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Research article

Removal and recovery of vanadium from alkaline steel slag leachates with anion exchange resins

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ABSTRACT

Leachable vanadium (V) from steel production residues poses a potential environmental hazard due to its mobility and toxicity under the highly alkaline pH conditions that characterise these leachates. This work aims to test the efficiency of anion exchange resins for vanadium removal and recovery from steel slag leachates at a representative average pH of 11.5. Kinetic studies were performed to understand the vanadium sorption process. The sorption kinetics were consistent with a pseudo-first order kinetic model. The isotherm data cannot differentiate between the Langmuir and Freundlich models. The maximum adsorption capacity (Langmuir value q_{\max}) was 27 mg V g^{-1} resin. In column anion exchange, breakthrough was only 14% of the influent concentration after passing 90 L of steel slag leachate with 2 mg L^{-1} V through the column. When eluting the column 57–72% of vanadium was recovered from the resin with 2 M NaOH. Trials on the reuse of the anion exchange resin showed it could be reused 20 times without loss of efficacy, and on average 69% of V was recovered during regeneration. The results document for the first time the use of anion exchange resins to remove vanadium from steel slag leachate. As an environmental contaminant, removal of V from leachates may be an obligation for long-term management requirements of steel slag repositories. Vanadium removal coupled with the recovery can potentially be used to offset long-term legacy treatment costs.

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1. Introduction

Steelworks slags are an important industrial by-product, with an annual global production of 170–250 million tonnes (USGS, 2015), and an estimated total production of 5 Gt since 1840 (WSA, 2015). The highest steel (and consequently steel slag) producers are, in descending order, China, EU, Japan, India, USA and Russia (WSA, 2015). Current slag management practices (landfill disposal or reuse as construction materials) produce alkaline leachates due to the hydration and dissolution of minerals such as free lime (CaO), calcium silicate phases and periclase (MgO) in the slag (Chaurand et al., 2007; Gomes et al., 2016b). Steel slags usually contain trace

amounts of potentially toxic metals (Chaurand et al., 2007), and as a result, leachates often contain up to $120 \text{ } \mu\text{g L}^{-1}$ of V (Mayes et al., 2008). Highly alkaline slag leachates can persist for more than 30 years in water bodies due to environmental weathering (Mayes et al., 2008; Riley and Mayes, 2015).

Vanadium is a group 5 transition metal that is widely used in the chemical and metal alloy industries (Keränen et al., 2013; Li et al., 2013; Mirazimi et al., 2015; Navarro et al., 2007; Zhou et al., 2011). It has three stable oxidation states: V(III), V(IV) and V(V) (ATSDR, 2012), and it is present in steel slag predominantly as V(IV), but during leaching it can be oxidized to V(V) (Chaurand et al., 2007), which is the most toxic form and a possible human carcinogen (IARC, 2006). The threshold for chronic V toxicity effects in freshwaters is $19 \text{ } \mu\text{g L}^{-1}$ and for acute toxicity is $280 \text{ } \mu\text{g L}^{-1}$ (NOAA, 2015). Soil and surface water contamination by V from basic slag and petroleum refinery fly ash has resulted in the poisoning of cattle (Frank et al., 1996) and geese (Rattner et al., 2006), respectively. Although it is an environmental contaminant, vanadium is

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also considered of critical importance to green technologies (Naden, 2013), namely for batteries to store renewable energies (Viebahn et al., 2015). As such, numerous researchers have investigated the accelerated leaching of V from slags (Hocheng et al., 2014; Mirazimi et al., 2015; Oty et al., 2014), but V recovery methods have yet to be firmly established.

Ion exchange resins have several advantages, compared with other recovery technologies, such as a high recovery rate, low cost, and simple operation (Zhao et al., 2010). They have been trialled for V recovery (or removal) from sulphuric acid leach solutions from stone coal (Li et al., 2013; Zeng et al., 2009), Bayer liquor (pH 7–8) (Zhao et al., 2010), ammoniacal industrial wastewater (neutral pH) (Keränen et al., 2013) and acid leaching solutions of spent catalysts (Nguyen and Lee, 2013). Promising results were also found for post-closure effluent and runoff bauxite residue disposal areas leachates at pH 11.5 (Gomes et al., 2016a). Until now, the capacity and performance of anion exchange resins for the recovery of vanadium from alkaline solutions such as steel slag leachates have not been studied.

The aim of this study was to test the efficiency of a basic anion exchange resin for vanadium removal and recovery from steel slag leachates. Alkaline leachates with pH 11.5 (representative average value for a steel slag leachate) and different vanadium concentrations were tested in batch tests. Column tests were undertaken to study breakthrough and elution of vanadium from the resins. The regeneration and reuse of the resin were also investigated to help inform practical management and valorisation of steel slag leachates.

2. Materials and methods

2.1. Chemicals

The steel slag leachate was produced in the laboratory via leaching a bulk sample of basic oxygen furnace (BOF) steel slag collected from

Yarborough, Scunthorpe, UK (53.588192N, –0.593582W) with deionised water (15 MΩ cm ELGA Purelab water). The steel slag solution was prepared in a 30 L vessel with deionised water and a liquid to solid (L/S) ratio of 10 (2 kg of steel slag for 20 L deionised water), and agitated periodically over a 48 h period, allowing for a sufficient rise in pH. The solution was allowed to settle to avoid a high suspended sediment load, and the vessel was kept sealed to prevent the contact with atmospheric CO₂. Table 1 shows the average composition of the synthetic steel slag leachate used in this study and compares it with the range of values found in steel slag leachate in the UK.

The steel slag solution was enriched with divanadium pentoxide (general-purpose grade, Fisher Chemical) to test different vanadium concentrations (0.1, 1.0 and 10 mg L⁻¹). These concentrations reflect a range from those documented during leaching under ambient environmental conditions (Roadcap et al., 2005) to those that could be anticipated from enhanced (bio-)leaching (Sjöberg et al., 2011).

The resin used in this study was Amberlite®IRA-400 (Sigma-Aldrich) which is a strong base anion exchange resin with quaternary ammonium functional groups (–N⁺R₃) in a polystyrene matrix and particle sizes of 600–750 μm. Before use, the resin was converted to the hydroxide form. It was washed with deionised water until the supernatant became clear and colourless, and then soaked in deionised water for 6 h, in 5 wt% NaOH solution for 4 h, and again washed with deionised water until the supernatant pH was in the range of 8–9 (Huang et al., 2010).

2.2. Batch experiments

Short duration batch tests to investigate the rate of V removal from solution were performed in conical flasks (250 mL) containing 10 g of wet resin in 150 mL of synthetic slag leachate solution at room temperature (20 ± 1 °C). The contents of the flasks were mixed using a magnetic stirrer at 150 rpm. Aqueous samples (10 mL) were taken after 1, 2, 3, 4, 5, 10, 15, 20, 25 and 30 min. Three

Table 1

Composition of the synthetic steel slag leachate and comparison with the range of values found in steel slag leachate in the UK (Hull et al., 2014; Mayes et al., 2008).

Determinand	Synthetic slag leachate (average values, n = 17)	Range of reported UK leachate values
pH	11.6 ± 0.7	10.3–11.9
Eh (V)	51.2 ± 109.1	361–700
Conductivity (μS cm ⁻¹)	1291 ± 1608	438–7879
Major elements (mg L⁻¹)		
Ca	74 ± 59.3	11–239
Mg	5.14 ± 5.1	1–12
K	2.93 ± 1.7	18–293
Na	17.64 ± 10.8	24–83
Al	5.72 ± 11.1	0.013–0.5
Si	1.53 ± 0.76	0.203–7.7
S	16.45 ± 11.64	na
Trace elements (μg L⁻¹)		
As	30 ± 31	na
Ba	140 ± 50	4.6–42.5
Cd	1 ± 0.3	<0.1–0.3
Co	1 ± 1.0	na
Cr	2 ± 1.6	<5–22
Cu	1 ± 0.8	<5–70
Fe	7 ± 4.4	54–920
Ga	<3	na
Li	6 ± 3.8	4.4–822
Mn	1.5 ± 2.3	5.4–160
Mo	<7	2.8–45
Ni	0.1 ± 0.1	0.3–70
Pb	2 ± 0.3	<5–70
Sr	99 ± 85	213–4000
V	12 ± 2.9	1.6–120
W	6 ± 9.3	na
Zn	5 ± 4.9	2–40

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