



## Removal of vanadium from aqueous solution using a red mud modified saw dust biochar

Bashir Ghanim, JOHN MURNANE, Lisa M.T. O'Donoghue, RONAN COURTNEY, TONY PEMBROKE, Thomas F. O' Dwyer

### Publication date

01-01-2020

### Published in

Journal of Water Process Engineering; 33, 101076

### Licence

This work is made available under the [CC BY-NC-SA 1.0](#) licence and should only be used in accordance with that licence. For more information on the specific terms, consult the repository record for this item.

### Document Version

1

### Citation for this work (HarvardUL)

Ghanim, B., MURNANE, J., O'Donoghue, L.M.T., COURTNEY, R., PEMBROKE, T. and O' Dwyer, T.F. (2020) 'Removal of vanadium from aqueous solution using a red mud modified saw dust biochar', available: <https://hdl.handle.net/10344/8722> [accessed 8 Feb 2023].

This work was downloaded from the University of Limerick research repository.

For more information on this work, the University of Limerick research repository or to report an issue, you can contact the repository administrators at [ir@ul.ie](mailto:ir@ul.ie). If you feel that this work breaches copyright, please provide details and we will remove access to the work immediately while we investigate your claim.

# **Removal of Vanadium from Aqueous Solution using a Red Mud modified Saw Dust Biochar**

Bashir Ghanim<sup>1,4</sup>, John G. Murnane<sup>3</sup>, Lisa O'Donoghue<sup>3</sup>, Ronan Courtney<sup>2,4</sup>, J. Tony Pembroke<sup>1,4</sup>, Thomas F. O'Dwyer<sup>1,4\*</sup>

<sup>1</sup>Department of Chemical Sciences, School of Natural Sciences, University of Limerick, Limerick, Ireland

<sup>2</sup>Department of Biological Sciences, School of Natural Sciences, University of Limerick, Limerick, Ireland

<sup>3</sup>School of Engineering, University of Limerick, Limerick, Ireland

<sup>4</sup>Bernal Institute, University of Limerick, Limerick, Ireland

\*Author to whom all correspondence should be addressed: Dr Thomas O'Dwyer, Chemical Sciences Dept., School of Natural Sciences, University of Limerick, Ireland.

E-mail: tom.odwyer@ul.ie

## **Abstract**

Adsorption studies were carried out on a red mud modified sawdust biochar material to assess its capacity in the removal of vanadium (V) from aqueous solution. In this study, a number of parameters which can potentially influence V(V) adsorption were investigated including equilibrium V(V) solution concentration, contact time for effective V(V) removal, temperature of the adsorption process, solution pH and ionic strength. The uptake of V(V) was shown to be heavily influenced by solution pH with maximum uptake ( $16.45 \text{ mg g}^{-1}$ ) achieved in the pH range of 3.5 - 5.5. The adsorption process was best described by the Langmuir model. The kinetics of the adsorption process indicated that V(V) uptake occurred within 60 minutes of contact and that pseudo-second order kinetics best described the kinetics of the overall adsorption process. There was a clear increase in V(V) uptake with increasing temperature (range 293 – 343 K) indicating an endothermic adsorption process and the level of uptake remained largely unchanged at solution salt concentrations of up to 0.1 M NaCl and competing cation concentrations of up to  $2000 \text{ mg L}^{-1}$  of sodium and  $200 \text{ mg L}^{-1}$  aluminium. The relatively weak interaction between V(V) and the modified biochar surface may indicate a possibility of recovery of the bound V(V) and subsequent regeneration of the adsorbent.

**Keywords:** Modified biochar, red mud, saw dust, Vanadium, adsorption, bauxite residue

## **1.0 Introduction**

Vanadium is a transition metal and its compounds are widely used in a variety of industries such as glass, textile, ceramic, steel and other manufacturing activities [1, 2]. While V is increasingly being considered an essential element for human health due to its ability to reduce cholesterol formation [3], its compounds can be potentially hazardous (carcinogenic effects) at high aqueous concentrations [4–6]. V enriched wastewaters can cause severe environmental issues, inhibiting plant growth and polluting groundwater [7]. V exists in various oxidation states in the environment, e.g. V(II), V(III), V(IV) and V(V), however, the most common valence state is V(V) which can be present as both cationic and anionic species depending on the solution pH [6, 8, 9]. V(V) removal and recovery from complex wastewater solutions presents a significant environmental challenge and various treatment options have been recently examined [5, 8, 10–12]. Amongst these methods, adsorption has gained a lot of recent favour and is commonly recommended as it possesses a number of advantages such as high removal efficiency, operational simplicity, potential for adsorbent recycling and economic viability. In addition, previous research using a range of adsorbents including

natural materials, treated materials and clays have shown that the adsorption process offers good potential for V(V) removal from wastewaters [2, 12–15]. Currently, there is a move towards biosorbent type materials for metal recovery based on the fact that they are naturally occurring and their supply is relatively abundant and cheap. Saw dust is a low-cost and abundant material which can be converted to its stable, carbon-rich, solid biochar form, via a pyrolysis process under oxygen-limiting conditions [16–22]. The surface properties of a biochar, which can be enhanced by adopting appropriate methods, are key factors in its usability as an adsorbent. Previous studies have shown that impregnation of biochar with metal oxides or clay minerals can lead to improvement of its adsorption properties and selectivity [18, 23, 24]. In these cases, the biochar acting as a good porous structure can host the distribution of the elements within its matrix. More recently biochar derived from saw dust and red mud has been proposed as an adsorbent for removing various inorganic pollutants from aqueous solutions [17, 25].

While much recent attention has focussed on the sustainable use of agricultural and industrial waste materials [26], clay and other waste materials have also been used as adsorbents for the removal of selected materials from polluted waste waters [27]. The use of these types of waste materials would also aid in reducing adsorption process cost and enhance their intrinsic value [17, 28, 29]. Bauxite residue, also referred to as red mud (RM), is a by-product generated during alumina processing from bauxite ore, via the Bayer process and is abundantly available at a number of global sites [30]. Consequently, large volumes of RM are produced each year with approximately 1 - 2 tonnes of residue being generated for every tonne of alumina produced [16, 30–32]. The RM generated needs to be stored in large disposal areas which, if not maintained correctly, can lead to contamination of the surrounding environment. Typically, RM is a strongly alkaline material with pH in the range of 10 - 13 and contains high levels of a range of metals such as Aluminium ( $\text{Al}_2\text{O}_3$  5-30 wt%), Iron ( $\text{Fe}_2\text{O}_3$  5-60 wt%), Calcium ( $\text{CaO}$  2-14 wt%) Silicon ( $\text{SiO}_2$  3-50%) and Sodium ( $\text{Na}_2\text{O}$  1-10 wt%). The red mud also contains significant quantities of valuable rare earth metals such as Scandium (0.12 wt%), Yttrium (0.01 wt%) and Vanadium (0.2 wt%) [17, 30, 34–36]. Given the open air storage method for the vast quantities of red mud waste, soil contamination presents as an immediate environmental issue. Over time, leaching from the red mud leads to a metal laden waste water which presents a further risk of surface and groundwater contamination. Aluminium leaching from red mud, particularly in the form of mobile aluminate ( $\text{Al}(\text{OH})_4^-$ ) has the potential to damage receiving soils and water bodies leading to inhibited plant growth while also functioning as a neurotoxin. Chromium

concentrations in the leachate, particularly in the hexavalent form have the potential to lead to carcinogenic impacts [37]. Thus, it is essential to find alternative options for red mud treatment and re-use. Based on previous studies RM has shown good binding affinity for heavy metals [17, 34, 38, 39]. Previous studies also show that red mud contains various elements including Fe as  $\text{Fe}_2\text{O}_3$ , which can reduce to Fe through thermal treatment between 450 and 850 °C [40] and thus, pyrolysing saw dust in the presence of Fe (from RM) can lead to production of adsorbent material which offers the potential for enhanced binding affinity for metal ions [34].

The aim of the present work was to prepare a red mud modified saw dust biochar and compare its capacity for V(V) removal from aqueous solutions with that of the unmodified saw dust biochar. Further investigation will centre on the influence of the key parameters of solution pH, initial V(V) concentration and solution temperature on adsorption performance of the red mud modified biochar system.

## **2.0 Experimental**

### **2.1 Materials**

Red mud (RM) was obtained from a European bauxite refinery and was stored in a sealed 1 L plastic container at room temperature in the laboratory. Saw dust was collected by chopping/grinding raw cypress timber to a particle size less than 1 mm and was also stored at room temperature in the laboratory. Ammonium metavanadate, sodium chloride, aluminium nitrate, hydrochloric acid (37%) and sodium hydroxide were purchased from Sigma–Aldrich.

### **2.2 Characterisation Methods**

Characterisation methods were conducted on a dry basis (db) using suitable standard methods (as described below) with all measurements performed in triplicate. The concentrations of metal ions were determined using an inductively coupled plasma-Agilent Technologies 5100 ICP-OES. Ash content was measured according to BS EN 14775:2009 (550 °C). Elemental composition of prepared biochar samples was conducted through acid digestion in a microwave system according to CEN/TS 15290:2006. The textural properties of prepared biochar samples were evaluated by  $\text{N}_2$  adsorption/desorption isotherms at 77 K using an automatic volumetric system (Quantachrome Instruments 1900 Corporate Drive). A Hitachi S-2700 Scanning Electron Microscopy (SEM) was used to investigate the surface morphologies of biochar samples. The chemical functional groups of prepared biochar samples were studied by Fourier Transform Infrared (FTIR) analysis using a Cary 630 FT-IR spectrometer. A D2976-71 pH meter was used to measure the solution pH.

### 2.3 Adsorbent Preparation

Saw dust samples were first washed with distilled water, oven dried at 105 °C for 24 h and then crushed and sieved to a particle size of <1.00 mm. RM samples were also dried at 105 °C for 24 h, powdered and sieved to a particle size of <0.75 mm. RM-modified sawdust biochar samples were produced using the method adopted by Wu et al., [17]. Briefly, RM suspensions were obtained by agitating 3 g of RM with 600 mL distilled water for 30 min in an orbital shaker (IKA 130 Basic). Subsequently, 15 g of saw dust was thoroughly mixed with the RM suspension, agitated for 24 h (orbital shaker) and filtered using Whatman filter paper grade 4. The residual wet material (RM-modified saw dust) was dried at 105 °C for 24 h before being pyrolysed at 700 °C for 10 min to produce a RM modified biochar (RM-BC). For comparison, unmodified biochar (BC) was also prepared from saw dust via pyrolysis under the same conditions. After cooling to room temperature, the biochar samples (RM-BC and BC) were washed with deionized water (x3) and oven dried at 105 °C for 24 h. They were crushed to <0.75 mm, and stored in an airtight container at room temperature in preparation for laboratory work.

### 2.4 Adsorbate solution preparation

Stock solutions containing V(V) ( $1000 \text{ mg L}^{-1}$ ) were prepared from analytical grade of Ammonium Metavanadate (Sigma-Aldrich). Stock solutions of aluminium nitrate ( $200 \text{ mg L}^{-1} \text{ Al(III)}$ ) and sodium chloride ( $2000 \text{ mg L}^{-1} \text{ Na(I)}$ ) were also prepared for the binary cation competition studies. All stock solutions were freshly prepared and the solutions used in the subsequent experiments were obtained from serial dilution of the stock solutions and the solution pH was adjusted using 0.1 M NaOH or HCl.

### 2.5 Point of zero charge

The points of zero charge ( $\text{pH}_{\text{pzc}}$ ) of both RM-BC and BC biochar samples were measured using the method adopted by Ghanim, [20]. Briefly, the  $\text{pH}_{\text{pzc}}$  of the biochar samples (RM-BC and BC) were determined using a 50 mL centrifuge tube containing 30 mL of 0.05 M NaCl. The initial pH in each tube was adjusted to a value in the range of 2 - 10 using 0.1 M HCl or NaOH solutions before the introduction of 0.1 g of biochar. The suspensions were then agitated for 24 h in an orbital shaker (IKA 130 Basic) at room temperature and the final pH of the solutions was measured. The difference between the initial and final pH values were plotted against the initial pH. The  $\text{pH}_{\text{pzc}}$  is the point of intersection of the resulting curve with the abscissa.

## 2.6 Batch adsorption experiments

To investigate the V(V) removal efficiency as a function of initial pH, batch adsorption experiments were carried out using 50 mL polypropylene centrifuge tubes containing 25 mL adsorbate solution with various initial solution pH's of between 2 and 12. In these experiments, initial V(V) concentration, dosage of adsorbent and temperature were 100 mg L<sup>-1</sup>, 2 g L<sup>-1</sup>, and 293 K, respectively. After 4 hr shaking, the supernatants were filtered through 0.45 µm syringe filters and final V(V) concentrations and pH were measured.

For kinetic experiments, the adsorption time was varied between 5 min and 24 h, adsorbent dosage of 50 mg (2 g L<sup>-1</sup>) was mixed with 25 ml of 10 mg L<sup>-1</sup> initial concentration of V(V) at pH 4 (optimum adsorption pH) and placed on a shaker (IKA 130 Basic) at room temperature. The supernatants were filtered through 0.45 µm syringe filters and final V(V) concentrations and pH were measured.

Isotherm experiments were conducted at various initial V(V) concentrations of 10 - 100 mg L<sup>-1</sup> under optimal conditions, adsorbent dosage of 2 g L<sup>-1</sup>, pH 4 and temperature 293 K. Once the contact time (4 h) was reached, the samples were filtered through 0.45 µm syringe filters and each final V(V) concentration and pH was measured. Cation competition experiments were conducted with binary solutions containing either Al(III) (50, 100, 150, 200 mg L<sup>-1</sup>) with V(V) (100 mg L<sup>-1</sup>) or Na(I) (250, 500, 1000, 2000 mg L<sup>-1</sup>) with V(V) (100 mg L<sup>-1</sup>). The influence of temperature and ionic strength on V(V) adsorption were studied with an initial concentration of 100 mg L<sup>-1</sup> and 2 g L<sup>-1</sup> of adsorbent at pH 4. Investigation of the temperature effect experiments were conducted between 293 and 343 K and the effect of ionic strength was carried out using 0.01, 0.05 and 0.1 M NaCl. After shaking for 4 h, the solutions were filtered through a 0.45 µm syringe filter and the final concentrations of V(V) and pH's were measured.

All batch adsorption experiments were conducted in triplicate. Adsorption capacity ( $q$ , mg g<sup>-1</sup>) for V(V) removal was obtained using Eq.1.

$$q = \left( \frac{C_0 - C_e}{W_t} \right) \times V \quad (1)$$

where  $C_e$  and  $C_0$  (mg L<sup>-1</sup>) are the equilibrium and the initial V(V) adsorbate concentrations, respectively,  $V$  (L) is the volume of solution and  $W_t$  (g) is the mass of adsorbent.

### 3.0 Results and Discussion

#### 3.1 Characterization of adsorbent

Adsorption processes depend strongly on the surface chemistry and morphology of the adsorbent [41] and the RM-BC and BC biochar characterisations (Table 1) revealed that the modification process led to enhanced adsorption properties in the RM-BC biochar. The surface area and pore volume of the RM-BC increased; however, there was a slight reduction in pore radius compared to that of BC biochar. The ash contents of both the BC and the RM-BC's varied significantly, the latter containing a much higher ash content of approximately 41% (w/w). It would be expected that this modified biochar, with the presence of RM elements such as Fe, Ti, Al and Ca, would yield higher ash content. This was supported by elemental composition results of RM-BC (Table 1) which indicated the presence of Fe (26.3 w/w%), Al (5.6 w/w%) and Ti (3.3 w/w%). More detailed information on surface morphologies and structural properties was obtained from the SEM images and EDS spectra of BC and RM-BC biochars those shown in Fig.1a and Fig.1b, respectively. Although there was no obvious difference in morphology of BC and RM-BC, the EDS results confirmed the presence of Fe, Al, Si, and Ti on surfaces of the RM-BC biochar. The surface morphology exhibited a dendritic structure with a relatively porous surface which can increase the accessibility to more adsorption sites for V(V) ions. As shown in Fig.2a, the point of zero charge of both the RM-BC and BC biochars remained approximately the same following the modification process (Table 1).

Table 1. Characterisation of Red Mud modified biochar (RM-BC) and unmodified biochar (BC).

| Parameter                                   | Biochar Type |   |
|---|--------------|---|
|   | BC           | RM-BC   |
| Surface Area ( $\text{m}^2 \text{g}^{-1}$ ) | 9.6          | 23.7  |
| Pore Volume ( $\text{cm}^3 \text{g}^{-1}$ ) | 413.4        | 666.3   |
| Pore Radius ( $\text{\AA}$ )                | 15.3         | 15.0  |
| Ash (%)                                     | 7.5          | 41.7  |
| Elemental Composition (%)                   | -            | Ca (5.4)<br>Fe (26.3)<br>Mg (0.2)<br>Ti (3.3)<br>Al (5.6) |
| $\text{pH}_{\text{pzc}}$                    | 6.2          | 6.3   |



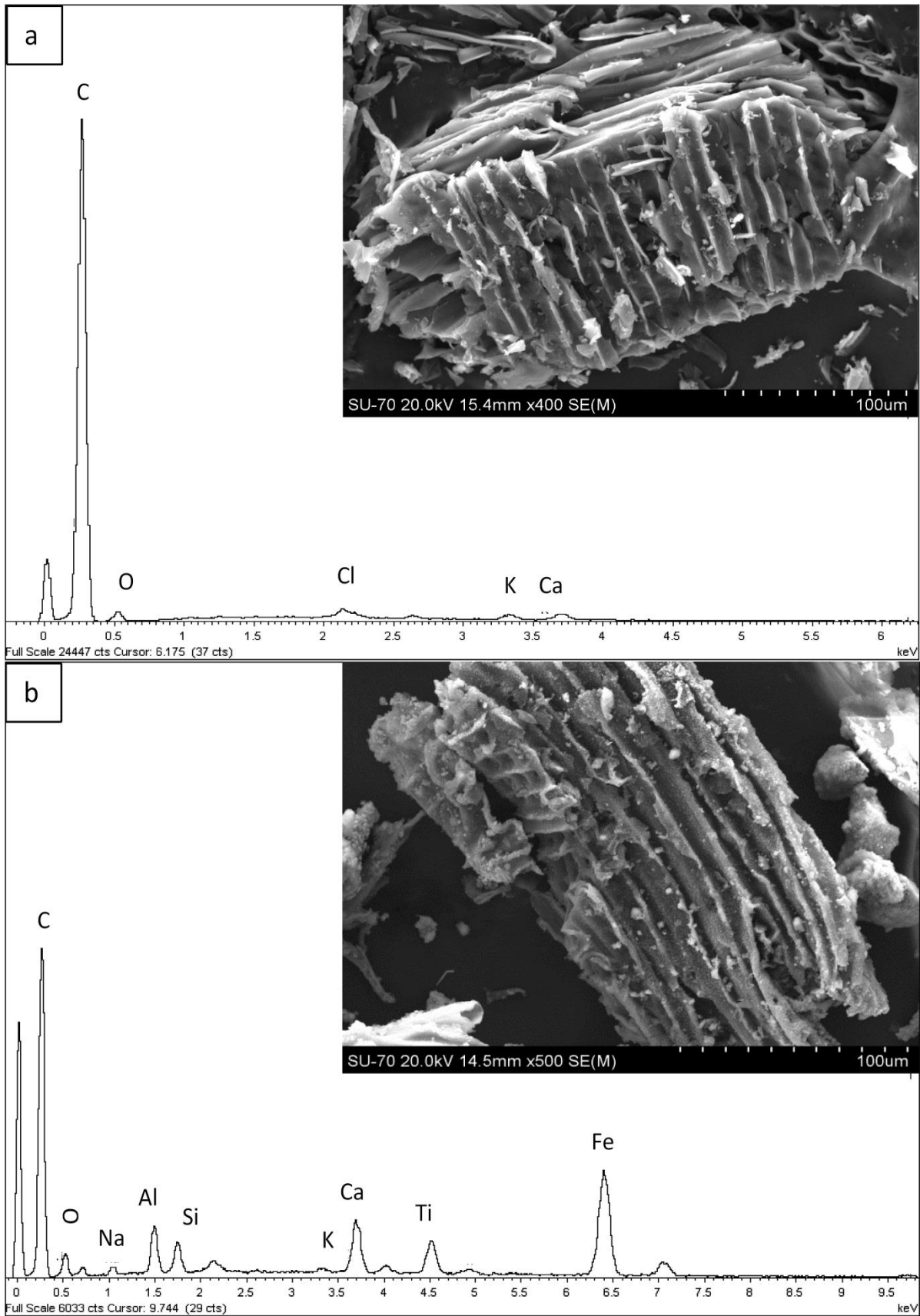


Figure 1. EDS Spectra and SEM Images of (a) Unmodified Biochar (BC) and (b) Red Mud modified Biochar (RM-BC).

### 3.2 Optimization of Adsorption Parameters

The solution chemistry and process conditions, such as solution pH, initial adsorbate concentration, contact time, ionic strength and temperature are important factors that may control the adsorption process [42]; thus, the effects of these factors on the V(V) removal were assessed and optimised.

### 3.3 Effect of solution pH

Solution pH is one of the most significant parameters controlling the adsorption process as it affects both the surface charge of the adsorbent and the speciation of the adsorbate [42]. A fundamental assessment of the RM-BC and BC biochars ability to adsorb V(V) from aqueous solution at various pH's was undertaken to estimate an optimum pH for the V(V) removal process. Fig.2b outlines the level of V(V) removal for each adsorbent as a function of solution pH. The adsorption patterns for both biochars over a wide solution pH range show very similar profiles. An optimum V(V) removal efficiency occurs at approximately pH 4.0 for both the RM-BC and BC biochars with significant decrease at pH's greater than pH 5.5 and less than pH 3.5. The RM-BC biochar shows a significantly increased V(V) uptake over the BC biochar over a wide pH range. Given the  $pH_{pzc}$  of 6.1 and 6.3 respectively for the BC and RM-BC biochars, it would be expected that the biochar surface would be positively charged below  $pH_{pzc}$  (pH 6.1, 6.3) and would become more positively charged as the pH drops to very low pH. For optimum adsorption, the adsorbing V(V) ion should preferably be in an anionic form. At pH's < 3, V(V) tends to exist as a  $VO^{2+}$  species in solution [7, 9]. Thus, it would be expected that the level of uptake of a positively charged V(V) species on a positively charged biochar adsorbent surface should be small due to increased electrostatic repulsion forces. This is confirmed in Fig.2b where the V(V) adsorption level is relatively low. As the solution pH rises to pH 4 and above, the V(V) species tend to be anionic in nature such as  $H_2VO_4^-$ ,  $H_2V_2O_7^{2-}$  and  $HVO_4^{2-}$  [7, 9]. This coincides with an increase in V(V) adsorption arising from an anionic adsorbing V(V) species binding to a positively charged biochar surface. Maximum uptake of V(V) on the RM-BC biochar occurs at approximately pH 4.0. Beyond pH 6, the level of V(V) uptake decreases significantly again as the V(V) is in an anionic state and the surface of the biochar becomes more negatively charged beyond its  $pH_{pzc}$ . Current observations were also supported by studies which assessed V adsorption onto sulfated Katira gum-cl-poly (acrylic acid) [8] and a modified lignocellulosic material [15].

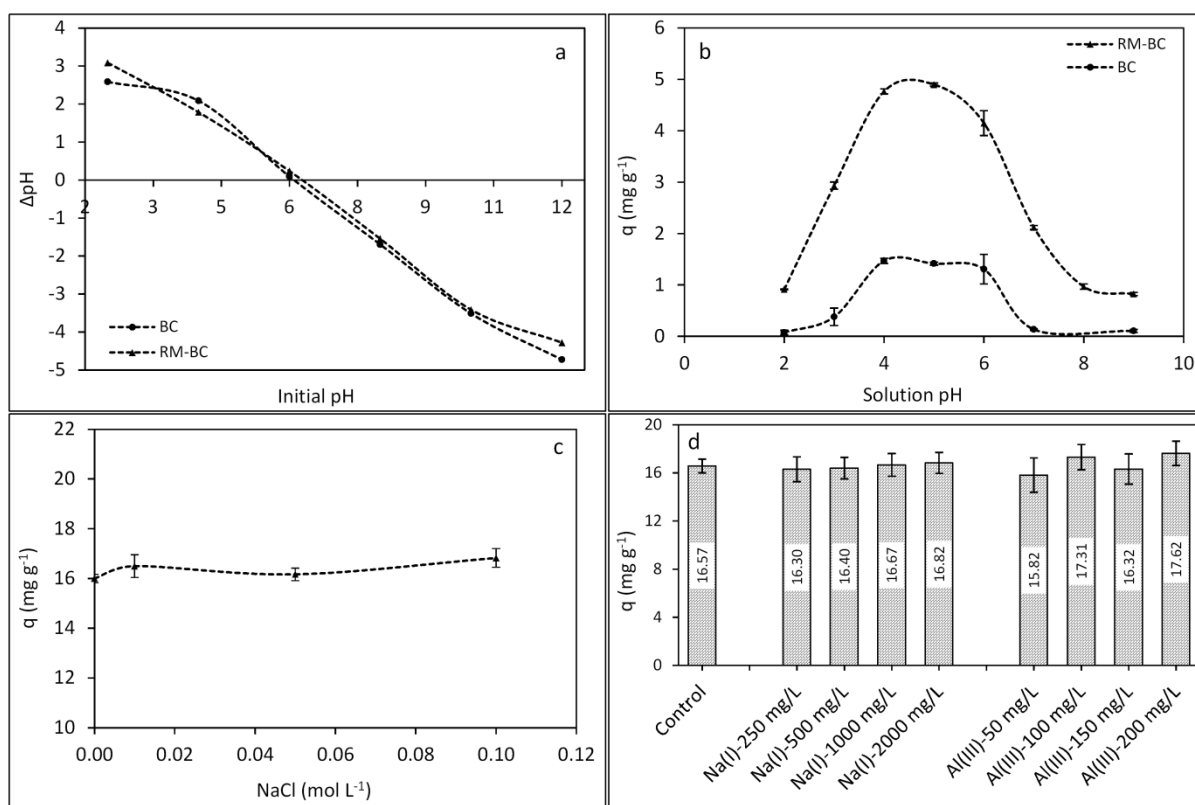


Figure 2. (a) Zero point charge of unmodified biochar (BC) and Red Mud modified Biochar (RM-BC); (b) Effect of solution pH; (c) Effect of Ionic strength on V(V) adsorption and (d) Effect of Competing Cation Competition on V(V) adsorption.

As evidenced from Fig.2b, the level of adsorption of V(V) on the RM-BC biochar is significantly greater than that of the BC biochar across a range of solution pH's. This observation confirmed that the RM modification significantly enhanced the V(V) removal by RM-BC biochar due to the impregnation of the biochar surface with the elemental compositions of RM. As the maximum adsorption capacity of the BC biochar ( $1.5 \text{ mg g}^{-1}$ ) for V(V) removal was considerably less than the RM-BC, no further experiments were carried out on the unmodified biochar (BC). Further work concentrated on a more in-depth study of the capacity of the RM-BC adsorbent to remove V(V) from aqueous solution.

### 3.4 Effect of ionic strength & competing cations

The influence of ionic strength of an aqueous solution can have significant impact on the uptake of a specific metal from solution [7]. Furthermore, RM residue, with high  $\text{Na}^+$  concentration, was used to develop a modified biochar used in this study, thus, it is important to assess the effects of ionic strength on adsorption of V(V) ions onto RM-BC. From Fig.2c,

minimal impact on the uptake level of V(V) by RM-BC biochar was observed at NaCl concentrations up to 0.1 M. Typical bauxite residue leachate solutions contain sodium concentrations of up to 1500 mg L<sup>-1</sup>, roughly equivalent to an NaCl concentration of approximately 0.025 M NaCl which is within the range used in this study. The results indicated a slight but insignificant increase in adsorption capacity of V(V) with increasing concentration of NaCl. A similar observation was reported for V(V) adsorption onto Kaolinite clay [7], and this work suggested that the presence of the Na<sup>+</sup> ions acted as bridges to facilitate the V(V) adsorption. Along with Na(I), as Al(III) is also present in bauxite residue leachate at significant concentrations of up to 200 mg L<sup>-1</sup>, it was also decided to evaluate its potential for interference in the V(V) adsorption process onto RM-BC. This work revealed that, even in the presence of up to 200 mg L<sup>-1</sup> Al(III) concentration, the adsorption of the V(V) was unhindered with uptake levels of V(V) on RM-BC remaining constant (Fig. 2(d)).

### 3.5 Adsorption Isotherm

To study the full extent and mechanism of V(V) adsorption on the RM-BC biochar, a full adsorption isotherm was carried out (Fig.3). As can be seen in Fig.3a, at low equilibrium concentrations, V(V) uptake was significant with uptake levels reaching a plateau at higher equilibrium V(V) concentrations of around 30 mg L<sup>-1</sup>. A maximum V(V) uptake level of 16.45 mg g<sup>-1</sup> was obtained. This uptake level compares favourably with the work of others who have found V adsorption levels of 0.98 mg g<sup>-1</sup> on montmorillonite [7] and 14.0 mg g<sup>-1</sup> on surface-modified lignocellulosic material [15].

A number of possible adsorption mechanisms including pore filling, ion-exchange, electrostatic interaction, surface precipitation and complexations are potentially viable processes [43]. FTIR analysis of both the RM-BC and BC biochar surfaces indicated a lack of any obvious functional groups on either surface, supporting the idea that the mechanism of adsorption is most likely either a simple electrostatic interaction between an anionic V(V) species and a positively charged modified biochar surface (at pH 4) or a possible pore filling mechanism. The latter possibility is supported by the fact that on moving from the BC to the RM-BC an increase in both the surface area and the pore volume is observed and a corresponding increase in V(V) adsorption is also evident (Fig.2b). However, there also exists the possibility that the elemental compositions of RM-BC support the idea that a complexation mechanism is possible and could play a significant role in the V(V) binding process. In this regard, it has been suggested that complexation was the primary mechanism

for V(V) removal using zero-valent iron as adsorbent [44]. One further mechanism that may be considered in the adsorption of V(V) is some form of precipitation or a combined adsorption/precipitation process. However, the likelihood of precipitation in the current study can most likely be discounted for a number of reasons. The adsorption processes were carried out at a pH (pH 4) where V(V) is fully soluble (Fig.2b) and the solution pH post adsorption was still in the soluble range for V(V). A range of studies have shown that the optimum pH for V(V) removal by adsorption is pH 4 [7, 9, 44]. Further, an uptake level of 16.6 mg g<sup>-1</sup> V(V) in this work is in a very realistic range for adsorption level whereas very high adsorption levels may be prone to the inadvertent inclusion of a precipitation mechanism. Lastly, the V(V) equilibrium concentrations (remaining soluble in solution post adsorption) were significant and there were no visible signs of precipitation in the equilibrium solution. The general shape of the isotherm plot can also be characterised as being a “Type I” isotherm plot which would be typical of an adsorption process where a limiting factor is present, which causes a levelling off in adsorption level at high adsorbate equilibrium concentrations. In the case of the V(V) adsorption, this limiting factor may correspond to a saturation of pore volume with the V(V), or a complete occupancy of suitable surface binding sites. In the first instance, both the linear and non-linear Langmuir and Freundlich models (Eqs.2&3 respectively) were applied to the adsorption isotherm data [6, 8, 45, 46].

$$q_e = \frac{K_L C_e}{1 + A_L C_e} \quad (2)$$

$$q_e = K_F C_e^{1/n} \quad (3)$$

where  $q_e$  is the amount of solute adsorbed in mg g<sup>-1</sup>,  $C_e$  is equilibrium concentration in solution in mg L<sup>-1</sup>,  $K_L$  and  $A_L$  are Langmuir constants. A plot of  $C_e/q_e$  versus  $C_e$  from the linear form of Eq.2 was used to determine the values of  $K_L$  (Intercept) and  $A_L/K_L$  (slope). Saturation coverage on the adsorbent was defined as  $K_L/A_L$ . The linearised form of the Freundlich isotherm model (Eq.3) simply assumes a logarithmic relationship between the level of adsorption and equilibrium sorbate concentration and can be defined as Eq.4.

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (4)$$

where  $K_F$  and  $n$  are Freundlich constants relating to adsorption capacity and adsorption energy respectively [47]. Fig.3 shows the adsorption of V(V) on RM-BC at 293K and associated Langmuir modelling.

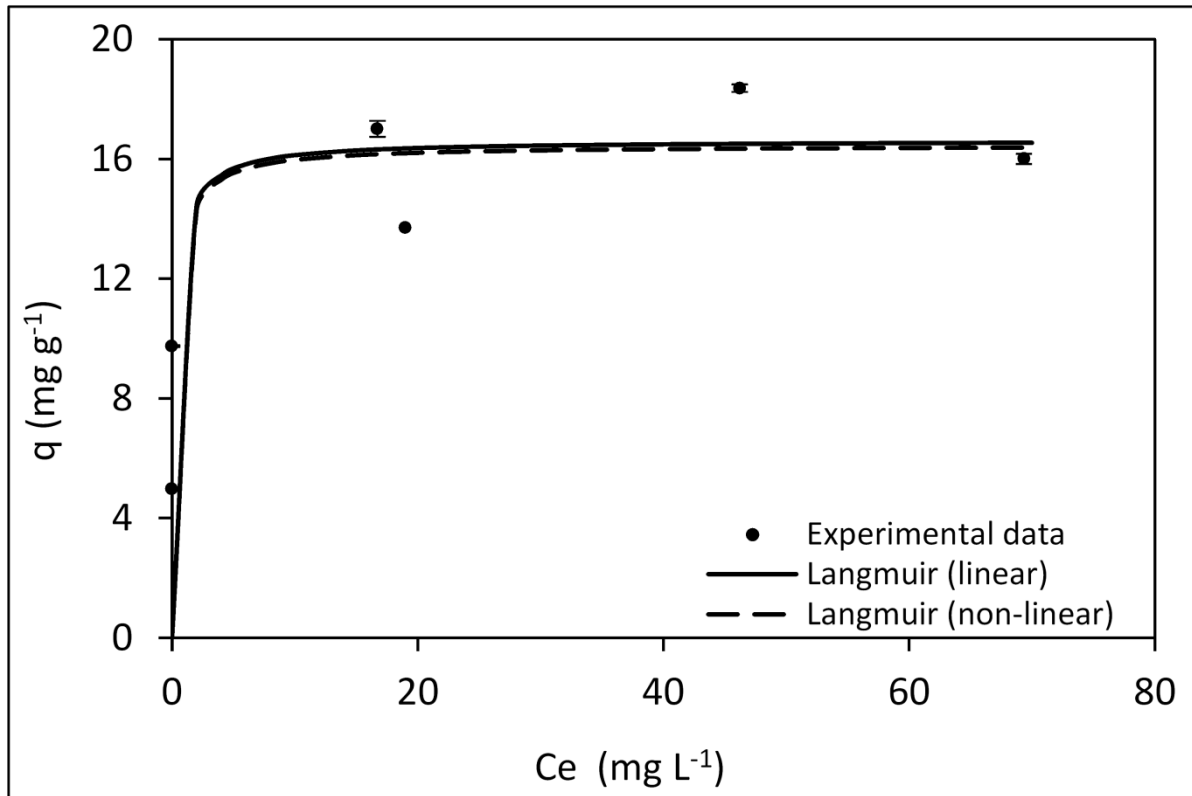


Figure 3. Adsorption of V(V) onto Red Mud modified Biochar (RM-BC) at 293 K.

Correlation co-efficient values ( $R^2$ ) of 0.989 and 1.00 at 293 K were obtained for the linearized and non-linearized Langmuir plots respectively while the Freundlich model yielded somewhat weaker co-efficients ( $R^2$ ) of 0.747 and 0.982 at 293 K with the linearized and non-linearized approaches respectively (Fig.3). The estimated parameters for each of the Langmuir and Freundlich plots are shown in Table 2. The  $K_L/A_L$  was used to estimate the saturation coverage of V(V) on the RM-BC adsorbent. The data obtained demonstrated that the Langmuir isotherm model provided the best fit for V(V) adsorption onto RM-BC. Both the linear and non-linear approaches to the Langmuir modelling showed a strong correlation. The plateau in V(V) uptake at higher equilibrium concentrations suggests a possible monolayer or saturation coverage of the surface by V(V). Similar observations for V(V) removal by montmorillonite [7] and zerovalent iron [44] respectively have been seen, while comparable findings for As adsorption onto RM modified biochar have also been reported [17].

Table 2. Langmuir & Freundlich constants for V(V) adsorption on Red Mud modified Biochar (RM-BC) at 293 K.

| <b>Langmuir Isotherm Data</b>   |                    |                               |                                |                                    |       |
|---------------------------------|--------------------|-------------------------------|--------------------------------|------------------------------------|-------|
|                                 | Temperature<br>(k) | $K_L$<br>(L g <sup>-1</sup> ) | $A_L$<br>(L mg <sup>-1</sup> ) | $K_L/A_L$<br>(mg g <sup>-1</sup> ) | $R^2$ |
| Linear                          | 293                | 3.42                          | 0.206                          | 16.60                              | 0.989 |
| Non-Linear                      | 293                | 3.33                          | 0.202                          | 16.45                              | 1.00  |
| <b>Freundlich Isotherm Data</b> |                    |                               |                                |                                    |       |
|                                 | Temperature<br>(K) | $K_F$<br>(L g <sup>-1</sup> ) | n                              | $R^2$                              |       |
| Linear                          | 293                | 7.20                          | 4.37                           | 0.747                              |       |
| Non-Linear                      | 293                | 7.64                          | 4.35                           | 0.982                              |       |

### 3.6 Adsorption Kinetics

Large scale adsorption systems require a detailed assessment of the optimum contact time between the adsorbate and adsorbent. Therefore, a kinetic evaluation of the rate of uptake of V(V) by the RM-BC biochar was necessary to yield the minimum contact time necessary for complete adsorption. As a means of defining the nature of the kinetic process for the adsorption of V(V) onto RM-BC biochar, the pseudo-first and second order reaction kinetic approaches were applied to the data and are presented in Table 3. Lagergren's pseudo-first-order (PFO) kinetic expression (Eq.5) and its linearised form (Eq. 6) can be outlined as follows [7, 8].

$$dq_t = k_1 (q_e - q_t) dt$$

$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \quad (5)$$

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (6)$$

The term  $k_1$  refers to the pseudo-first order rate constant for the V(V) adsorption process ( $\text{min}^{-1}$ ). Pseudo-second order (PSO) kinetics (Eq.7) can be used to assess the dependency of the process on the adsorbed V(V) concentration [48].

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \quad (7)$$

where  $k_2$  is the overall rate constant for the V(V) adsorption process [ $\text{L (mg min}^{-1})$ ],  $q_e$  ( $\text{mg g}^{-1}$ ) and  $q_t$  ( $\text{mg g}^{-1}$ ) are the amount of V(V) adsorbed at equilibrium and at any time  $t$ , respectively. The linearized form of the pseudo second order equation can be represented as in Eq.8  $k_2 q_e^2$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (8)$$

The initial sorption rate,  $h$ , as  $t \rightarrow 0$  can be defined as

$$h = k_2 q_e^2 \quad (9)$$

Preliminary adsorption tests on the rate of V(V) uptake by the RM-BC biochar indicated that the adsorption process is relatively fast with maximum adsorption and equilibrium conditions being reached within approximately 60 min of contact (Fig.4). This figure also indicates that the pseudo-second order approach provides a considerably better fit to the experimental data than the pseudo-first order approach. Comparison of the linearized and non-linearized approaches to the pseudo second order kinetics indicates a slightly higher  $R^2$  value of 0.996 for the linearized approach compared to 0.956 for the non-linear method. Equilibrium V(V) uptake in both cases were similar at  $4.82 \text{ mg g}^{-1}$  and  $5.23 \text{ mg g}^{-1}$  for linear and non-linear respectively.



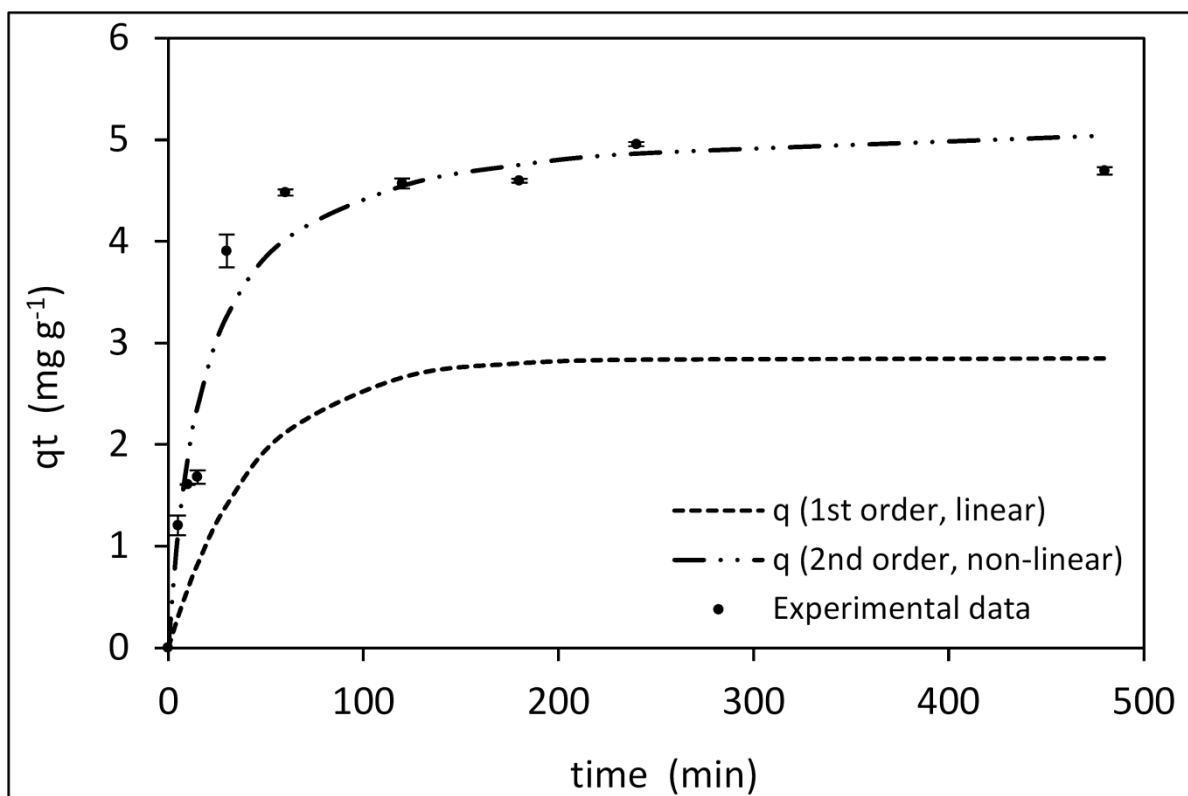


Figure 4. Effect of contact time on V(V) uptake by Red Mud modified Biochar (RM-BC) (initial V(V) concentration of  $10 \text{ mg L}^{-1}$ )

The initial V(V) adsorption rate,  $h$ , the equilibrium V(V) adsorption capacity,  $q_e$ , and the pseudo-second-order rate constant,  $k_2$ , can be determined experimentally from the slope and intercept by plotting  $t/q_t$  against  $t$  [8]. Fig.4 shows the appropriate non-linear second-order plot for V(V) adsorption on RM-BC biochar. The kinetic parameters identified using each model are presented in Table 3. The plot shows a correlation co-efficient ( $R^2$ ) of 0.996 for the pseudo second order model as opposed to a much weaker pseudo first order correlation co-efficient ( $R^2$ ) of 0.824 giving a strong indication that the adsorption of V(V) by RM-BC biochar follows a pseudo second order kinetics process.

Table 3. Kinetics of V(V) adsorption onto Red Mud modified Biochar (RM-BC) using the pseudo-first order and pseudo-second order approaches at 293 K.

| Pseudo-second order Kinetic parameters |       |                      |                      |                  |
|--|-------|----------------------|----------------------|------------------|
| Initial Vanadium                       | $R^2$ | Equilibrium Vanadium | Rate Constant, $k_2$ | Initial sorption |
|  |       |                      |                      |                  |

|                                       | Concentration<br>(mg L <sup>-1</sup> )                        |                | Uptake<br>(mg g <sup>-1</sup> )                            | (g mg <sup>-1</sup> min <sup>-1</sup> )                                     | Rate, h<br>(mg g <sup>-1</sup> min <sup>-1</sup> ) |
|---------------------------------------|---|----------------|--|---|--|
| Linear                                | 10  | 0.996          | 4.89   | 1.81 x 10 <sup>-2</sup>   | 0.435  |
| Non-linear                            | 10  | 0.956          | 5.23   | 1.06 x 10 <sup>-2</sup>   | 0.290  |
| Pseudo-first order Kinetic Parameters |   |                |  |   |  |
|                                       | Initial<br>Vanadium<br>Concentration<br>(mg L <sup>-1</sup> ) | R <sup>2</sup> | Equilibrium<br>Vanadium<br>Uptake<br>(mg g <sup>-1</sup> ) | Rate<br>Constant, k <sub>1</sub><br>(g mg <sup>-1</sup> min <sup>-1</sup> ) |  |
| Linear                                | 10  | 0.824          | 2.84   | 2.27 x 10 <sup>-2</sup>   |  |

### 3.7 Adsorption Thermodynamics

To determine the thermodynamic parameters of V(V) adsorption on the RM-BC, the effect of temperature was assessed by carrying out the adsorption process at 293, 303, 313, 323, 333 and 343 K. Adsorption increased with increasing temperature indicating an endothermic binding process. A similar observation was reported for uranium onto Ferric nitrate modified red mud [34]. Using the Van't Hoff equation (Eq.10), a plot of ln K versus 1/T was used as the starting point to calculate the standard enthalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ) changes for the binding process [5]. The  $\Delta H^\circ$  and the  $\Delta S^\circ$  values were calculated from the slope and intercept respectively from Fig.5. These computed values along with the Gibbs free energy change ( $\Delta G^\circ$ ) value were subsequently calculated from Eq.11 and are presented in Table 4.

$$\ln K = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (10)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (11)$$

Where  $\Delta H^\circ$  (kJ mol<sup>-1</sup>),  $\Delta G^\circ$  (kJ mol<sup>-1</sup>) and  $\Delta S^\circ$  (kJ mol<sup>-1</sup> K<sup>-1</sup>), R is the universal gas constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup>) and T (K) is the absolute temperature.

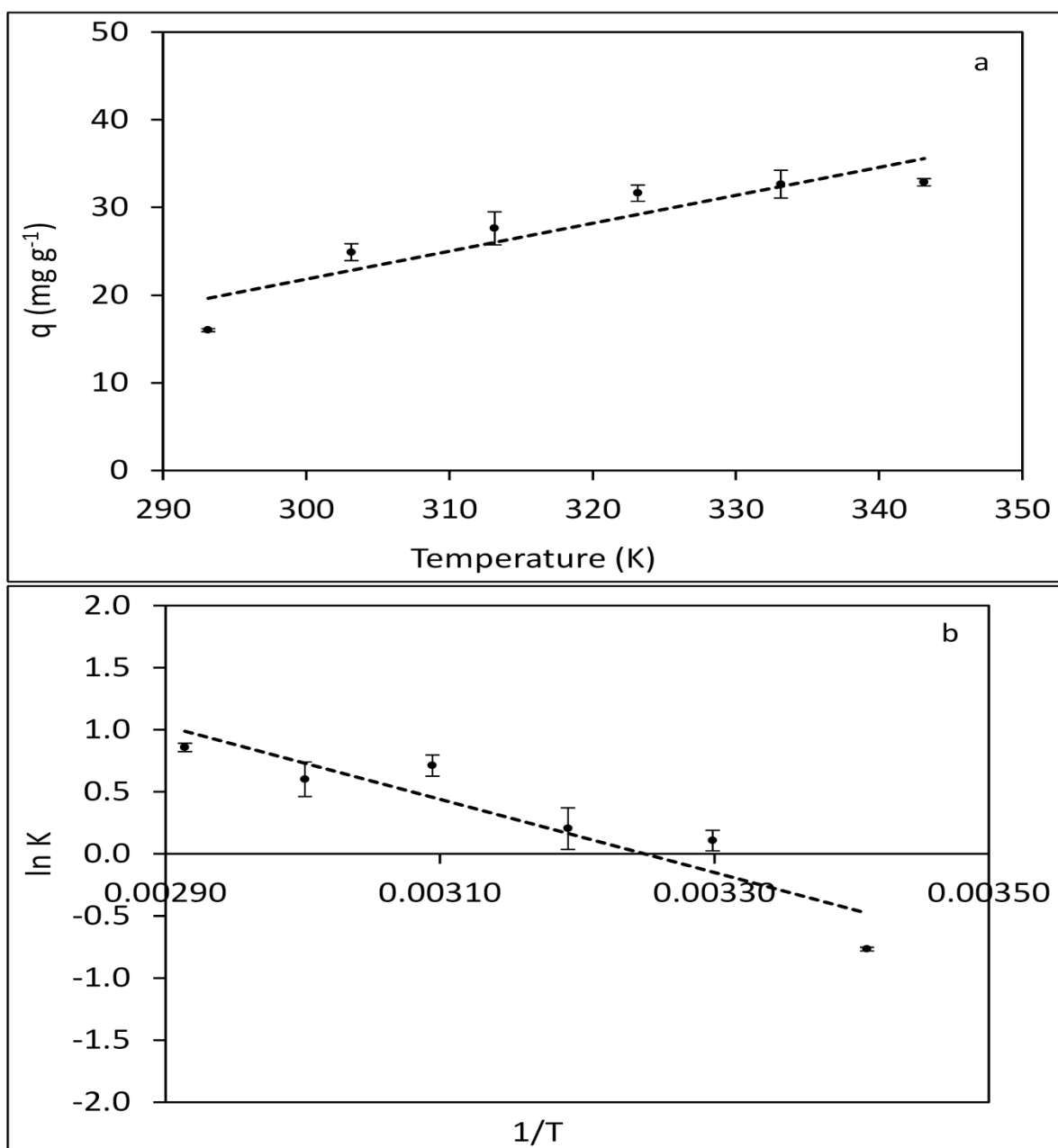


Figure 5. (a) Effect of temperature and (b) Arrhenius plot for adsorption of V(V) onto Red Mud modified Biochar (RM-BC) at 293, 303, 313, 323, 333 and 343 K.

Table 4. Thermodynamic parameters for the adsorption of V(V) on Red Mud modified Biochar (RM-BC) at 293, 303, 313, 323, 333 and 343 K.

| $\Delta G^{\circ}$ (kJ mol <sup>-1</sup> ) |       |       |       |       |       | $\Delta H^{\circ}$ (kJ mol <sup>-1</sup> ) | $\Delta S^{\circ}$ (J mol <sup>-1</sup> K <sup>-1</sup> ) |
|--|-------|-------|-------|-------|-------|--|---|
| 293 K                                      | 303 K | 313 K | 323 K | 333 K | 343 K |  |   |
| 1.87                                       | -0.27 | -0.53 | -1.91 | -1.67 | -2.45 | 24.53                                      | 97.71   |

---

The increasingly negative values of  $\Delta G^\circ$  with increasing temperature indicate that as the temperature of the adsorption process increases, the V(V) adsorption process onto the RM-BC biochar becomes more spontaneous. This is also clearly supported by the fact that the  $\Delta H^\circ$  is positive, therefore the adsorption process is endothermic and that the addition of heat to the adsorption process system increases the level of V(V) uptake. The magnitude of the enthalpy change suggests that the nature of the V(V) binding is relatively weak and in the physisorption range of binding. A positive entropy change ( $\Delta S^\circ$ ) also indicates an increase in randomness at the solid-solution interface during adsorption of V(V) [49].

#### **4.0 Conclusions**

Currently there is an increased need to focus on developing new and relatively cheap biosorbent materials for the removal of a range of metal contaminants from aqueous waste solutions. Specifically, in this study, a red mud modified sawdust biochar was prepared and its ability to adsorb vanadium from aqueous solution was evaluated.

The adsorption isotherm for modified RM-BC biochar indicated an uptake capacity of 16.45 mg g<sup>-1</sup> vanadium. The adsorption process closely followed the Langmuir approach and the Type I adsorption profile indicated a very clear vanadium adsorption saturation point for the modified biochar. The mechanism was most likely a pore-filling or weak electrostatic interaction between the vanadium and the modified biochar surface. The heat change accompanying adsorption of the vanadium on the modified biochar was endothermic and its magnitude (+24.5 kJ mol<sup>-1</sup>) suggests that the nature of the interaction was effectively physisorption and weak in nature. The extent of the vanadium uptake was significantly influenced by the aqueous solution pH and an optimum pH of pH 4.0 was observed. The adsorption level was largely unaffected by a range of solution ionic strengths up to 0.1M NaCl. In competitive binary adsorption studies between V(V) and either Na(I) or Al(III), the V(V) adsorption level remained largely unchanged even at high competing cation concentrations.

While application of abundant supplies of biosorbent materials to remove metals from wastewater is gaining increasing attention, there are a number of practical considerations to be addressed with each biosorbent material before it can be applied on a large scale. In the case of this research work, the potential practical application of the red mud modified sawdust biochar as a biosorbent for removal of vanadium from waste streams has been demonstrated and offers significant potential due to it being derived from both a readily available biosorbent material source (sawdust) and an existing solid waste (red mud). In

practical application, in order to effect the significant vanadium adsorption capacity observed in this work, it would be necessary to carry out a pre-adsorption pH adjustment of aqueous waste streams to approximately pH 4.0. Given the relatively weak interaction between the vanadium and the modified biochar surface, the possibility of recovery of the bound vanadium and the ultimate regeneration of the adsorbent may be feasible.

### **Acknowledgements:**

The authors acknowledge support from the Geological Survey of Ireland (GSI, project no. 2018-ERAMIN2-002), the Irish Environmental Protection Agency (EPA) and an EU ERA-MIN2 award to the EU Biomimic Consortium (ID 86).

### **5.0 References**

- [1] Ryabina, A., Shevchenko, V., Adsorption Properties of an Aluminum Powder Modified with Vanadium Pentoxide. *RUSS J PHYS CH A* 2018, 92, 2302–2308.
- [2] Zhang, L., Liu, X., Xia, W., Zhang, W., Preparation and characterization of chitosan-zirconium (IV) composite for adsorption of vanadium (V). *INT J BIOL MACROMOL* 2014, 64, 155–161.
- [3] Del Carpio, E., Hernández, L., Ciangherotti, C., Coa, V.V., et al., Vanadium: History, chemistry, interactions with alpha-amino acids and potential therapeutic applications. *COORDIN CHEM REV* 2018, 372, 117–140.
- [4] Oyewo, O.A., Onyango, M.S., Wolkersdorfer, C., Adsorptive Performance of Surface-Modified Montmorillonite in Vanadium Removal from Mine Water. *MINE WATER ENVIRON* 2017, 36, 628–637.
- [5] Omidinasab, M., Rahbar, N., Ahmadi, M., Kakavandi, B., Ghanbari, F., Kyzas, G., Martinez, S., Jaafarzadeh, N., Removal of vanadium and palladium ions by adsorption onto magnetic chitosan nanoparticles. *ENVIRON SCI POLLUT R* 2018, 25, 34262–34276.
- [6] Leiviskä, T., Khalid, M.K., Sarpola, A., Tanskanen, J., Removal of vanadium from industrial wastewater using iron sorbents in batch and continuous flow pilot systems. *J ENVIRON MANAGE* 2017, 190, 231–242.
- [7] Zhu, H., Xiao, X., Guo, Z., Han, X., Liang, Y., Zhang, Y., Zhou, C., Adsorption of vanadium (V) on natural kaolinite and montmorillonite: characteristics and mechanism. *APPL CLAY SCI* 2018, 161, 310–316.
- [8] Jana, S., Ray, J., Jana, D., Mondal, B., Bhanjab, S., Tripathy, T., Removal of vanadium (IV) from water solution by sulfated Katira gum-cl-poly (acrylic acid) hydrogel. *COLLOID SURFACE A* 2019, 566, 70–83..

- [9] Zhang, R., Leiviskä, T., Tanskanen, J., Gao, B., Yue, Q., Utilization of ferric groundwater treatment residuals for inorganic-organic hybrid biosorbent preparation and its use for vanadium removal. *CHEM ENG J* 2019, *361*, 680–689.
- [10] Spanka, M., Mansfeldt, T., Bialucha, R., Chromium, molybdenum, vanadium, and fluoride sorption from steelwork slag eluates by different mineral additives. *INT J ENVIRON SCI TE* 2018, *15*, 1381–1392.
- [11] Gomes, H.I., Funari, V., Mayes, W.M., Rogerson, M., Prior, T., Recovery of Al, Cr and V from steel slag by bioleaching: Batch and column experiments. *J ENVIRON MANAGE* 2018, *222*, 30–36.
- [12] Gomes, H.I., Jones, A., Rogerson, M., Greenway, G.M., Lisbona, D., Burke, I., Mayes, W., Removal and recovery of vanadium from alkaline steel slag leachates with anion exchange resins. *J ENVIRON MANAGE* 2017, *187*, 384–392.
- [13] Anirudhan, T., Radhakrishnan, P., Adsorptive performance of an amine-functionalized poly (hydroxyethylmethacrylate)-grafted tamarind fruit shell for vanadium (V) removal from aqueous solutions. *CHEM ENG J* 2010, *165*, 142–150.
- [14] He, Q., Si, S., Zhao, J., Yan, H., Sun, B., Cai, Q., Yu, Y., Removal of vanadium from vanadium-containing wastewater by amino modified municipal sludge derived ceramic. *SAUDI J BIOL SCI* 2018, *25*, 1664–1669.
- [15] Thamilarasi, M.J.V., Anilkumar, P., Theivarasu, C., Sureshkumar, M.V., Removal of vanadium from wastewater using surface-modified lignocellulosic material. *ENVIRON SCI POLLUT R* 2018, *25*, 26182–26191.
- [16] Murnane, J.G., Ghanim, B., O'Donoghue, L., Courtney, R., O'Dwyer, T.F., Pembroke, J.T., Advances in Metal Recovery from Wastewaters Using Selected Biosorbent Materials and Constructed Wetland Systems, in: *Water and Wastewater Treatment*, IntechOpen, 2019.
- [17] Wu, C., Huang, L., Xue, S.-G., Huang, Y.-Y., Hartley, W., Cui, M-Q., Wong, M-H., Arsenic sorption by red mud-modified biochar produced from rice straw. *ENVIRON SCI POLLUT R* 2017, *24*, 18168–18178.
- [18] Sizmur, T., Fresno, T., Akgül, G., Frost, H., Moreno-Jiménez, E., Biochar modification to enhance sorption of inorganics from water. *BIORESOURTE TECHNOL* 2017, *246*, 34–47.
- [19] Ahsan, M.A., Islam, M.T., Hernandez, C., Castro, E., Katlaa, S., Kimb, H., Linb, Y., Curryc, M., Gardea-Torresdeya, J., Noveron, J., Biomass conversion of saw dust to a functionalized carbonaceous materials for the removal of Tetracycline, Sulfamethoxazole and Bisphenol A from water. *J ENVIRON ENG* 2018, *6*, 4329–4338.
- [20] Ghanim, B., Investigation of the effects of hydrothermal carbonisation process parameters on the produced hydrochar properties and its applications, PhD Thesis, University of Limerick, Ireland, 2018.

- [21] Khasri, A., Bello, O.S., Ahmad, M.A., Mesoporous activated carbon from *Pentace* species sawdust via microwave-induced KOH activation: optimization and methylene blue adsorption. *RES CHEM INTERMEDIAT* 2018, *44*, 5737–5757.
- [22] Sun, L., Chen, D., Wan, S., Yu, Z., Performance, kinetics, and equilibrium of methylene blue adsorption on biochar derived from eucalyptus saw dust modified with citric, tartaric, and acetic acids. *BIORESOURCE TECHNOL* 2015, *198*, 300–308.
- [23] Yao, Y., Gao, B., Fang, J., Zhang, M., Chen, H., Zhou, Y., Creamer, A., Sun, Y., Yang, L., Characterization and environmental applications of clay-biochar composites. *CHEM ENG J* 2014, *242*, 136–143.
- [24] Sharififard, H., Pepe, F., Aprea, P., de Gennaro, B., Chemical modification of activated carbon surface with iron functional groups for efficient separation of vanadium: batch and column study. *RES CHEM INTERMEDIAT* 2017, *43*, 6553–6570.
- [25] Yoon, K., Cho, D.-W., Tsang, Y.F., Tsang, D.C., Kwon, E., Song, H., Synthesis of functionalised biochar using red mud, lignin, and carbon dioxide as raw materials. *CHEM ENG J* 2019, *361*, 1597–1604.
- [26] Mo, J., Yang, Q., Zhang, N., Zhang, W., Zheng, Y., Zhang, Z., A review on agro-industrial waste (AIW) derived adsorbents for water and wastewater treatment. *J ENVIRON MANAGE* 2018, *227*, 395–405.
- [27] Awad, A.M., Shaikh, S.M., Jalab, R., Gulied, M.H., Nasser, M., Benamor, A., Adham, S., Adsorption of Organic Pollutants by Natural and Modified Clays: A Comprehensive Review. *SEP PURIF TECHNOL* 2019, *228*, 115719.
- [28] Cusack, P.B., Healy, M.G., Ryan, P.C., Burke, I.T., Donoghue, L., Ujaczki, E., Courtney, R., Enhancement of bauxite residue as a low-cost adsorbent for phosphorus in aqueous solution, using seawater and gypsum treatments. *J CLEAN PROD* 2018, *179*, 217–224.
- [29] Bhatnagar, A., Minocha, A.K., Pudasainee, D., Chung, H.-K., Kim, S.-H., Kim, S.-H., Lee, G., Min, B., Jeon, B.-H., Vanadium removal from water by waste metal sludge and cement immobilization. *CHEM ENG J* 2008, *144*, 197–204.
- [30] Cusack, P.B., Courtney, R., Healy, M.G., O'Donoghue, L.M., Ujaczki, E., An evaluation of the general composition and critical raw material content of bauxite residue in a storage area over a twelve-year period. *J CLEAN PROD* 2019, *208*, 393–401.
- [31] Li, Y., Haynes, R.J., Chandrawana, I., Zhou, Y.-F., Properties of seawater neutralized bauxite residues and changes in chemical, physical and microbial properties induced by additions of gypsum and organic matter. *J ENVIRON MANAGE* 2018, *223*, 489–494.
- [32] Ren, J., Chen, J., Han, L., Wang, M., Yang, B., Du, P., Li, F., Spatial distribution of heavy metals, salinity and alkalinity in soils around bauxite residue disposal area. *SCI TOTAL ENVIRON* 2018, *628*, 1200–1208.

- [33] Avdibegovic, D., Regadio, M., Binnemans, K., Efficient separation of rare earths recovered by a supported ionic liquid from bauxite residue leachate. *RSC ADV* 2018, 8, 11886–11893.
- [34] Wu, W., Chen, D., Li, J., Su, M., Chen, N., Enhanced adsorption of uranium by modified red muds: adsorption behavior study. *ENVIRON SCI POLLUT R* 2018, 25, 18096–18108.
- [35] Zou, Q., An, W., Wu, C., Li, W., Fu, A., Xiao, R., Chen, H., Xue, S., Red mud-modified biochar reduces soil arsenic availability and changes bacterial composition. *ENVIRON CHEM LETT* 2018, 16, 615–622.
- [36] Ujaczki, É., Feigl, V., Molnár, M., Cusack, P., Curtin, T., Courtney, R., O'Donoghue, L., Davris, P., Hugi, C., Evangelou, M., Balomenos, E., Lenz, M., Re-using bauxite residues: benefits beyond (critical raw) material recovery. *J CHEM TECHNOL BIOT* 2018, 93, 2498–2510.
- [37] Milacic, R., Zuliani, T., Scancar, J., Environmental impact of toxic elements in red mud studied by fractionation and speciation procedures. *SCI TOTAL ENVIRON* 2012, 426, 359–365.
- [38] Atasoy, A., Bilgic, B., Adsorption of copper and zinc ions from aqueous solutions using montmorillonite and bauxite as low-cost adsorbents. *MINE WATER ENVIRON* 2018, 37, 205–210.
- [39] Gupta, V.K., Sharma, S., Removal of cadmium and zinc from aqueous solutions using red mud. *ENVIR SCI TECH* 2002, 36, 3612–3617.
- [40] Das, B., Mohanty, K., A review on advances in sustainable energy production through various catalytic processes by using catalysts derived from waste red mud. *RENEW ENERG* 2019, 143, 1791 - 1811.
- [41] Xu, L., Tian, J., Wu, H., Fang, S., Lu, Z., Ma, C, Sun, W., Hu, Y., Anisotropic surface chemistry properties and adsorption behavior of silicate mineral crystals. *ADV COLLOID INTERFAC* 2018, 256, 340–351.
- [42] Chen, Y., Liang, W., Li, Y., Wu, Y., Chen, Y., Xiao, W., Zhao, L., Zhang, J., Li, H., Modification, application and reaction mechanisms of nano-sized iron sulfide particles for pollutant removal from soil and water: A review. *CHEM ENG J* 2018, 362, 144-159.
- [43] Amin, M., Alazba, A., Shafiq, M., Application of biochar derived from date palm biomass for removal of lead and copper ions in a batch reactor: Kinetics and isotherm scrutiny. *CHEM PHYS LETT* 2019, 722, 64–73.
- [44] Bello, A., Leiviskä, T., Zhang, R., Tanskanen, J., Maziarz, P., Matusik, J., Bhatnagar, A., Synthesis of zerovalent iron from water treatment residue as a conjugate with kaolin and its application for vanadium removal. *J HAZARD MATER* 2019, 374, 372–381
- [45] Freundlich, H.M.F., Over the Adsorption in Solution. *J PHYS CHEM* 1926.



- [46] Langmuir, I., The adsorption of gases on plane surfaces of glass, mica and platinum. *J AM CHEM SOC* 1918, *40*, 1361–1403.
- [47] Ortiz, N., Pires, M., Bressiani, J., Use of steel converter slag as nickel adsorber to wastewater treatment. *WASTE MANAGE* 2001, *21*, 631–635.
- [48] Xing, B., McGill, W.B., Dudas, M.J., Maham, Y., Sorption of phenol by selected biopolymers: isotherms, energetics, and polarity. *ENVIR SCI TECH* 1994, *28*, 466–473.
- [49] Namasivayam, C., Ranganathan, K., Recycling of “waste” Fe (III)/Cr (III) hydroxide for the removal of nickel from wastewater: adsorption and equilibrium studies. *WASTE MANAGE* 1994, *14*, 709–716