

## Removal of V(V) ions from aqueous solutions using oxidized multi-walled carbon nanotubes

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### ABSTRACT

In this paper, multi-walled carbon nanotubes (MWCNTs) were oxidized and used as an adsorbent for the removal of vanadium (V(V)) ions from aqueous solution. Oxidized MWCNTs were characterized by scanning electron microscope and Brunauer–Emmett–Teller measurements. The effects of various parameters such as solution pH (1.0–8.0), adsorbent dose (0.001–0.08 g), contact time (7.0–150 min), and temperature (25–55 °C) were investigated. The results demonstrated that the maximum percentage of V(V) adsorption was found at pH 5.0 and 90 min contact time with 0.03 g oxidized MWCNTs. Kinetic adsorption data were analyzed using the first-order model and the pseudo-second-order model. The regression results showed that the adsorption kinetics were more accurately represented by the pseudo-second-order model. The equilibrium data in aqueous solutions were fitted to Langmuir, Freundlich, and Tempkin isotherms and the equilibrium adsorption of V(V) was best described by the Freundlich isotherm model.

**Key words** | adsorption, oxidized multi-walled carbon nanotube, removal efficiency, vanadium

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### INTRODUCTION

Heavy metals represent one of the major ecological problems inducing detrimental effects on both human and environmental health (Sun *et al.* 2014). The World Health Organization (WHO) estimates that about 25% of the diseases facing humans today occur due to long-term exposure to environmental pollution, including air, soil, and water pollution (Wong *et al.* 2003; Bagheri *et al.* 2012). Rapid industrial development is resulting in increasing levels of heavy metal residues in biological and environmental samples. The vanadium (V(V)) ion is one of the heavy metal ions causing environmental pollution specifically in water (Dai *et al.* 2012; Cheng *et al.* 2014). Once absorbed, V(V) can be accumulated in the body and greatly threaten the health of a human. V(V) has been widely used in various industries such as steel, ceramic, glass, and textile, and facilities such as oil refineries and power plants, which can release large quantities of V(V) ions to the aquatic ecosystem. These V(V) ions can enter the human body through the food chain and may cause breathing disorders and

paralysis, and may have negative effects on the liver and kidney (Zhang *et al.* 2014). Removal of heavy metals from water has been a major preoccupation for many years. A number of methods have been studied for the removal of V(V) ions from water, such as precipitation, coagulation, adsorption, ultrafiltration, reverse osmosis, and membrane separation (Sobhanardakani *et al.* 2013; Wang *et al.* 2013). The disadvantage of the precipitation method is production of sludge that needs further processing after precipitation. Reverse osmosis is an expensive method. Adsorption is one of the best methods reported for removal of pollutants (Gong *et al.* 2009; Wang *et al.* 2011; Xu *et al.* 2012). Carbon materials, agricultural and industrial wastes, biomaterials, and other adsorbents have been reported for V(V) adsorption (Xin *et al.* 2012). Recently, the application of carbon nanotubes (CNTs) in environmental remediation and pollutant removal has become a focus for research due to their excellent properties, such as high surface area, good adsorption, and layered structures (Yu & Fugetsu 2010; Tang *et al.*

2012). CNTs include single-wall CNTs and multi-wall (MW) CNTs, the latter comprising a number of layers (Chiang & Wu 2010). The adsorption capacity of CNTs can be improved by oxidation with  $\text{KMnO}_4$ ,  $\text{H}_2\text{O}_2$ ,  $\text{NaOCl}$ , or  $\text{HNO}_3$ , any of which removes impurities, increases the surface area, and introduces oxygen-containing functional groups, thus altering adsorption characteristics (Sheng *et al.* 2010).

In the present study, oxidized MWCNTs were used for removal of V(V) ions from aqueous solution. The effects of pH, oxidized MWCNT dose, contact time, and temperature on adsorption capacity of oxidized MWCNTs have been investigated. Based on these studies, the Langmuir, Freundlich, and Tempkin isotherm models were used to fit the equilibrium data. Finally, the adsorption kinetics were evaluated.

## METHODOLOGY

### Chemicals and reagents

All chemicals and reagents were purchased from Merck (Darmstadt, Germany). MWCNTs with length 5–15  $\mu\text{m}$ , outer diameter 50–80 nm, inner diameter 5–10 nm, purity  $\geq 95\%$  were purchased from Sigma–Aldrich (Madrid, Spain).

A stock solution of V(V) was prepared by dissolving 2.296 g of the powder in 1,000 mL double-distilled water. V(V) solutions of initial concentrations of 24–48  $\text{mg L}^{-1}$  were prepared by diluting the stock solution in appropriate proportions. Double-distilled water was used in all experiments.

### Apparatus

Heavy metal concentrations were measured using inductively coupled plasma optical emission spectrometry (Verian710-Es, Australia). A pH meter (780, Metrohm, Zofingen, Switzerland), equipped with a combined Ag/AgCl glass electrode was used for pH measurements. Morphology and structure of the MWCNTs were characterized by scanning electron microscope (SEM-EDX, XL30 and Philips, Eindhoven, The Netherlands). Specific surface area (SSA) was defined by  $\text{N}_2$  adsorption–desorption porosimetry (77 K) using a porosimeter (Bel Japan, Inc., Osaka, Japan).

### Oxidation of MWCNTs

For oxidation, 2 g MWCNTs were placed in a 1 L round-bottom flask with reflux condenser, and 300 mL concentrated nitric acid (65%) were added. The mixture was refluxed for 48 h at 120 °C, cooled to room temperature, diluted with 500 mL double-distilled water, and vacuum-filtered through filter paper (3 mm porosity, Whatman, Maidstone, UK). Washing was repeated until the pH became neutral, followed by drying in a vacuum oven at 100 °C (Muataz *et al.* 2010).

### Batch adsorption experiments

For the batch adsorption experiments 0.7 mL of 1 mM V(V) solution were transferred into a 25 mL stoppered conical flask. The pH of the solution was adjusted to 7.0 using 0.1  $\text{mol L}^{-1}$  HCl and/or 0.1  $\text{mol L}^{-1}$  NaOH solutions. Then, 0.03 g of adsorbent were added, and the solution was shaken at room temperature for 90 min to facilitate adsorption of the metal ions onto the oxidized MWCNTs. Then, the metal-loaded oxidized MWCNTs were separated from the mixture using Whatman filter paper with a pore diameter of 42  $\mu\text{m}$ . Finally, concentrations of the V(V) ions which remained in the solution were determined by inductively coupled plasma optical emission spectrometry (Verian710-Es, Australia) and the concentrations of the V(V) ions remaining in the adsorbent phase ( $q_e$ ,  $\text{mg g}^{-1}$ ) were calculated using Equation (1)

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where  $q_e$  ( $\text{mg g}^{-1}$ ) is the equilibrium adsorption capacity,  $C_0$  and  $C_e$  ( $\text{mg L}^{-1}$ ) are the metal concentrations initially and at equilibrium, respectively,  $V$  (L) is the volume of solution, and  $W$  (g) is the weight of adsorbent (Yu *et al.* 2013).

Finally, the V(V) removal percent ( $R\%$ ) was calculated by Equation (2) (Bhaumik *et al.* 2012)

$$R(\%) = \frac{C_0 - C_e}{C_0} \times 100 \quad (2).$$

## RESULTS AND DISCUSSION

### Characterizations of oxidized MWCNTs

Figure 1 shows the morphological structure of oxidized MWCNTs. SEM clearly suggests the crystalline tubular structure of nanotubes.

SSAs are commonly reported as Brunauer–Emmett–Teller (BET) surface areas obtained by applying the theory of BET to nitrogen adsorption–desorption isotherms measured at 77 K. This is a standard procedure for the determination of the SSA of a sample. The SSA of a sample is determined by physical adsorption of a gas onto the surface of the solid and by measuring the amount of adsorbed gas corresponding to the monomolecular layer on the surface. The data are treated according to the BET theory (Brunauer *et al.* 1938; Walton & Snurr 2007).

The results of the BET method showed that the SSAs of MWCNTs and oxidized MWCNTs were 115 and 158  $\text{m}^2 \text{g}^{-1}$ , respectively.

Pore size distributions of MWCNTs and oxidized MWCNTs were measured using the Barrett–Johner–Halenda method. The average pore diameter and pore volume were 29 nm and 0.17  $\text{cm}^3 \text{g}^{-1}$  for MWCNTs, and 36 nm and 0.24  $\text{cm}^3 \text{g}^{-1}$  for oxidized MWCNTs, respectively.

The results indicated that the pore volume and average pore diameter of MWCNTs are less than oxidized

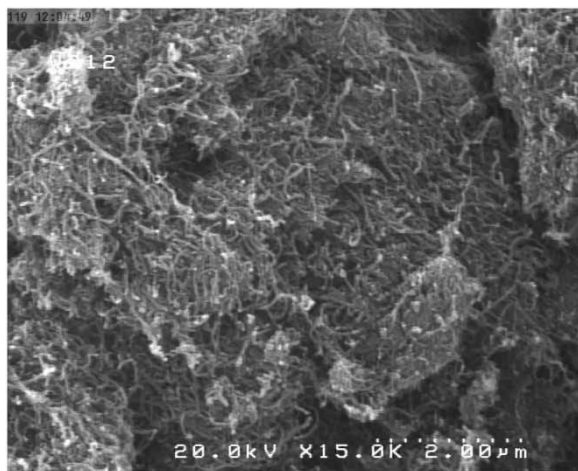


Figure 1 | SEM image of oxidized MWCNTs.

MWCNTs. This can be comprehended considering the structure change of oxidized MWCNTs with nitric acid, which can easily break up the MWCNTs into smaller pieces with a large number of defects on their surface, open the tips, and probe the holes through the MWCNTs (Li *et al.* 2003a).

### Optimization of adsorption

Primary study shows that the adsorption efficiency depends strongly on the solution pH, oxidized MWCNT dose, contact time, and temperature.

### Effect of pH

In the adsorption of heavy metal ions, the pH of the aqueous solution is one of the main influences, and an appropriate pH value can improve the adsorption efficiency. The influence of pH on the adsorption of V(V) was investigated in the pH range of 1.0–8.0 with a stirring time of 90 min and V(V) concentration fixed at 30  $\text{mg L}^{-1}$ . The results are shown in Figure 2. It was observed that the adsorption percentage of V(V) increased by increasing the aqueous solution pH from 1.0 to 5.0, and a maximum adsorption for the V(V) was obtained at pH 5.0. When the pH was further increased from 6.0 to 8.0, the adsorption percentage decreased. The

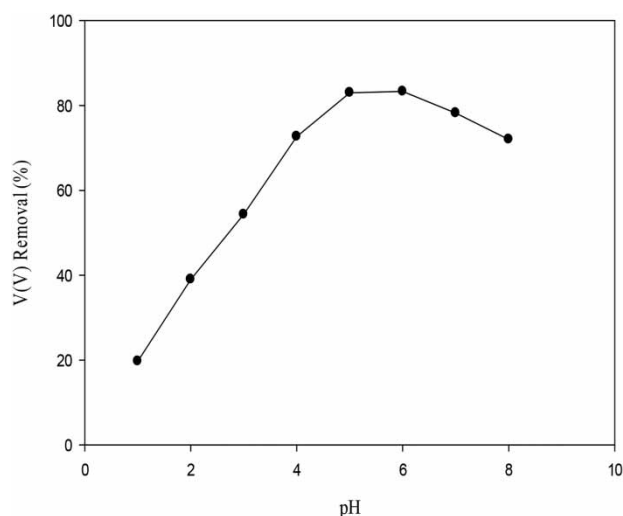
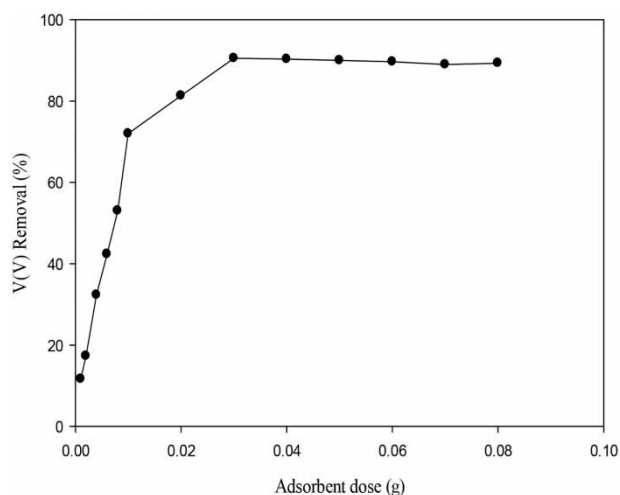


Figure 2 | Effect of pH on the removal of V(V) from aqueous solution by oxidized MWCNTs ( $C_0 = 30 \text{ mg L}^{-1}$ , contact time = 90 min, dose of oxidized MWCNTs = 0.03 g, and temperature = 25 °C).

pH of point of zero charge ( $\text{pH}_{\text{zpc}}$ ) is an important property and indicates the electrical neutrality of the adsorbent and surface at a particular value of pH;  $\text{pH}_{\text{zpc}}$  for the oxidized MWCNTs was determined at around 4.0 (Yang *et al.* 2009). When the pH is low ( $<\text{pH}_{\text{zpc}}$ ), the decrease in the adsorption efficiency of V(V) can be attributed to the increase in the proton concentration. A proton can compete with V(V) in the adsorption mechanism. Therefore, by increasing the pH ( $>\text{pH}_{\text{zpc}}$ ), the positive charge of the surface decreases and the repulsion between the positive surface and V(V) ions decreases too, which leads to a higher amount of adsorption. When the pH of the solution is higher than 6.0, the decreased adsorption efficiency of V(V) ions might result from the other (V(V)) oxidation states that form at high pH, such as  $\text{V}_3\text{O}_9^{3-}$ ,  $\text{HVO}_4^{2-}$ , and  $\text{HV}_2\text{O}_7^{3-}$  and which might affect the adsorption capacity on the oxidized MWCNTs. Thus, pH 5.0 was adopted for further studies. A similar behavior has been reported for V(V) adsorption on chitosan-zirconium(IV) (Li *et al.* 2003b; Zhang *et al.* 2014).

### Effect of adsorbent dose

The adsorbent dose is an important parameter in adsorption studies because it determines the capacity of the adsorbent for a given initial concentration of metal solution. The effect of amount of oxidized MWCNTs on the V(V) removal at  $30 \text{ mg L}^{-1}$  is shown in Figure 3. It is observed that the removal



**Figure 3** | Effect of dose of oxidized MWCNTs on the removal of V(V) from aqueous solution by oxidized MWCNTs ( $C_0 = 30 \text{ mg L}^{-1}$ , solution pH = 5, contact time = 90 min, and temperature =  $25^\circ\text{C}$ ).

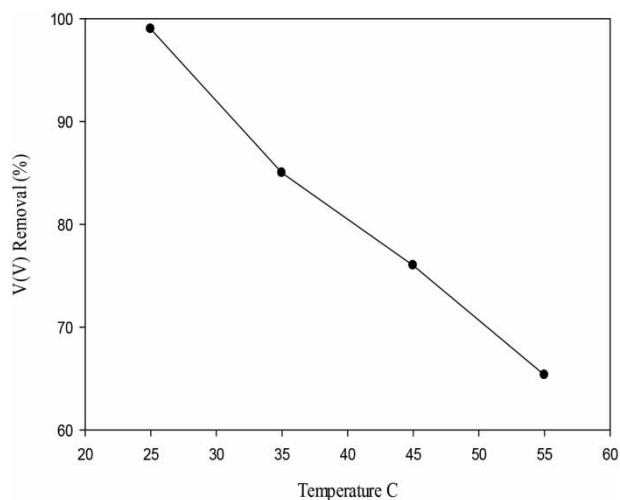
efficiency increases from 11.5 to 90.5% with an increase in adsorbent dose from 0.001 to 0.03 g and the maximum adsorption was observed at 0.03 g. This is due to an increase in the surface area and availability of more active sites for adsorption. Hence, 0.03 g of oxidized MWCNTs was used in all experiments. The results are in agreement with those reported in the literature (Afkhani *et al.* 2010; Dai *et al.* 2012).

### Effect of temperature

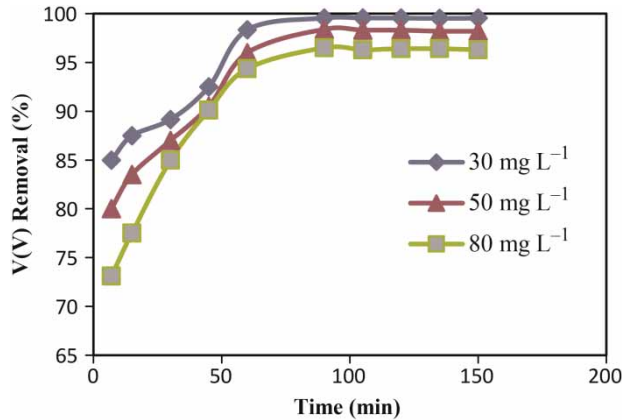
The effect of the temperature on the adsorption of V(V) ions was studied in the range  $25\text{--}55^\circ\text{C}$  using oxidized MWCNTs as an adsorbent and at the V(V) concentration of  $30 \text{ mg L}^{-1}$  (Figure 4). The experimental results showed that the adsorption capacity decreases with increase in the solution temperature. This indicates that the adsorption of V(V) ions on oxidized MWCNTs is exothermic in nature. The decrease in the rate of adsorption with the increase in temperature may be attributed to the weakening of adsorption forces between the active sites of the adsorbents and adsorbate species and also between the adjacent molecules of the adsorbed phases.

### Adsorption kinetics

The effect of adsorption time on the removal of V(V) is shown in Figure 5. The results of time optimization showed that adsorption of V(V) ions by oxidized



**Figure 4** | Effect of temperature on the removal of V(V) from aqueous solution by oxidized MWCNTs ( $C_0 = 30 \text{ mg L}^{-1}$ , solution pH = 5, dose of oxidized MWCNTs = 0.03 g, and contact time = 90 min).



**Figure 5** | Effect of contact time on the removal of V(V) from aqueous solution by oxidized MWCNTs ( $C_0 = 30, 50,$  and  $80 \text{ mg L}^{-1}$ , solution pH = 5, dose of oxidized MWCNTs = 0.03 g, and temperature =  $25^\circ \text{C}$ ).

MWCNTs increased with time and reached equilibrium at about 90 min. A rapid adsorption was observed within 7 min which shows the availability of a large number of vacant sites. Subsequently, the diminishing availability of the remaining active sites and the decrease in the driving force led to the slow adsorptive process. A similar phenomenon has been observed in the adsorption of heavy metal from aqueous solutions on chitosan (Kolodynska 2011).

To investigate the kinetics of adsorption, three different initial concentrations of V(V) were chosen: 30, 50, and  $80 \text{ mg L}^{-1}$ . The adsorption kinetics data of V(V) ions were analyzed using a first-order kinetic model and a pseudo-second-order kinetic model.

The first-order model can be expressed as Equation (3)

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

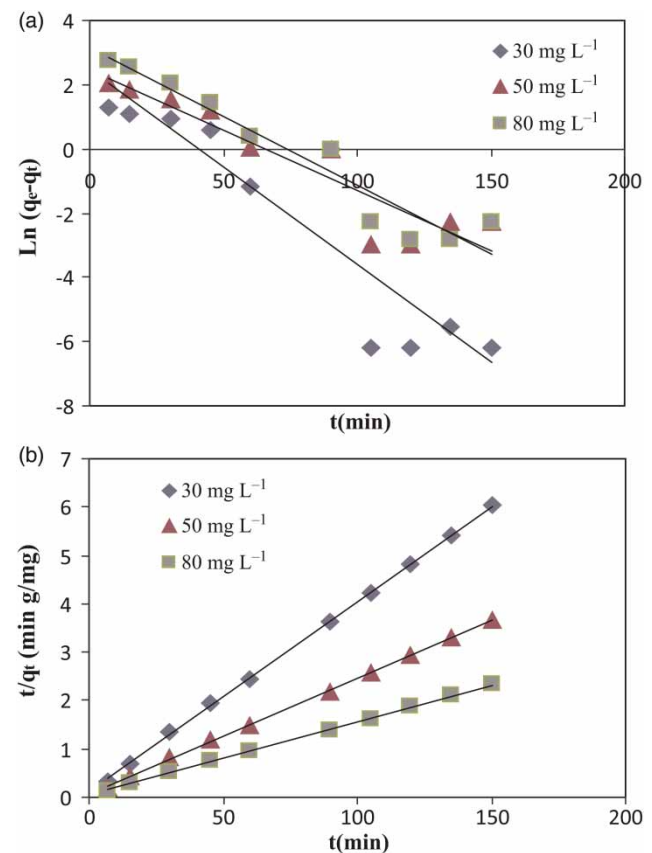
where  $q_e$  and  $q_t$  ( $\text{mg g}^{-1}$ ) are the adsorption capacity at equilibrium and time  $t$  (min), respectively; and  $k_1$  ( $\text{min}^{-1}$ ) is the first-order rate constant (Zhang *et al.* 2011).

The pseudo-second-order model can be expressed as Equation (4)

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

where  $k_2$  ( $\text{mg}^{-1} \text{g min}^{-1}$ ) is the pseudo-second-order rate constant (Azizian 2004). The correlation coefficients and

constants of Equations (3) and (4) were obtained from Figure 6 at different concentrations and are listed in Table 1. The correlation coefficient ( $R^2$ ) of the pseudo-second-order model is higher than that of the first-order model; moreover, the  $q_{e,\text{cal}}$  (i.e. calculated) value for the pseudo-second-order model is more similar to the experimental value ( $q_{e,\text{exp}}$ ). The results demonstrate that adsorption data are well represented by the pseudo-second-order kinetic model. This also confirmed that the adsorption mechanism depended on the adsorbate and adsorbent and the rate-limiting step may be a chemical sorption involving valence forces through sharing or exchanging of electrons. The  $k_2$  values for V(V) adsorption were calculated to be 0.014, 0.006, and  $0.004 \text{ mg}^{-1} \text{g min}^{-1}$ , respectively, for 30, 50, and  $80 \text{ mg L}^{-1}$  V(V) adsorption. The low value of the rate constant ( $k_2$ ) suggested that the adsorption rate decreased with the increase in time and



**Figure 6** | (a) First-order kinetic plot and (b) pseudo-second-order kinetic plot for the adsorption of V(V) onto oxidized MWCNTs at  $25^\circ \text{C}$ .



the adsorption rate was proportional to the number of unoccupied sites.

## Adsorption isotherms

The equilibrium isotherms for adsorption of V(V) by oxidized MWCNTs were investigated by varying initial concentrations of V(V) from 24 to 48 mg L<sup>-1</sup> at pH 5.0 and at 25 °C. From various isotherm equations that may be used to analyze adsorption data in the aqueous phase, the Langmuir equilibrium isotherm, Freundlich equilibrium isotherm, and Temkin equilibrium isotherm are the most common models. The Langmuir isotherm model can be expressed as Equation (5) (Geethakarathi & Phanikumar 2012)

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m b_1} \quad (5)$$

where  $q_e$  (mg g<sup>-1</sup>) is the amount of adsorbed material at equilibrium,  $C_e$  (mg L<sup>-1</sup>) is the equilibrium concentration of the V(V) in solution,  $q_m$  (mg g<sup>-1</sup>) is the maximum capacity of adsorbent and  $b_1$  is a constant. The essential features of the Langmuir adsorption isotherm can be expressed in terms of a dimensionless constant called the separation factor or equilibrium parameter ( $R_L$ ), which is defined by Equation (6)

$$R_L = \frac{1}{1 + bC_0} \quad (6)$$

where  $b$  (L mg<sup>-1</sup>) is the Langmuir constant and  $C_0$  (mg L<sup>-1</sup>) is the highest metal concentration. The value of  $R_L$  indicates the type of the isotherm to be unfavorable ( $R_L > 1$ ), linear ( $R_L = 1$ ), favorable ( $0 < R_L < 1$ ), or irreversible ( $R_L = 0$ ). As shown in Table 2, the calculated value of  $R_L$  was found to be between 0 and 1. This implies that the adsorption of V(V) ions on oxidized MWCNTs from aqueous solutions is favorable under the conditions used in this study.

The linear form of the Temkin isotherm is expressed as Equation (7) (Mishra et al. 2010)

$$q_e = b \ln K_T + b \ln C_e \quad (7)$$

where  $K_T$  is the equilibrium binding constant (L mg<sup>-1</sup>) corresponding to the maximum binding energy and constant  $b$  is related to the heat of adsorption.

The Freundlich model is usually appropriate for heterogeneous adsorption. The linear form of the Freundlich isotherm model can be expressed as Equation (8) (Dawood & Sen 2012)

$$\ln q_e = \frac{1}{n} \ln C_e + \ln K_F \quad (8)$$

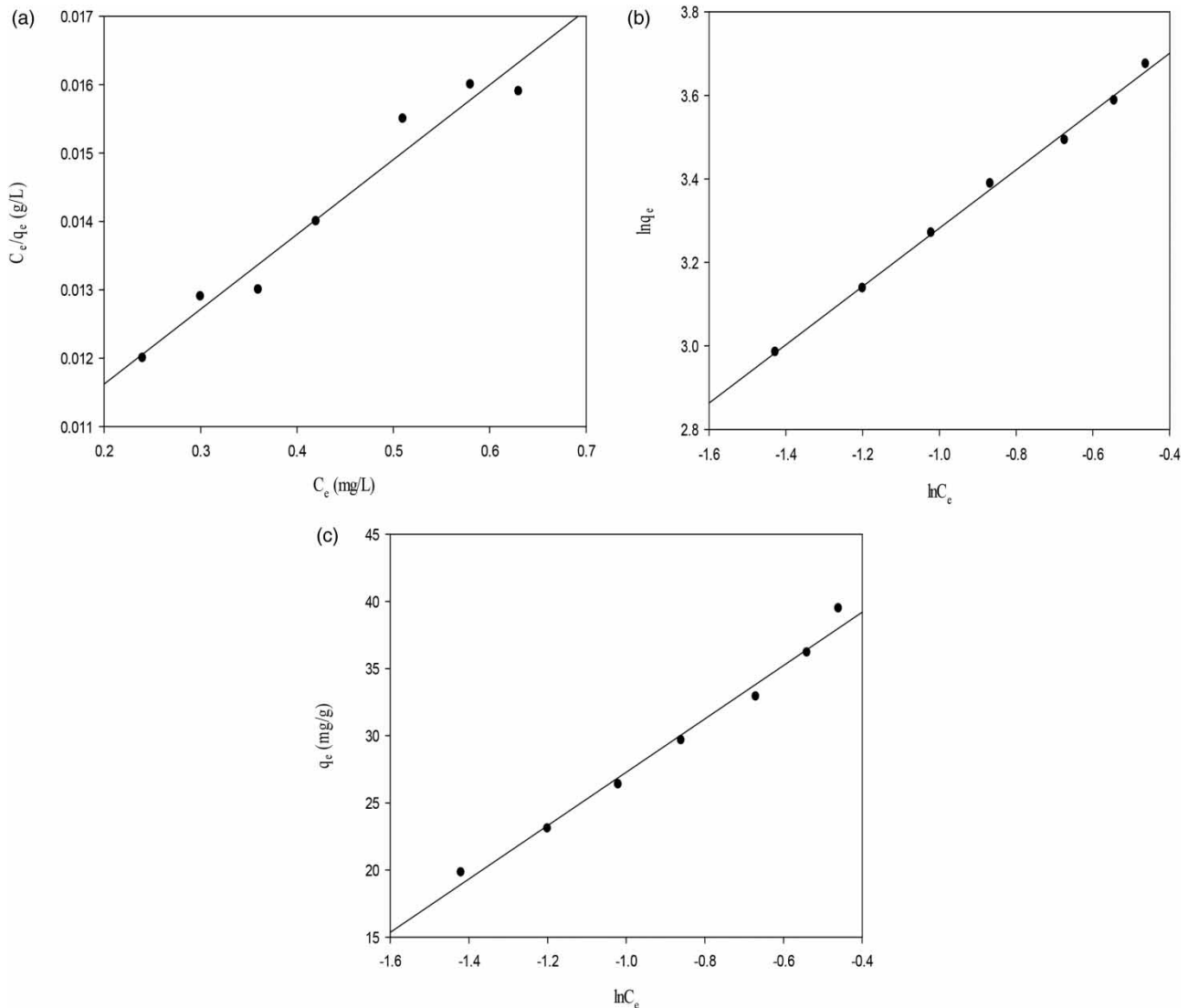
where  $K_F$  (mg<sup>1-(1/n)</sup> L<sup>1/n</sup> g<sup>-1</sup>) is the Freundlich constant and  $n$  is the heterogeneity factor. Figure 7 shows the lines fitted to the experimental data, and the relative parameters calculated from the three models are listed in Table 2. The correlation coefficients ( $R^2$ ) for the Langmuir, Freundlich, and Temkin models were 0.959, 0.997, and 0.985,

**Table 1** | First-order and pseudo-second-order kinetic model parameters for the adsorption of V(V) ions onto oxidized MWCNTs at 25 °C

$C_0$ (mg L <sup>-1</sup> )	$q_e$ exp (mg g <sup>-1</sup> )	First-order kinetic model			Pseudo-second-order kinetic model		
		$q_{e1}$ (mg g <sup>-1</sup> )	$k_1$ (min <sup>-1</sup> )	$R^2$	$q_{e2}$ (mg g <sup>-1</sup> )	$k_2$ (mg <sup>-1</sup> g min <sup>-1</sup> )	$R^2$
30	24.88	11.72	0.06	0.829	25.64	0.014	0.999
50	41.02	11.42	0.037	0.864	43.47	0.006	0.999
80	64.35	22.82	0.042	0.931	66.66	0.004	0.999

**Table 2** | Isotherm parameters of adsorption of V(V) onto oxidized MWCNTs

Metal V(V)	Langmuir				Freundlich			Temkin		
	$b$ (L mg <sup>-1</sup> )	$q_m$ (mg g <sup>-1</sup> )	$R_L$	$R^2$	$K_F$ (mg <sup>1-(1/n)</sup> L <sup>1/n</sup> g <sup>-1</sup> )	$n$	$R^2$	$K_T$ (L mg <sup>-1</sup> )	$b$	$R^2$
	1.11	100	0.031	0.959	53.51	1.432	0.997	2.37	19.87	0.985



**Figure 7** | (a) Langmuir, (b) Freundlich, and (c) Temkin isotherms for the adsorption of V(V) onto oxidized MWCNTs at 25 °C.

respectively. Based on the obtained correlation coefficient it was found that the equilibrium data can be described by the Freundlich isotherm. In general, values  $n > 1$  illustrated that adsorbate was favorably adsorbed on an adsorbent, while  $n < 1$  indicated that adsorbate was unfavorably adsorbed on an adsorbent. In our study, the  $n$  value was higher than 1, which indicated that adsorption intensity was good over the whole range of concentrations from 24 to 48 mg L<sup>-1</sup>. The high  $n$  and  $K_F$  values suggest that the V(V) ions are favorably adsorbed onto the oxidized MWCNTs, and also that there was easy separation of the metal from the aqueous solutions. The  $K_F$  value could be acceptable and workable as

a new potential and low-cost adsorption system. The Freundlich isotherm model assumes that a multi-layer adsorption exists on the oxidized MWCNTs.

## CONCLUSION

The present study demonstrates that oxidized MWCNTs are effective adsorbents for the adsorption of V(V) from aqueous solutions. The effects of adsorption parameters, such as the pH, amount of oxidized MWCNTs used, temperature, and contact time were studied and optimized. The amount

of V(V) removal was found to increase with increasing pH (pH 5) and with an increase in adsorbent mass from 0.001 to 0.03 g. Temperature data suggest that the adsorption of V(V) on oxidized MWCNTs is an exothermic process. The kinetic batch experiments indicated that more than 99.5% of the V(V) was absorbed onto the oxidized MWCNTs within 90 min, and the pseudo-second-order kinetic model could explain the adsorption process. In addition, the equilibrium adsorption capacity of V(V) ions onto the oxidized MWCNT adsorbent was determined to be over 100 mg g<sup>-1</sup> and the adsorption process was better explained by the Freundlich model.

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