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

S. Sobhanardakani, R. Zandipak, Z. Fili, M. Ghoochian, R. Sahraei and A. Farmany

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

S. Sobhanardakani
Department of the Environment, Hamedan Branch,
Islamic Azad University,
Hamedan, Iran

R. Zandipak
Z. Fili
M. Ghoochian
Young Researchers & Elite Club, Hamedan Branch,
Islamic Azad University,
Hamedan, Iran

R. Sahraei
Department of Chemistry,
Ilam University,
Ilam, Iran

A. Farmany (corresponding author)
Department of Chemistry, Hamedan Branch,
Islamic Azad University,
Hamedan, Iran
E-mail: *a.farmany@iauh.ac.ir*

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 absorption, 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 $KMnO_4$, H_2O_2, NaOCl, or 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 μm, outer diameter 50–80 nm, inner diameter 5–10 nm, purity ≥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 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 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 mol L^{-1} HCl and/or 0.1 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 μm. 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, mg g^{-1}) were calculated using Equation (1)

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

where q_e (mg g^{-1}) is the equilibrium adsorption capacity, C_0 and C_e (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)

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

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 $m^2 g^{-1}$, 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 $cm^3 g^{-1}$ for MWCNTs, and 36 nm and 0.24 $cm^3 g^{-1}$ for oxidized MWCNTs, respectively.

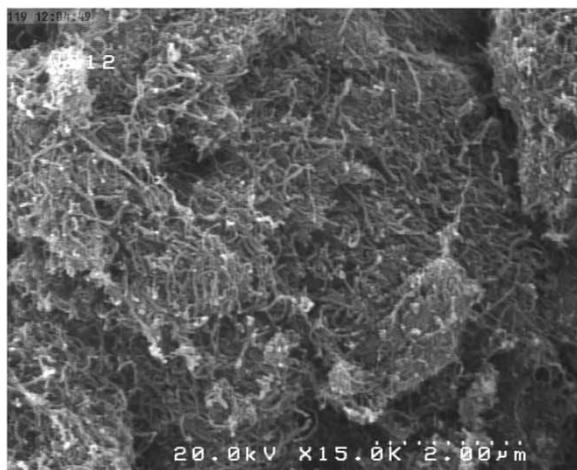The results indicated that the pore volume and average pore diameter of MWCNTs are less than oxidized MWCNTs. This can be comprehended considering the structure change of oxidized MWCNTs with nitric acid, which can easily break up the MWCNTs into smaller pieces with a large number of defects on their 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 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
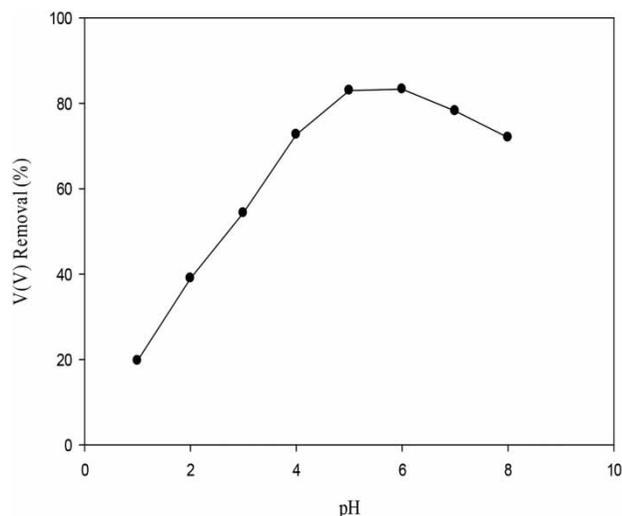

Figure 1 │ SEM image of oxidized MWCNTs.

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

pH of point of zero charge (pH_{zpc}) is an important property and indicates the electrical neutrality of the adsorbent and surface at a particular value of pH; pH_{zpc} for the oxidized MWCNTs was determined at around 4.0 (Yang *et al.* 2009). When the pH is low ($<pH_{zpc}$), 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 ($>pH_{zpc}$), 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 $V_3O_9^{3-}$, HVO_4^{2-}, and $HV_2O_7^{3-}$ 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 mg L^{-1} is shown in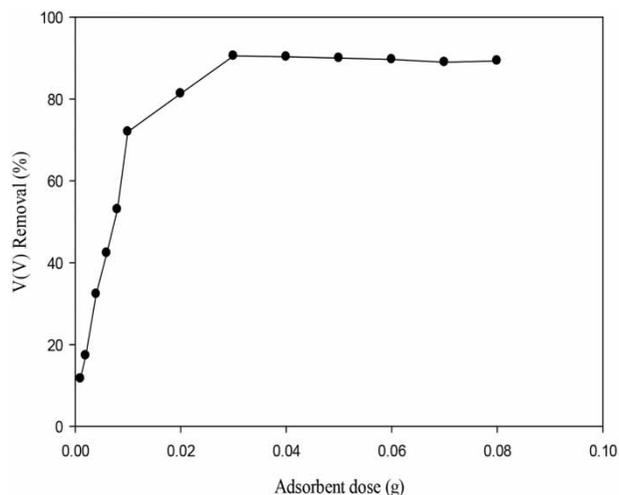 Figure 3. It is observed that the removal efficiency increases from 11.5 to 90.5% with an increase in adsorbent dose from 0.001 to 0.03 g and the maximum adsorption was observed at 0.03 g. This is due to an increase in the surface area and availability of more active sites for adsorption. Hence, 0.03 g of oxidized MWCNTs was used in all experiments. The results are in agreement with those reported in the literature (Afkhami *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 25–55 °C using oxidized MWCNTs as an adsorbent and at the V(V) concentration of 30 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
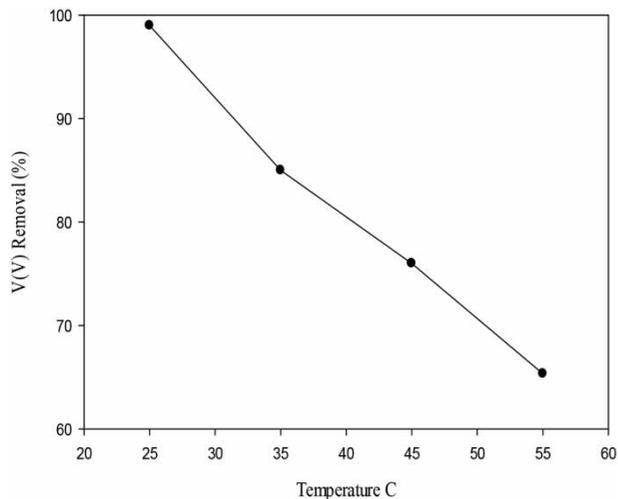

Figure 3 | Effect of dose of oxidized MWCNTs on the removal of V(V) from aqueous solution by oxidized MWCNTs ($C_0 = 30$ mg L^{-1}, solution pH = 5, contact time = 90 min, and temperature = 25 °C).

Figure 4 | Effect of temperature on the removal of V(V) from aqueous solution by oxidized MWCNTs ($C_0 = 30$ mg L^{-1}, solution pH = 5, dose of oxidized MWCNTs = 0.03 g, and contact time = 90 min).
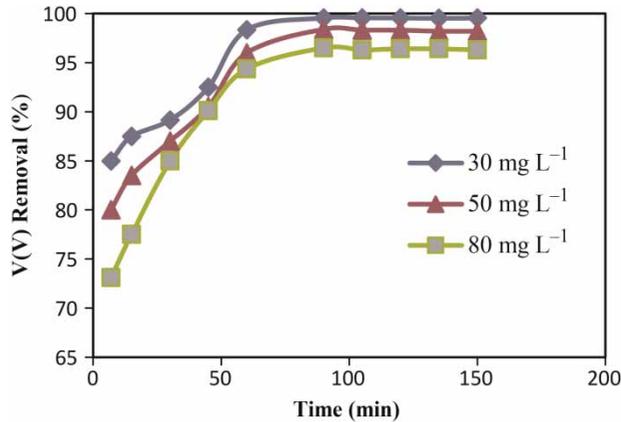
Figure 5 │ Effect of contact time on the removal of V(V) from aqueous solution by oxidized MWCNTs ($C_0 = 30$, 50, and 80 mg L^{-1}, solution pH = 5, dose of oxidized MWCNTs = 0.03 g, and temperature = 25 °C).

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 (Kołodynska 2011).

To investigate the kinetics of adsorption, three different initial concentrations of V(V) were chosen: 30, 50, and 80 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)

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

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

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

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{4}$$

where k_2 (mg^{-1}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 $q_{e,\mathrm{cal}}$ (i.e. calculated) value for the pseudo-second-order model is more similar to the experimental value ($q_{e,\mathrm{exp}}$). 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 mg^{-1}g min^{-1}, respectively, for 30, 50, and 80 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
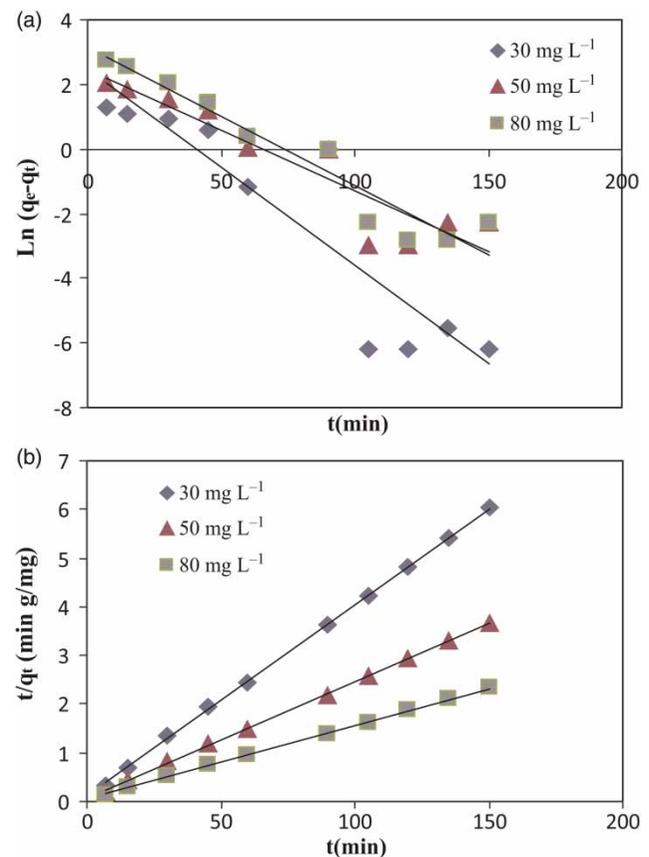

Figure 6 │ (a) First-order kinetic plot and (b) pseudo-second-order kinetic plot for the adsorption of V(V) onto oxidized MWCNTs at 25 °C.

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^{-1} 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) (Geethakarthi & Phanikumar 2012)

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m b_1} \tag{5}$$

where q_e (mg g^{-1}) is the amount of adsorbed material at equilibrium, C_e (mg L^{-1}) is the equilibrium concentration of the V(V) in solution, q_m (mg g^{-1}) 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)

$$R_L = \frac{1}{1 + bC_0} \tag{6}$$

where b (L mg^{-1}) is the Langmuir constant and C_0 (mg L^{-1}) 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)

$$q_e = b \ln K_T + b \ln C_e \tag{7}$$

where K_T is the equilibrium binding constant (L mg^{-1}) 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)

$$\ln q_e = \frac{1}{n} \ln C_e + \ln K_F \tag{8}$$

where K_F (mg$^{1-(1/n)}$ L$^{1/n}$ g^{-1}) 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

		First-order kinetic model			Pseudo-second-order kinetic model		
C_0 (mg L^{-1})	q_e exp(mg g^{-1})	q_{e1} (mg g^{-1})	k_1 (min^{-1})	R^2	q_{e2} (mg g^{-1})	k_2 (mg^{-1}g min^{-1})	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

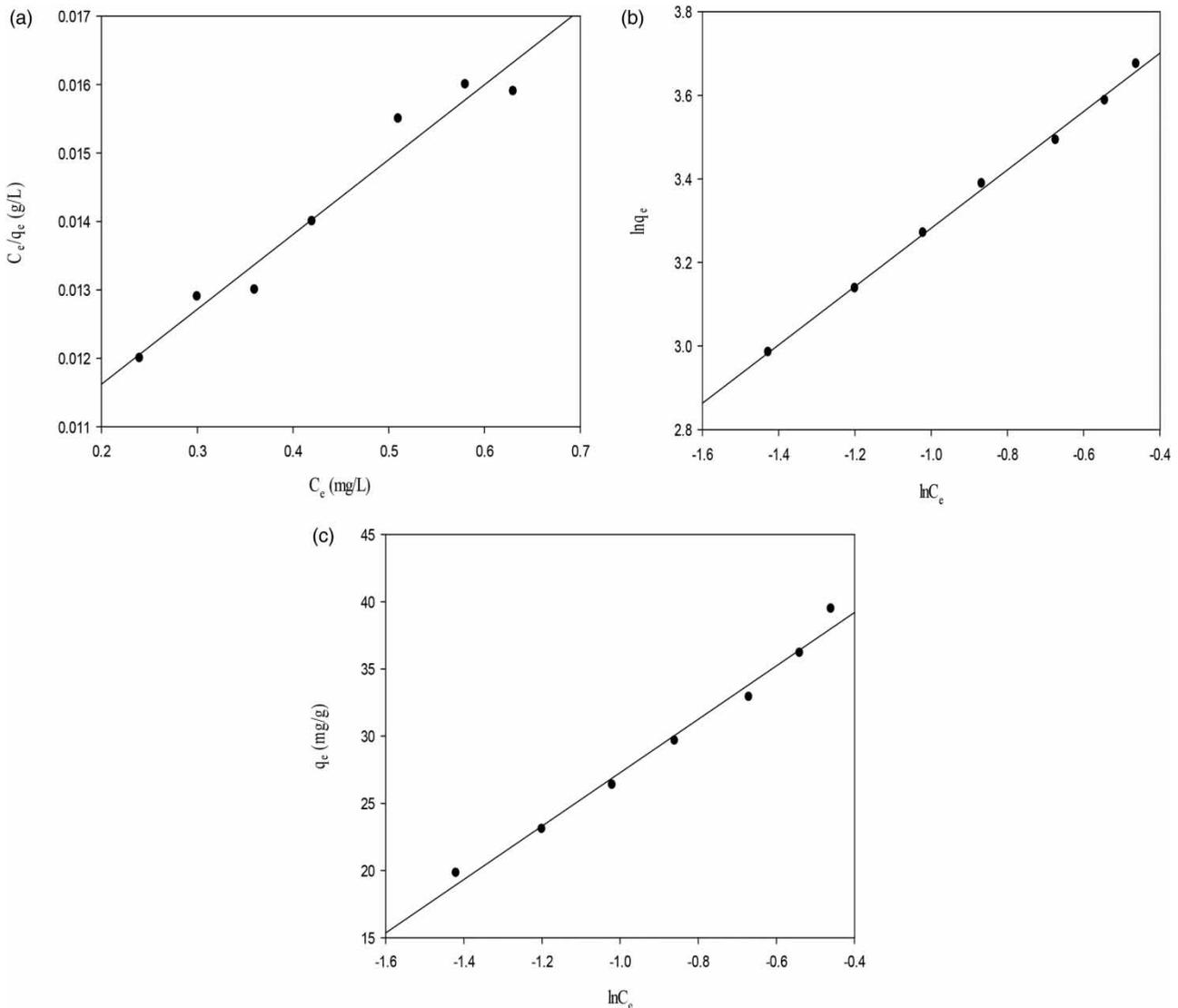|	Langmuir				Freundlich			Temkin		
Metal V(V)	b (L mg^{-1})	q_m (mg g^{-1})	R_L	R^2	K_F (mg$^{1-(1/n)}$ L$^{1/n}$ g^{-1})	n	R^2	K_T(L mg^{-1})	b	R^2
	1.11	100	0.031	0.959	53.51	1.432	0.997	2.37	19.87	0.985

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^{-1}. 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^{-1} and the adsorption process was better explained by the Freundlich model.

REFERENCES

Afkhami, A., Saber Tehrani, M. & Bagheri, H. 2010 Modified maghemite nanoparticles as an efficient adsorbent for removing some cationic dyes from aqueous solution. *Desalination* **263**, 240–248.

Azizian, S. 2004 Kinetic models of sorption: a theoretical analysis. *J. Colloid Interface Sci.* **276**, 47–52.

Bagheri, H., Afkhami, A., Saber-Tehrani, M. & Khoshsafar, H. 2012 Preparation and characterization of magnetic nanocomposite of Schiff base/silica/magnetite as a preconcentration phase for the trace determination of heavy metal ions in water, food and biological samples using atomic absorption spectrometry. *Talanta* **97**, 87–95.

Bhaumik, M., Maity, A., Srinivasu, V. V. & Onyango, M. S. 2012 Removal of hexavalent chromium from aqueous solution using polypyrrole-polyaniline nanofibers. *Chem. Eng. J.* **181–182**, 323–333.

Brunauer, S., Emmett, P. H. & Teller, E. 1938 Adsorption of gases in multimolecular layers. *J. Am. Chem. Soc.* **60**, 309–319.

Cheng, C., Wang, J., Yang, X., Li, A. & Philippe, C. 2014 Adsorption of Ni(II) and Cd(II) from water by novel chelating sponge and the effect of alkali-earth metal ions on the adsorption. *J. Hazard. Mater.* **264**, 332–341.

Chiang, Y. & Wu, P. 2010 Adsorption equilibrium of sulfur hexafluoride on multi-walled carbon nanotubes. *J Hazard. Mater.* **178**, 729–738.

Dai, B., Cao, M., Fang, G., Liu, B., Dong, X., Pan, M. & Wang, S. 2012 Schiff base-chitosan grafted multiwalled carbon nanotubes as a novel solid-phase extraction adsorbent for determination of heavy metal by ICP-MS. *J. Hazard. Mater.* **219–220**, 103–110.

Dawood, S. & Sen, T. K. 2012 Removal of anionic dye Congo red from aqueous solution by raw pine and acid-treated pine cone powder as adsorbent: equilibrium, thermodynamic, kinetics, mechanism and process design. *Water Res.* **46**, 1933–1946.

Geethakarthi, A. & Phanikumar, B. R. 2012 Characterization of tannery sludge activated carbon and its utilization in the removal of azo reactive dye. *Environ. Sci. Pollut. Res.* **19**, 656–665.

Gong, J. L., Wang, B., Zeng, G. B., Yang, C. P., Niu, C. G., Niu, Q. Y., Zhou, W. J. & Liang, Y. 2009 Removal of cationic dyes from aqueous solution using magnetic multi-wall carbon nanotube nanocomposite as adsorbent. *J. Hazard. Mater.* **164**, 1517–1522.

Kołodynska, D. 2011 Chitosan as an effective low-cost sorbent of heavy metal complexes with the polyaspartic acid. *Chem. Eng. J.* **173**, 520–529.

Li, Y. H., Wang, S. & Luan, Z. 2003a Adsorption of cadmium (II) from aqueous solution by surface oxidized carbon nanotubes. *Carbon* **41**, 1057–1062.

Li, Y. H., Ding, J., Luan, Z., Di, Z., Zhu, Y., Xu, C., Wu, D. & Wei, B. 2003b Competitive adsorption of Pb^{2+}, Cu^{2+} and Cd^{+2} ions from aqueous solutions by multiwalled carbon nanotubes. *Carbon* **41**, 2787–2792.

Mishra, A. K., Arockiadoss, T. & Ramaprabhu, S. 2010 Study of removal of azo dye by functionalized multi walled carbon nanotubes. *Chem. Eng. J.* **162**, 1026–1034.

Muataz, A. T., Omer, Y. B., Bassam, A. T., Alaadin, B., Faraj, A. B. & Mohamed, F. 2010 Effect of carboxylic group functionalized on carbon nanotubes surface on the removal of lead from water. *Bioinorg. Chem. Appl.* **2010**, 1–9.

Sheng, G. D., Shao, D. D., Ren, X. M., Wang, X. Q., Li, J. X., Chen, Y. X. & Wang, X. K. 2010 Kinetics and thermodynamics of adsorption of ionizable aromatic compounds from aqueous solutions by as-prepared and oxidized multiwalled carbon nanotubes. *J. Hazard. Mater.* **178**, 505–516.

Sobhanardakani, S., Parvizimosaed, H. & Olyaie, E. 2013 Heavy metals removal from wastewaters using organic solid waste-rice husk. *Environ. Sci. Pollut. Res.* **20**, 5265–5271.

Sun, Y. F., Chen, W. K., Li, W. J., Jiang, T. J., Liu, J. H. & Liu, Z. G. 2014 Selective detection toward Cd^{2+} using Fe_3O_4/RGO nanoparticle modified glassy carbon electrode. *J. Electroanal. Chem.* **714–715**, 97–102.

Tang, W., Zeng, G., Gong, J., Liu, Y., Wang, X., Liu, Y., Liu, Z., Chen, L., Zhang, X. & Tu, D. 2012 Simultaneous adsorption of atrazine and Cu (II) from wastewater by magnetic multi-walled carbon nanotube. *Chem. Eng. J.* **211–212**, 470–478.

Walton, K. S. & Snurr, R. Q. 2007 Applicability of the BET method for determining surface areas of microporous metal–organic frame works. *J. Am. Chem. Soc.* **129**, 8552–8556.

Wang, H., Yuan, X., Wu, Y., Huang, H., Zeng, G., Liu, Y., Wang, X., Lin, N. & Qi, Y. 2013 Adsorption characteristics and behaviors of graphene oxide for Zn(II) removal from aqueous solution. *Appl. Surf. Sci.* **279**, 432–440.

Wang, X. S., Zhu, L. & Lu, H. J. 2011 Surface chemical properties and adsorption of Cu (II) on nanoscale magnetite in aqueous solutions. *Desalination* **276**, 154–160.

Wong, K. K., Lee, C. K., Low, K. S. & Haron, M. J. 2003 Removal of Cu and Pb by tartaric acid modified rice husk from aqueous solutions. *Chemosphere* **50**, 23–28.

Xin, X., Wei, Q., Yang, J., Yan, L., Feng, R., Chen, G., Du, B. & Li, H. 2012 Highly efficient removal of heavy metal ions by amine-functionalized mesoporous Fe_3O_4 nanoparticles. *Chem. Eng. J.* **184**, 132–140.

Xu, P., Zeng, G. M., Huang, D. L., Feng, C. L., Hu, S., Zhao, M. H., Lai, C., Wei, Z., Huang, C., Xie, G. X. & Liu, Z. F. 2012 Use of iron oxide nanomaterials in wastewater treatment: a review. *Sci. Total Environ.* **424**, 1–10.

Yang, S., Li, J., Shao, D., Hu, J. & Wang, X. 2009 Adsorption of Ni(II) on oxidized multi-walled carbon nanotubes: effect of contact time, pH, foreign ions and PAA. *J. Hazard. Mater.* **166**, 109–116.

Yu, H. & Fugetsu, B. 2010 A novel adsorbent obtained by inserting carbon nanotubes into cavities of diatomite and applications for organic dye elimination from contaminated water. *J. Hazard. Mater.* **177**, 138–145.

Yu, J. X., Wang, L. Y., Chi, R. A., Zhang, Y. F., Xu, Z. G. & Guo, J. 2013 A simple method to prepare magnetic modified beer yeast and its application for cationic dye adsorption. *Environ. Sci. Pollut. Res.* **20**, 543–551.

Zhang, L., Song, X., Liu, X., Yang, L., Pan, F. & Lv, J. 2011 Studies on the removal of tetracycline by multi-walled carbon nanotubes. *Chem. Eng. J.* **178**, 26–33.

Zhang, L., Liu, X., Xia, W. & Zhang, W. 2014 Preparation and characterization of chitosan-zirconium(IV) composite for adsorption of vanadium(V). *Int. J. Biol. Macromol.* **64**, 155–161.