



## 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  $27 \text{ mg V g}^{-1}$  resin. In column anion exchange, breakthrough was only 14% of the influent concentration after passing 90 L of steel slag leachate with  $2 \text{ mg L}^{-1}$  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  $120 \mu\text{g L}^{-1}$  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  $19 \mu\text{g L}^{-1}$  and for acute toxicity is  $280 \mu\text{g L}^{-1}$  (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 also considered of critical importance to green technologies

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(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 CO<sub>2</sub>. 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<sup>-1</sup>). 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<sup>+</sup>R<sub>3</sub>) 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 initial V concentrations of 0.1, 1 and 10 mg L<sup>-1</sup> were investigated at

**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 <sup>-1</sup> )	1291 ± 1608	438–7879
<b>Major elements (mg L<sup>-1</sup>)</b>		
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
<b>Trace elements (μg L<sup>-1</sup>)</b>		
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

na – not available.

pH 11.5. Further batch experiments with initial V concentrations of 0.1 and 50 mg L<sup>-1</sup> were conducted for 30 min without intermediate sampling to establish the adsorption isotherms.

### 2.3. Column experiments

Column experiments were conducted in a 1.8 cm diameter × 35 cm height acrylic (Plexiglas) tube in which the hydroxyl-conditioned resin was wet-packed. The resin bed was backwashed with 200 mL of deionised water, allowed to stand for 20 min, and then flushed with deionised water, before the introduction of the steel slag leachate enriched with V<sub>2</sub>O<sub>5</sub> (pH 11.1 ± 0.15) at a flow-rate of 6 and 10 mL min<sup>-1</sup> (see Table 2 for details). Samples of the column effluent were collected every 30 min in Test 1 and every 12 h in Test 2, and analysed to determine vanadium concentrations.

After the synthetic slag solution had been passed through the column, it was flushed with 200 mL of deionised water, and then eluted with 2M NaOH (200 mL) at a flow rate of 6 mL min<sup>-1</sup>. The eluent was collected in 10 mL fractions.

### 2.4. Reuse of the resin and V recovery

To assess the possibility of reusing the ion exchange resin and recovering the V, one gram of hydrated resin was stirred at 150 rpm for 30 min with 10 mL of the steel slag leachate enriched with V<sub>2</sub>O<sub>5</sub> to 50 mg L<sup>-1</sup>. The solution was decanted off and sampled for V analysis. The resin was then mixed with 10 mL of NaOH 2M and stirred for 30 min. The NaOH was decanted off and analysed for V. Finally, the resin was mixed with 50 mL of deionised water stirred for 5 min, and the solution was decanted off and discarded. These operations were repeated 20 times using the same resin. After ten cycles, only samples from alternate cycles were analysed. Between the cycles of ten repetitions, the resin was stored in deionised water.

### 2.5. Analyses

The electrical conductivity, oxidation-reduction potential (Eh), total suspended solids (TDS) and pH of the synthetic slag leachate were measured with an Ultrameter II Psi6 (Myron L. Company). All aqueous samples (10 mL) were filtered (0.22 µm, MCE Membrane Millex HA) and preserved with a few drops of HNO<sub>3</sub> (Romil SpA™ Super Purity Acid). Vanadium was analysed using a Perkin Elmer Optima 5300 DV Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES). The wavelength measured was 290.880 nm and the detection limit was 2 µg L<sup>-1</sup>. A certified reference material (CRM-ES AT-1529, lot number 1319108) was used for quality control.

**Table 2**  
Experimental parameters of the column experiments.

Parameters	Test 1	Test 2
Feed grade target ion - vanadium (mg L <sup>-1</sup> )	5	2
Flow velocity (cm h <sup>-1</sup> )	141	236
Flow direction	downwards	downwards
Resin volume (mL)	1.3	13
Bed volume – BV (L)	0.0013	0.013
Bed depth (cm)	0.5	5
Flow rate (BV h <sup>-1</sup> )	283	47
Residence time (min)	0.21	1.27
Duration (h)	5	150

Notes: BV = Bed volume (L) = Bed dept (cm) × Column crosssectional area (cm<sup>2</sup>)/1000.

Residence time (min) = [bed depth (cm)/flow velocity (cm/h)] × 60.

### 2.6. Data analysis

Hydrochemical data were analysed using the software PHREEQC Interactive v.3.1.7.9213 (USGS) with MINTEQA4 database to determine the speciation of the most important elements, to calculate saturation indices and examine the stability of the stock solutions.

## 3. Results

### 3.1. Effect of contact time

The effect of the contact time between the synthetic leachate and the resin on the removal of V from solution in the batch tests, and using different initial V concentrations is shown in Fig. 1A. Rapid initial sorption was observed in the first minute of all experiments, and all experiments reached a steady state within the 30 min test period. After t = 2 min, the V concentration was below the detection limit (0.002 mg L<sup>-1</sup>) when the initial concentration was 0.1 mg L<sup>-1</sup>. The same happened at t = 4 min for 1 mg L<sup>-1</sup> and t = 10 min for 10 mg L<sup>-1</sup>.

High removal percentages (94–96%) were observed in all tests after only 3 min. At each V concentration, the V removal rate was similar except for the 0.1 mg L<sup>-1</sup> V (Table 3) that had a slightly higher removal in the first 3 min. The pH values in the steel slag leachate were stable over the 30 min test period, with an average difference of 0.07 between the initial and final values of the steel slag leachate.

The kinetics of V sorption on the resin was studied from the time versus percentage removal curves. The rate of sorption was analysed using the model proposed by Lagergren (Eqn. (1)) (Mustafa et al., 2010):

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (1)$$

where  $k_1$  (min<sup>-1</sup>) is the sorption rate constant,  $q_t$  is the amount adsorbed at time  $t$  (min) and  $q_e$  denotes the amount adsorbed at equilibrium, both in mg g<sup>-1</sup>. The rate constants ( $k_1$ ) for the tested conditions were calculated from the linear least square method and are given in Table 3 along with the coefficient of determination ( $r^2$ ). The best fits were obtained for the 10 mg L<sup>-1</sup> V concentration (Fig. 1B), but the rate constants obtained are similar. On average, V is adsorbed at a 1.1 min<sup>-1</sup> rate constant.

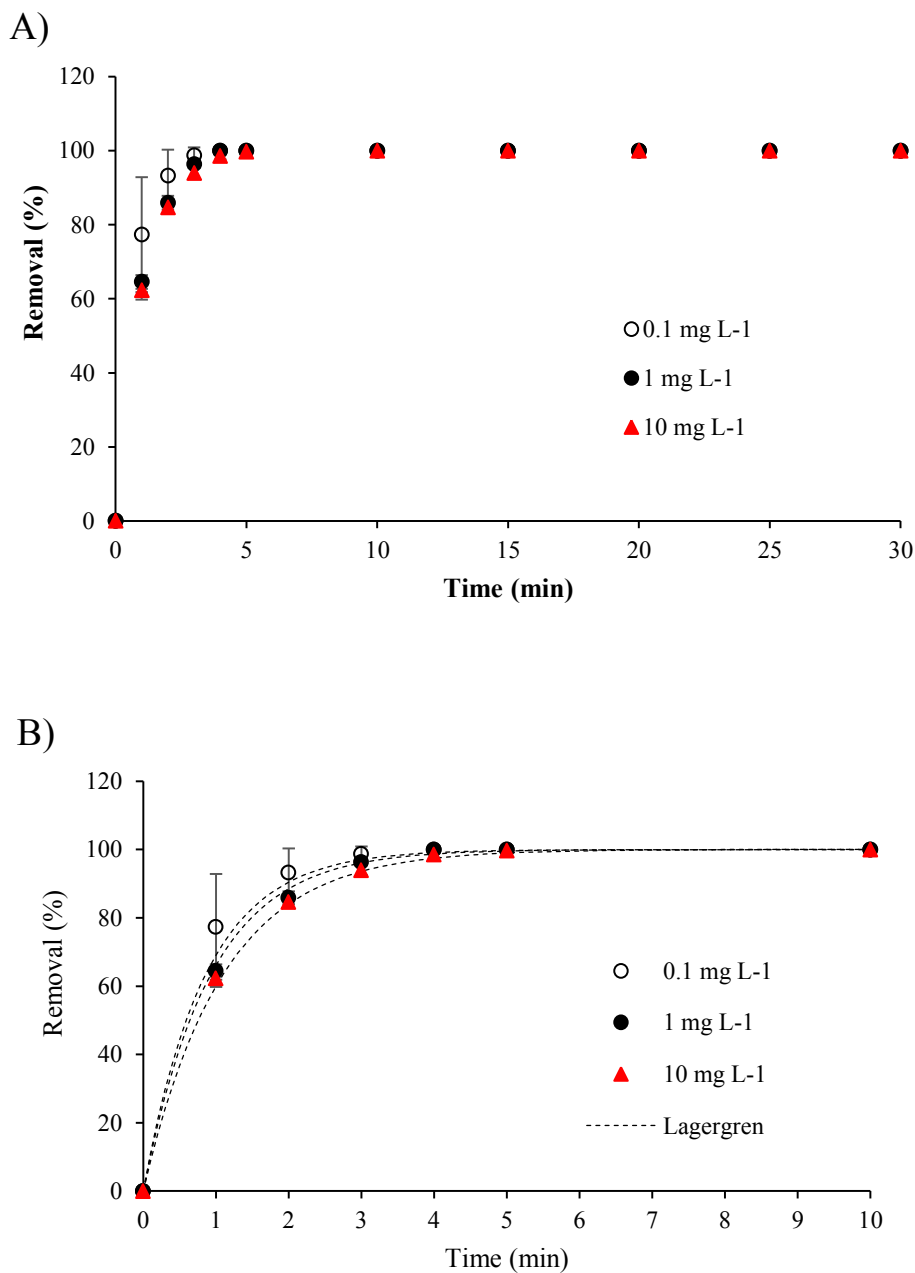
### 3.2. Vanadium adsorption isotherms

The experimental data for V adsorption to the resin were fitted with Langmuir and Freundlich adsorption isotherms. The Langmuir isotherm assumes monolayer adsorption onto a surface with a finite number of identical sites, homogeneous distribution of sorption sites and sorption energies, without interactions between the sorbed molecules, and is described by:

$$q_e = \frac{b q_{\max} C_e}{1 + b C_e} \quad (2)$$

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

Alternatively, the Freundlich adsorption isotherm describes the adsorption equilibrium onto a heterogeneous surface with uniform energy (non-ideal adsorption), and is expressed by:



**Fig. 1.** A) Removal of vanadium in the ion exchange resin in time with different initial vanadium concentrations. B) Pseudo-first order kinetics curves (Lagergren). Data plotted as average concentrations in the steel slag leachate; error bars indicate standard deviation, and when not visible, they are within the width of the marker symbol.

**Table 3**  
Rate constants and coefficient of determination ( $r^2$ ) for V removal at different initial concentrations, at pH 11.5 in the steel slag leachate.

Initial pH	Initial [V] (mg L <sup>-1</sup> )	$k_1$ (min <sup>-1</sup> )	$r^2$
11.5	0.1	1.173	0.992
	1	1.083	0.993
	10	0.916	0.999

$$q_e = K_f C_e^{1/n} \tag{3}$$

where  $q_e$  and  $C_e$  are the equilibrium concentrations of metal in the adsorbed (mg g<sup>-1</sup>) and liquid phases (mg L<sup>-1</sup>), respectively.  $K_f$  and

$n$  are the Freundlich constants that are related to adsorption capacity and intensity, respectively.

Table 4 and Fig. 2 show how the Langmuir and Freundlich isotherms fitted to the experimental data. The values of the Langmuir dimensionless constant,  $b$  and the Freundlich constant  $1/n$  were less than 1, which revealed that the exchange process was favourable (Namasivayam and Sangeetha, 2006). The Langmuir and Freundlich isotherms were both a good fit to the data. The maximum adsorption capacity value ( $q_{max}$ ) required to fit a Langmuir isotherm to the data was 27.4 mg V g<sup>-1</sup> resin.

### 3.3. Breakthrough volumes and V recovery

The results of the column test on the anion exchange resin using vanadate enriched steel slag leachate are shown in Fig. 3.

**Table 4**  
Langmuir and Freundlich isotherm constants and coefficient of determination ( $R^2$ ) for adsorption of V at pH 11.5 in the steel slag leachate.

pH	Langmuir isotherm			Freundlich isotherm		
	$q_{\max}$ ( $\text{mg g}^{-1}$ )	B ( $\text{L mg}^{-1}$ )	$R^2$	$K_f$	n	$R^2$
11.5	27.4	0.004	0.999	0.118	1.087	0.999

Conventionally, the breakthrough capacity (BTC) of a column is defined as the resin loading at the point when the effluent concentration is 10% of  $C_0$  (Tavakoli et al., 2013). Complete “breakthrough” occurs when the column is exhausted, and the effluent concentration is equal to the influent concentration. In test 1, where the influent V concentration was  $5 \text{ mg L}^{-1}$ , the breakthrough capacity was reached at  $0.18 \text{ mg V per cm}^3$  of resin (27 bed volumes that correspond to 35 mL feed solution). After 1000 bed volumes, the concentration of V stabilizes, and no complete breakthrough happens, although it reaches ~90%. In test 2, with an input concentration of  $2 \text{ mg L}^{-1}$  and a resin volume of  $13 \text{ cm}^3$ , a 13% breakthrough occurred with  $10 \text{ mg V per cm}^3$  of resin (~4000 bed volumes that correspond to 50 L of steel slag leachate) (Fig. 3). After ~7000 bed volumes (90 L), the breakthrough was only 14%. In the tested conditions, no complete breakthrough was reached.

The V recovery when the columns were eluted with 2.0 M NaOH is shown in Fig. 4. In test 1, with the small volume of resin, vanadium was recovered faster, with the peak concentration obtained after 38 mL of eluent passed through the column, whereas in test 2 (larger volume of resin) it took 115 mL for the peak elution concentration to be obtained. In test 1, V recovery was 57% after completing the column elution, whereas, in test 2, 72% of V was recovered. Other ions that were in the steel slag leachate that may compete with V for sites on the resin Si, Al, and S were also detected in the column eluent, however, these were at far lower concentrations than V (Fig. 4).

### 3.4. Reuse of the resin and V recovery

Fig. 5 shows the percentages of vanadium removal and recovery in the resin reuse trials. It can be seen that the resin was reused 20 times without loss of efficacy for vanadium removal ( $99.9 \pm 0.1\%$ ) from steel slag leachate. Recovery of vanadium from the resin was complete, with an average value of  $69.2 \pm 13.1\%$  (Fig. 5), although no

downward trend could be observed. The removal of potential competing elements also present in the steel slag leachate showed that the resin was selective toward V removal, with the removal of aluminium ( $72 \pm 19\%$ ) and silica ( $72 \pm 15\%$ ) being less efficient.

### 3.5. Geochemical modelling

Table 5 presents the dominant V species under the tested conditions in the batch trials and shows that at pH 11.5, the dominant V solution species is hydrogen vanadate ( $\text{HVO}_4^{2-}$ ). The second dominant species is orthovanadate ( $\text{VO}_4^{3-}$ ) in the 0.1 and  $10 \text{ mg L}^{-1}$  concentrations, whereas for  $1 \text{ mg L}^{-1}$  is dihydrogen vanadate ( $\text{H}_2\text{VO}_4$ ). The lowest concentrations were found for  $\text{H}_2\text{VO}_4$ , hydrogen divanadate ( $\text{HV}_2\text{O}_7^{3-}$ ) and divanadate ( $\text{V}_2\text{O}_7^{4-}$ ) for 0.1, 1 and  $10 \text{ mg L}^{-1}$ , respectively. Vanadium speciation at the different concentrations tested could have influenced the removal capacity of the resin. However, the dominant V species in all concentrations tested is  $\text{HVO}_4^{2-}$ .

## 4. Discussion

The results show that V can be removed from steel slag leachate at pH 11.5. Vanadium sorption rate can be predicted by a pseudo first order rate equation with a single value of the rate constant ( $1.1 \text{ min}^{-1}$ ). The isotherm data cannot differentiate between the Langmuir and Freundlich models, both fitting well to vanadium adsorption.

For the vanadium removal, hydrogen vanadate ( $\text{HVO}_4^{2-}$ ), the predominant form of V in the steel slag leachates, replaces the  $\text{OH}^-$  attached to the exchanging sites of the resin (Eqn. (4)), where ROH represents the resin in the hydroxide form (Gomes et al., 2016a):



The resin regeneration involves the elution of the resin with a strongly basic solution, in this case, aqueous sodium hydroxide (NaOH 2M). During regeneration, the trapped negative ions are flushed out and replaced by  $\text{OH}^-$ , renewing the exchange capacity of the resin (eq. (5)) (Gomes et al., 2016a).

The fact that not all the V was readily recoverable from the columns tests (Fig. 5) suggests the attenuation of some of the V in a

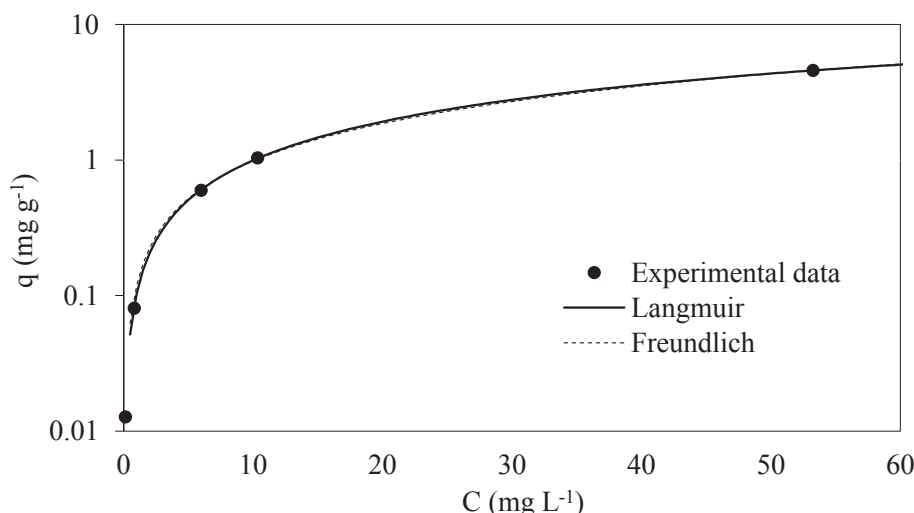
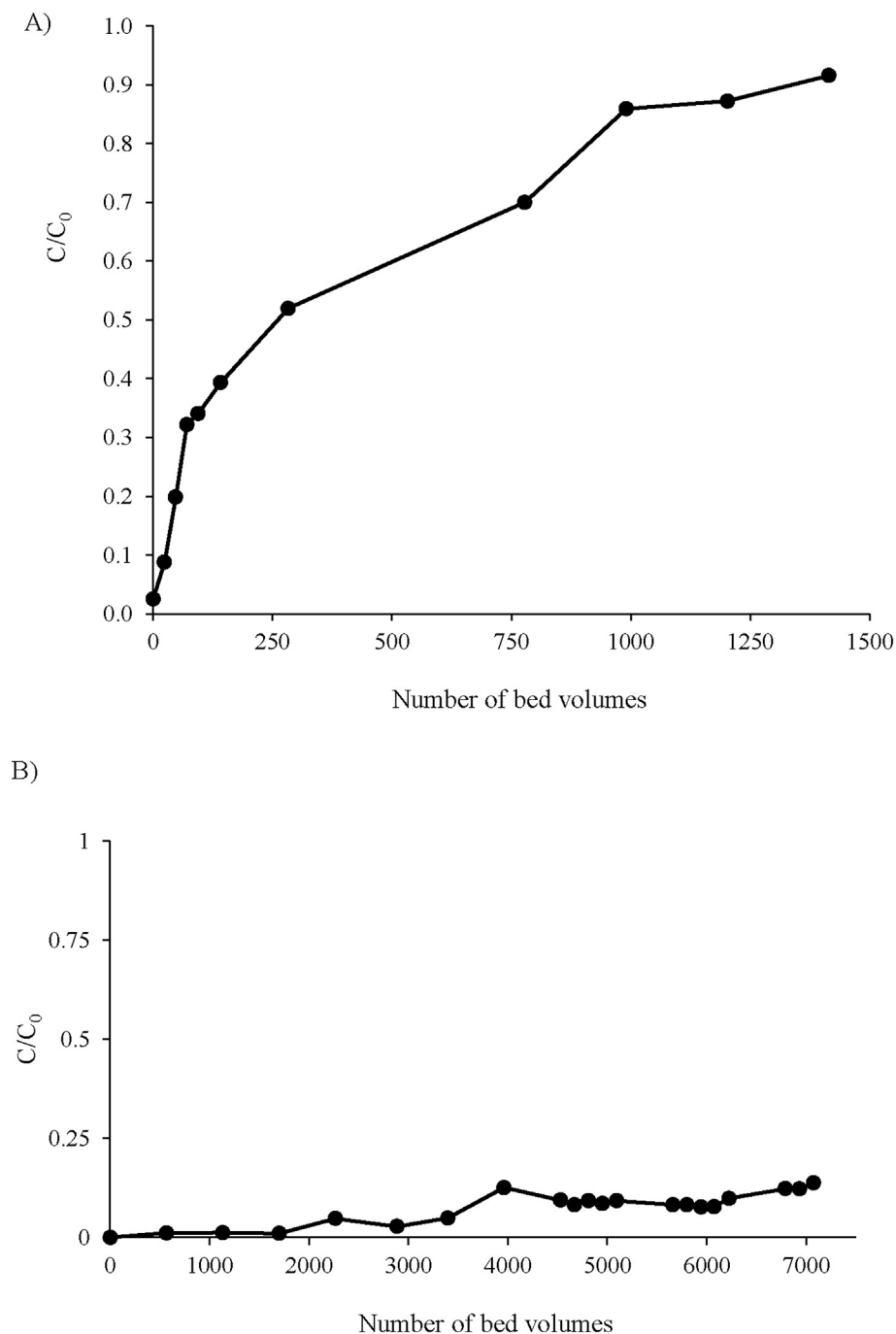


Fig. 2. Isotherm curves for the batch tests.



**Fig. 3.** Breakthrough of vanadium in A) test 1 and B) test 2 for a feed grade concentration of 5 and 2 mg L<sup>-1</sup> in steel slag leachate, respectively.

non-exchangeable form. At least part of this non-exchangeable inventory is likely to be associated with the secondary mineral deposits in the column. Modest levels of V removal from aqueous solution has been documented previously in alkaline environments with rapidly precipitating secondary mineral phases (Burke et al., 2013; Mayes et al., 2008), with Ca-vanadate phases considered to be critical in controlling V solubility at high pH (Cornelis et al., 2008). The secondary phases identified in the column are dominated by calcite (see Supplementary Information), with no other phases identified. Such mineralogical analyses do not preclude the presence of Ca-vanadates in the samples below XRD detection limits (~10% volume) however, as vanadates can form a thin layer

on the surface of fine grained calcite, not individual crystals, they can be hardly detectable by XRD. Modelling in PHREEQC suggested that V oxides and hydroxide phases are not saturated. However, some Ca vanadate phases such as Ca<sub>2</sub>V<sub>2</sub>O<sub>7</sub> are very close to saturation (Supplementary Information) which may indicate they are a possible sink for V, but further analyses would be required to elucidate the specific form of these V sinks. Any secondary carbonate phases and Ca-vanadates (if present) would be expected to be stable during elution (given the alkaline pH), which would be consistent with the V recovery percentages in the region of 70%.

For maximum efficacy of the ion exchange resin, vanadium must bind more strongly to the resin than the displaced OH<sup>-</sup> and also the

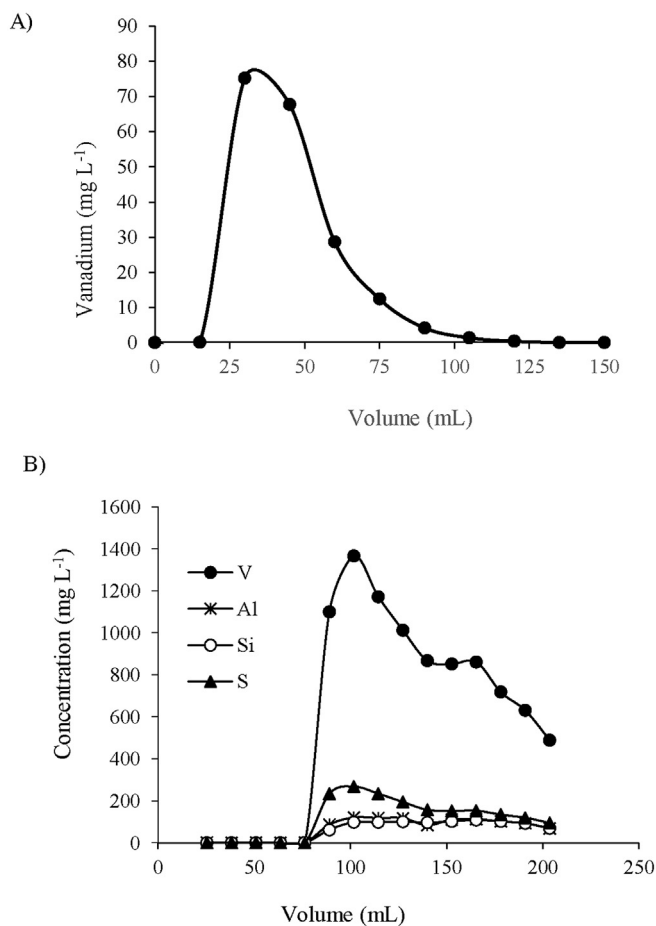


Fig. 4. Elution curves of V from the column with 2.0 M NaOH in test 1 with A) a 0.0013 L bed volume of resin and B) test 2 with a 0.013 L bed volume of resin.

competing ions present in the leachate. Anion exchange resins generally show affinity for  $\text{SO}_4^{2-} > \text{NO}_3^- > \text{Br}^- > \text{Cl}^- > \text{HCO}_3^-$  (Clifford and Zhang, 1995; Harland, 1994). Amberlite<sup>®</sup>IRA-400, in particular, shows affinity for  $\text{AsO}_4^{3-} > \text{PO}_4^{3-} > \text{SO}_4^{2-} > \text{Cl}^- > \text{OH}^-$  (Korkisch,

Table 5

Dominant vanadium species and molality (inside brackets, mol kg<sup>-1</sup>) at pH 11.5 modelled in PHREEQC using the MINTEQA2 database with the concentrations trialled in the batch tests.

Initial V concentration (mg L <sup>-1</sup> )	pH 11.5
0.1	<b>HVO<sub>4</sub><sup>2-</sup> (1.956 × 10<sup>-6</sup>)</b> VO <sub>4</sub> <sup>3-</sup> (5.197 × 10 <sup>-9</sup> ) H <sub>2</sub> VO <sub>4</sub> <sup>-</sup> (1.807 × 10 <sup>-9</sup> )
1.0	<b>HVO<sub>4</sub><sup>2-</sup> (1.673 × 10<sup>-5</sup>)</b> H <sub>2</sub> VO <sub>4</sub> <sup>-</sup> (1.695 × 10 <sup>-6</sup> ) HV <sub>2</sub> O <sub>3</sub> <sup>3-</sup> (1.284 × 10 <sup>-8</sup> )
10.0	<b>HVO<sub>4</sub><sup>2-</sup> (1.906 × 10<sup>-4</sup>)</b> VO <sub>4</sub> <sup>3-</sup> (5.385 × 10 <sup>-7</sup> ) V <sub>2</sub> O <sub>4</sub> <sup>4-</sup> (3.327 × 10 <sup>-7</sup> )

1989; Tang et al., 2013). Further testing is needed to assess the competition by phosphates, arsenates, aluminates and silicates with vanadate in Amberlite<sup>®</sup>IRA-400 in a complex stock solution such as steel slag leachate. In the batch tests, we observed Al and Si removal from the steel slag leachate, which could also have affected the resin capacity to remove V (Fig. 6), as they compete for the exchange sites. However, V(V) ions, which are likely to predominate at higher pH (Cornelis et al., 2008) are more readily exchanged than Si(IV) and Al(III) ions at the same pH values (Huang et al., 2010).

The use of ion exchange beds with steel slag leachate prior to passive treatment systems like aeration cascades or wetlands (Mayes et al., 2009) could allow the removal and recovery of V. The use of sorbents and waste materials as filter and to remove metals, and specifically V, from waters is well documented at bench scale (Hua et al., 2015; Naeem et al., 2007; Namasivayam and Sangeetha, 2006; Westholm et al., 2014), but limited application can be found in pilot and full-scale applications. The use of ion exchange resins could allow the removal of V from steel slag leachate and its potential recovery for recycling, releasing potential economic gains, or, at least, offering some cost offset for remediation operating expenditure at legacy sites.

The concentrations of V in the recovered solution after elution with NaOH (Fig. 5) are of the same order of magnitude as other industrial stocks, such as an ammonia strip solution (Sahu et al., 2013) and oil fly ash leachate (Navarro et al., 2007). Selective precipitation of V can be obtained in a two step procedure – addition

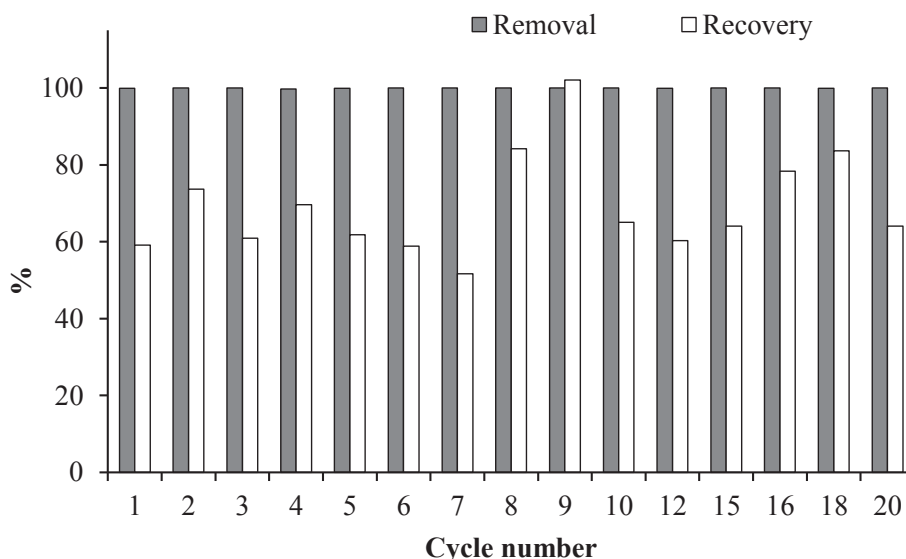


Fig. 5. Removal and recovery of vanadium from steel slag leachate enriched with 50 mg L<sup>-1</sup> after 20 cycles of sorption and regeneration.

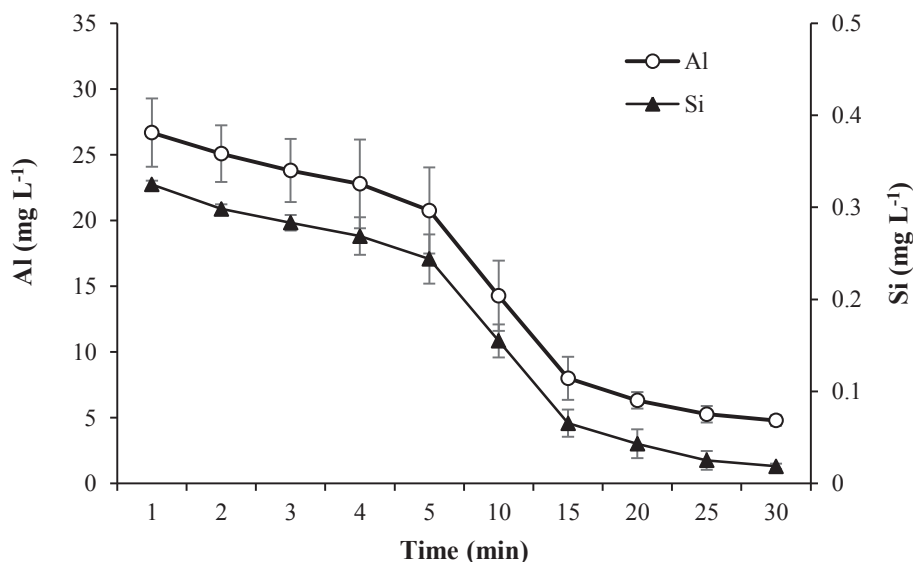


Fig. 6. Concentrations of Al and Si during the batch tests at pH 11.5. Data plotted as average concentrations in the steel slag leachate; error bars indicate standard deviation.

of sulphuric acid to pH 8, followed by the addition of ammonium chloride, and further pH buffering to pH 5, to precipitate ammonium vanadate (Navarro et al., 2007).

Upscaling the use of ion exchange resins to field conditions is important to assess their efficacy and potential constraints under environmental conditions. Resin fouling may be a concern for full-scale implementation (Paul Chen et al., 2002; Shuang et al., 2013), with secondary carbonates likely to be of particular significance for steel slag leachates (Mayes et al., 2008; Roadcap et al., 2005). As such, efforts to minimise atmospheric CO<sub>2</sub> ingress into resin recovery systems are likely to be critical for ensuring system longevity. Pre-filtration (e.g. sand filters) can, however, help to remove fouling compounds and preserve bed life (Crittenden et al., 2012).

Although resins can be regenerated, the process produces waste solutions with high pH and a high concentration of metals. Treatment residuals may include backwash, rinse water, and aged/ineffective resins. Liquid disposal options may include discharge to a water treatment plant, and aged/ineffective resins will need to be properly managed and disposed.

## 5. Conclusions

The results demonstrate that anion exchange resins can be used for metal removal and recovery from steel slag leachates at pH 11.5, which is important for both the treatment of hazardous alkaline leachates and the recovery of metals of critical importance. Vanadium has been effectively removed and recovered from alkaline steel slag leachates with anionic exchange resins in both batch and column tests. Future research should optimise operating parameters such as flow rate and bed height, or the use of a multiple column system for a pilot scale unit, which will permit evaluation of efficiency and cost-effectiveness of anion exchange resins under field conditions.

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## Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jenvman.2016.10.063>.

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