substrate contains 12% and 8% organic matter respectively and B) average pH across the CW cells, with pH threshold of 9 denoted on both graphs. Error bars denote standard deviation.*

at the outflow of the second cells in both treatments, with the 12% OM system showing a greater reduction of V within the first cell (Fig. 4). There was an efflux of Na from both systems (inflow= 42.2±11.7 mg L^{-1}, 12% OM= 56.01±19.4 mg L^{-1}, 8% OM=50.54±17.9 mg L^{-1}) but it is likely that this was due to release of Na from the substrate material as the system adjusted to increased pH.

Discussion

Passive nature-based solutions are increasingly becoming the preferred design of choice for remediation and treatment of industrial leachates, particularly where long term post closure management is required. However ongoing monitoring of CW systems for pH reduction and trace element removal is often reported through sporadic sampling campaigns across a systems operation, with limited published data on systems over 10 years old (Pat-Espadas *et al.* 2018). The single cell pilot demonstrates the capacity of CWs to consistently reduce the pH of alkaline BR leachate from ~11.5 to pH<9 over a 10-year period. With over 2000 pH sampling dates from commissioning to present this dataset provides one of the most continuous monitoring datasets for any CW, and the longest, to the authors knowledge, for an alkaline system. Possible mechanisms of pH reduction are microbial respiration, production of organic acids and carbonation, which have all been supported by elevated microbial activity and biomass and carbonates formed within the system (Higgins *et al.* 2018; Hudson *et al.* 2023a).

Reductions of influent Al, As and V in the 10-year-old single celled pilot CW indicates that the system is still providing the additional benefit of reducing trace element load. The removal rates of Al concur with other findings in alkaline steel slag systems (Gomes *et al.* 2019), as well as acidic coal mine drainage (Hedin 2020) and with domestic wastewaters (Kröpfelová *et al.* 2009). V removal efficiency exceeds that reported in field scale CWs treating steel slag leachate (Gomes *et al.* 2019) and municipal water (Kröpfelová *et al.* 2009), and is comparable to rates reported in lab investigations (Chi *et al.* 2024; Zhang *et al.* 2024). Albeit removal efficiency of Na has decreased in the single cell system, the quantity of Na (110 mg L^{-1}) is still far below the threshold of 200 mg L^{-1} for Drinking Water (Environmental Protection Agency 2014). Trace removal processes within these wetlands include precipitation as oxides, sedimentation and microbial processes, with limited plant uptake displayed (Higgins *et al.* 2017; Hudson *et al.* 2023b; O'Connor and Courtney 2020).

Multicell monitoring reveals that the substrate with the 12% OM had a higher pH reduction, with average outflow pH 0.3 units less than that of the 8% mix. This field scale approach corroborates with lab scale studies (Buckley *et al.* 2016), demonstrating the concept is scalable. Removal of trace elements, of Al and V remained high over the 6 months, but further monitoring is needed to determine whether rates are maintained over a longer period. V retention was shown to be greater in the first cell of the 12% OM substrate when compared with the 8% OM mix (Fig. 4). This result is corroborated with a batch study which shows that V retention increases for substrates that contain higher proportions of compost (Hudson *et al.* 2024). This effect is also seen in modified biochars where enhanced surface area and pore volume, and surface modification of the biochar

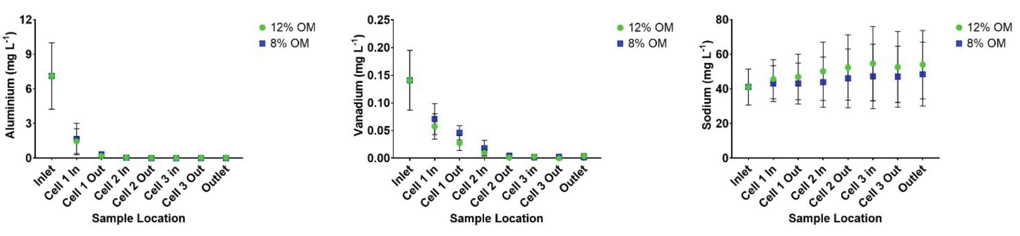

Figure 4 Average water concentrations of Al, V and Na within the two multi-celled systems. Error bars denote standard deviation.

increase the amount of adsorption sites and the opportunity to optimise the removal of V from waters (Ghanim *et al.* 2020). V removal is also noted to be correlated with the organic carbon in natural wetlands (Shaheen *et al.* 2016; Telfeyan *et al.* 2017), supporting the findings and rationale behind employment of increased organic matter to increase removal by adsorption.

Monitoring of these pilots over time is essential to determine the point at which the primary objective of pH reduction is no longer achieved, if indeed such a point is reached. As it stands, the use of a predominantly topsoil only system has achieved successful pH reduction over the past 10 years in the single cell. The new multi-cell systems require long term monitoring to determine whether pH reduction is achieved to a greater degree in one of the treatment types, and with greater co-benefits (i.e. trace element removal). At present, the multi-cell design appears to give the added benefit of the second cell acting as a polishing bed to remove any trace elements (Al and V) still present, with pH already being below the necessary pH 9 limit in the first cell outlet. It is hypothesised that the second and third cells may help increase the lifespan of a treatment system compared with a single cell CW, as trace elements can be accumulated in the second and third beds upon saturation of the first. However, only continued future monitoring will determine whether this occurs.

Passive treatment systems such as CWs can provide cost savings to operators and regulators over time due to reduced operational costs. Similarly, CWs are more environmentally friendly compared to active treatment systems which have emissions due to reagent and electricity generation and transport and require routine sludge disposal. Additionally, such systems provide a potential means of capture of rare earth elements that may otherwise be released to the environment, and further investigation into such retrieval of these elements from wetland substrates is needed.

Conclusions

Monitoring of a single cell CW treating alkaline bauxite residue leachate has demonstrated effective pH reduction from > 11 to pH 7.14 over a 10-year sampling period. Additionally, reductions in trace elements Al, As and V have been sustained. New multicell CWs comparing substrate mixes have so far demonstrated effective pH reduction, with a 12% organic matter content substrate producing an additional 0.3 unit reduction when compared with an 8% organic matter content. So far, the multicell configuration demonstrates enhanced capture of trace elements Al and V, with the first cell removing most and the second cell removing any remaining traces from the outflow of the first. Further monitoring is needed to determine whether effluent quality will be maintained over time and whether differences in treatment efficiencies arise due to differing substrate organic matter contents.

Acknowledgements

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