



## Research article

# Potential use of two filter media in constructed wetlands for simultaneous removal of As, V and Mo from alkaline wastewater - Batch adsorption and column studies

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## ARTICLE INFO

## Article history:

Received 5 January 2018

Received in revised form

22 March 2018

Accepted 7 April 2018

## Keywords:

Mono-element adsorption

Multi-element adsorption

Mo

As

V

Chemisorption

Constructed wetland

Water treatment sludge

Bauxite

## ABSTRACT

The potential to use water treatment sludge and bauxite as active filter media in constructed wetlands to remove As, V and Mo from alkaline drainage originating from seawater-neutralized bauxite processing residue was evaluated in laboratory batch and column studies. Batch adsorption studies showed that increasing the electrolyte concentration from 0.01 to 0.30 M NaCl (the typical electrolyte strength of the drainage) increased adsorption of all three oxyanions onto both media while increasing initial pH from 6.7 to 8.3 (the typical pH of drainage) and using granules (1–2 mm dia.) rather than ground material (<0.2 mm) both decreased adsorption. Kinetic studies showed that while ionic strength had little effect on the contact time required to reach maximum adsorption, increased initial pH increased the time to reach maximum adsorption for Mo on both media and increased particle size increased the time required for maximum adsorption of all three oxyanions onto both media. In batch experiments, at initial elemental concentrations of 1 and 50 mg L<sup>-1</sup>, adsorption from multi-element solutions (compared with single element ones) was reduced in the order: Mo » As > V. In continuous flow column studies from single element solutions (1 mg L<sup>-1</sup>), breakthrough curves for Mo occurred first and greater than three times more eluent passed through the columns before breakthrough of V and then As occurred. When multi-element solutions were used, less volume of eluent was required for breakthrough of all three anions and the volume required before breakthrough of As was greatly reduced compared to that for V. The possibility that the strong ability of V to compete with As and particularly Mo could cause desorption of previously adsorbed Mo and As and their movement through a wetland filter needs to be further investigated. It was concluded that molybdate is the least strongly held oxyanion and that a decrease in solution pH within the wetland would greatly improve Mo removal efficiency.

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## 1. Introduction

Bauxite processing residues are characterized by high pH (11–13) and high salinity and sodicity (Jones and Haynes, 2011; Power et al., 2011) and the drainage from residue storage areas can pose a potential environmental risk. Seawater neutralization is used by an increasing number of alumina refineries located close to the marine environment in order to lower the pH of residues (and drainage) to 9.0 or below (Kirwin et al., 2013). Despite this, drainage from some seawater neutralized storage areas has been shown to be high in Al, Mo, As, V and Ga and to have a pH of about 8.3

(Department of Environment and Heritage Protection, 2012). The drainage from residue storage areas may need to be treated for many decades after closure of the refinery so cost-effective, passive methods of treatment are desirable.

A cost-effective, passive option for management of wastewater is the use of constructed wetlands (Haynes, 2015) and they have already been used successfully to lower the pH of drainage from bauxite residue storage areas (Buckley et al., 2016). Although constructed wetlands are routinely used to remove organic compounds from wastewater, they are increasingly being used to remove inorganic contaminants such as heavy metals from wastewater streams (Haynes, 2015; Hua and Haynes, 2016). In wetlands, inorganic contaminants are removed from the wastewater stream by bulk precipitation and/or adsorption/precipitation reactions with

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the surfaces of the filter matrix. Since, common filter materials used in constructed wetlands such as sands and gravels do not have a high adsorption capacity so the capacity of wetlands to remove inorganic contaminants can tend to decrease over time and/or be highly variable (Hua and Haynes, 2016). The removal efficiency of wetlands for inorganic ions can be greatly improved with the use of active filter materials which have reactive Fe/Al hydrous oxide adsorption surfaces that specifically adsorb ions from solution (Haynes, 2015).

A previous exploratory study (Hua et al., 2015) showed that bauxite (mainly Al oxide) and alum water treatment sludge (mainly Al hydroxide) were suitable materials to adsorb arsenate, vanadate and molybdate and were potentially suitable active filter materials for a constructed wetland or an active filter installation. Factors such as pH, ionic strength, adsorbent particle size and competition between contaminant ions for adsorption sites can influence adsorption. In addition, results can differ between batch studies (where complete equilibrium is achieved between ions in solution and those adsorbed) and continuous flow column experiments (where complete equilibrium is not established) (Westholm et al., 2014; Haynes, 2015). These factors need to be investigated before the potential for use of active filter materials in constructed wetlands to remove Mo, V and As from alkaline drainage from bauxite residue storage areas can be fully assessed.

In this study, adsorption of Mo, V and As from mono- and multi-element solutions onto water treatment sludge and bauxite at different ionic strengths (0.01 and 0.30 M), pH (6.7 and initially 8.3) and particle sizes (<0.2 and 1–2 mm dia.) is investigated in batch adsorption studies. In addition, mono- and multi-element adsorption is compared in batch and continuous flow column studies.

## 2. Materials and methods

### 2.1. Sample description

Water treatment sludge was collected from the Seqwater Mount Crosby Water Treatment Plant (Brisbane) and bauxite (originating from the Weipa deposit in north Queensland) was obtained from Rio Tinto Alcan. Samples were dried and ground to two particle size classes (<0.20 mm and 1–2 mm).

Elemental composition of materials was measured by inductively coupled plasma mass spectrometry (ICP-MS) after digestion in a microwave system with HNO<sub>3</sub>, HCl and HF (CEM, 1993). Specific surface area of samples was determined by the BET/N<sub>2</sub> adsorption method, and zero point of charge (PZC) was determined using a Laser Zeta metre. Materials were subjected to X-ray diffraction analysis to determine their mineralogy. Effective cation exchange capacity, pH and electrical conductivity (EC) (1:5 material/water ratio) were determined as described by Rayment and Higginson (1992).

### 2.2. Adsorption experiments

Adsorption isotherms for Mo, V and As were performed in a batch system to determine (a) the effect of electrolyte concentration (0.01 M versus 0.30 M NaCl) at a pH adjusted to 6.7, (b) the effect of pH adjustment (to pH 6.7 versus no adjustment - initial solution pH 8.3) at an electrolyte concentration of 0.30 M and (c) the effect of ground adsorbent (<0.20 mm dia.) versus particulate adsorbent (1–2 mm dia.) at 0.3 M electrolyte concentration and no pH adjustment (initial solution pH 8.3). The reason these treatments were chosen was that in a previous exploratory batch adsorption study (Hua et al., 2015) adsorption conditions were standardized by using a background electrolyte of 0.01 M NaCl, pH adjusted to 6.7 and the use of ground (<0.20 mm dia.) adsorbent

material. However, the ionic strength of the leachate from the bauxite residue storage areas is typically about 0.30 M NaCl, the pH of leachates is around 8.3 (Department of Environment and Heritage Protection, 2012). And in a wetland large particles of adsorbent (i.e. 1–2 mm dia.) are required to maintain the hydraulic conductivity (Haynes, 2015).

Six different initial concentrations of Mo, V and As ranging from 2 to 640 mg L<sup>-1</sup> (twice the desired final concentration) were prepared using Na<sub>2</sub>MoO<sub>4</sub>, NaVO<sub>3</sub> and Na<sub>2</sub>HAsO<sub>4</sub> at pH 6.7 and 8.3. For the pH 6.7 treatment, the procedure used was the same as that previously described (Hua et al., 2015). 200 mg of adsorbent was weighed into 50-mL centrifuge tubes and 10 mL of 0.02 M or 0.60 M NaCl (at pH 6.7) was added. The mixtures were shaken for 1 h. The mixture was then readjusted to pH (6.7) using HCl. Once the pH stabilized, 10 mL of an individual heavy metal solution, in aqueous solution, was added and the pH was adjusted again. During the adsorption period (2 h), the solution pH was checked and readjusted if necessary, every 30 min. For the pH 8.3 (without pH readjustment) treatment 20 mL of 0.01 M or 0.30 M NaCl (at pH 8.3) containing six different initial concentrations of Mo, V and As ranging from 1 to 320 mg L<sup>-1</sup> were added to 200 mg of waste material in 50-mL centrifuge tubes and shaken for 2 h. The resulting solutions were centrifuged (4000 rpm for 10 min) and the filtered supernatant was analysed for the appropriate element by ICP-MS. Preliminary experiments showed that a 2-h contact time was adequate to reach equilibrium. The percentage of metal adsorbed was calculated from the difference between that added and that remaining in solution.

Adsorption data (equilibrium metal concentration versus quantity adsorbed) were fitted to the Langmuir and Freundlich equations (Apak, 2002). The Freundlich equation explains adsorption onto a heterogeneous surface with uniform energy:

$$q_e = K_f C_e^{\frac{1}{n}} \quad (1)$$

where  $q_e$  and  $C_e$  are the equilibrium concentrations of metal in the adsorbed (mmol g<sup>-1</sup>) and liquid phases (mmol L<sup>-1</sup>), respectively,  $K_f$  and  $n$  are the Freundlich constants which are related to adsorption capacity and intensity, respectively. The Langmuir equation is based on monolayer adsorption on active sites of the adsorbent:

$$q_e = bq_{\max}C_e/(1 + bC_e) \quad (2)$$

where  $q_e$  and  $C_e$  are equilibrium concentrations of metal in the adsorbed (mmol g<sup>-1</sup>) and liquid phases (mmol L<sup>-1</sup>), respectively.  $q_{\max}$  and  $b$  are the Langmuir constants which are related to the adsorption capacity and energy of adsorption, respectively.

### 2.3. Adsorption kinetics

The effects of electrolyte concentration (0.01 M vs 0.30 M NaCl), adsorbent particle size (<0.01 M vs 0.30 M NaCl) and pH adjustment (adjusted to pH 6.7 vs an initial pH of 8.3) on adsorption kinetics were examined using a contact time varying from 10 to 300 min, a dosage level of 10 g L<sup>-1</sup> and an initial concentration of Mo, V and As of 1 mg L<sup>-1</sup>. Procedures were as described above for adsorption isotherms (section 2.2). The data was fitted to pseudo-first-order and pseudo-second-order kinetic models. The pseudo-first order equation is represented by:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \quad (3)$$

The pseudo-second-order equation can be represented as:

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