Robati *Journal Of Nanostructure in Chemistry* 2013, **3**:55
http://www.jnanochem.com/content/3/1/55

Journal of Nanostructure in Chemistry
a SpringerOpen Journal

ORIGINAL **Open Access**

Pseudo-second-order kinetic equations for modeling adsorption systems for removal of lead ions using multi-walled carbon nanotube

Dariush Robati

Abstract

This study investigated the lead ion removal of the multi-walled carbon nanotubes (MWCNTs) and oxidized multi-walled carbon nanotubes (MWCNT-COOH). The main purpose of this work is to study the possibilities on the removal of Pb(II) ions from aqueous solutions using MWCNTs and MWCNT-COOH surfaces as adsorbents. Removal of Pb(II) ions was investigated using solutions with different concentrations in the range 10 to 100 mg/L. In this study, removal of Pb(II) ions on surfaces has been investigated by atomic absorption spectrophotometry. The microstructure of carbon nanotubes were characterized using scanning electron microscopy. Three different kinetic theories were applied to experimental data. The kinetic rates were modeled using the pseudo-first-order, four-type linear pseudo-second-order, and intraparticle diffusion. The pseudo-second-order model was found to explain the adsorption kinetics most effectively. The results indicated a significant potential of the multi-walled carbon nanotube as an adsorbent for Pb(II) ion removal.

Keywords: Oxidized multi-walled carbon nanotubes; Kinetics models; Pb(II) ions; Multi-walled carbon nanotube; Removal

Background

Exposure to heavy metal ions can cause a variety of adverse health impacts, including serious damages to the immune system, central nervous system, and reproductive system [1]. The contamination of groundwater by heavy metal ions is a major problem in many countries around the world [2]. For example, Pb(II) is a major harmful pollutant to the biosphere, and even trace amounts of it pose a detrimental risk to human health. Although lead is an essential element for the normal metabolism of many living organisms, it is believed that excess lead may be harmful to mankind. So the determination of heavy metal ions is still an intensively active research area [3-5]. Lead is one of the most harmful heavy metals. It has toxic effects on human, animals, and the plants. The main lead pollution resources are battery manufacturing, acid metal plating, ceramic and glass industries, tetraethyl lead manufacturing, and other industries. Lead has fatal effects on the kidney, the nervous system, the liver, and the brain [6]. Therefore, lead must be removed from water. Adsorption is one of the commonly used purification technologies. It is easy to apply and is an economical process. Carbon nanotubes (CNTs) are carbon allotropes consisting of sp^2-hybridized carbons, like fullerene and graphene as well as graphite. Since CNTs were discovered by Iijima in 1991, they have existed in a wide variety of forms, i.e., single-walled carbon nanotubes, double-walled carbon nanotubes, few-walled carbon nanotubes, and multi-walled carbon nanotubes (MWCNTs) [7]. Because of so many outstanding performances, CNTs exhibit a great promise for potential applications in many technological fields such as hydrogen storage, catalyst supports, chemical sensors, and nanoelectronic devices [8]. The known ability of CNTs to establish electrostatic interactions and their large surface areas can facilitate the adsorption of many kinds of pollutants from water, such as aniline, phenol, and their substitutes and sodium chloride, as well as several divalent metal ions [9-11]. Surface

---

Correspondence: d_robati@iiau.ac.ir
Department of Chemistry, Eslamshahr Branch, Islamic Azad University, Eslamshahr, Iran

© 2013 Robati; licensee Springer. This is an Open Access article distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/2.0), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

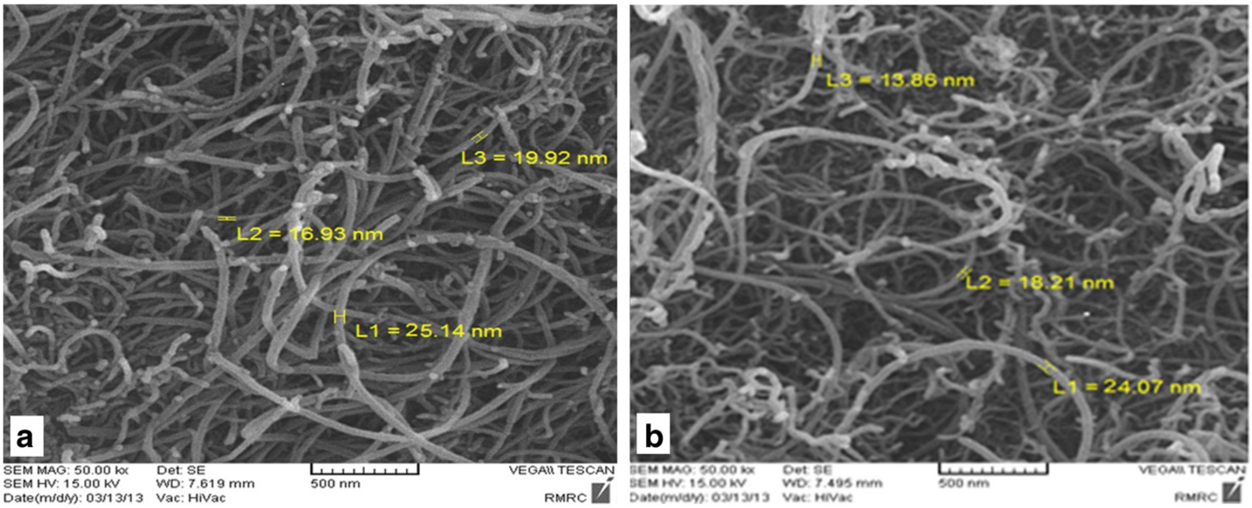

Figure 1 **SEM images of multi-walled carbon nanotubes (MWCNTs) (a) and oxidized multi-walled carbon nanotubes (MWCNT-COOH) (b).**

modifications of CNTs have been applied recently to enhance the dispersion property and adsorption capacities of CNTs. Oxidation of CNTs have been widely reported [12]. During oxidation, the surface characteristics are altered due to the introduction of new functional groups (e.g., COOH, OH) [12]. Many other functional groups could also be appropriate for metal ion adsorption [13,14]. The goals of this research were to evaluate the removal of behavior of Pb(II) by the MWCNTs and oxidized multi-walled carbon nanotubes (MWCNT-COOH). Three different kinetic theories were applied to experimental data. The kinetic rates were modeled using the pseudo-first-order, four-type linear pseudo-second-order, and intraparticle diffusion.

Methods

MWCNT (purity, >95%; diameter 1 to 2 nm; length, 5 to 30 nm; surface area, approximately 400 m^2/g; and

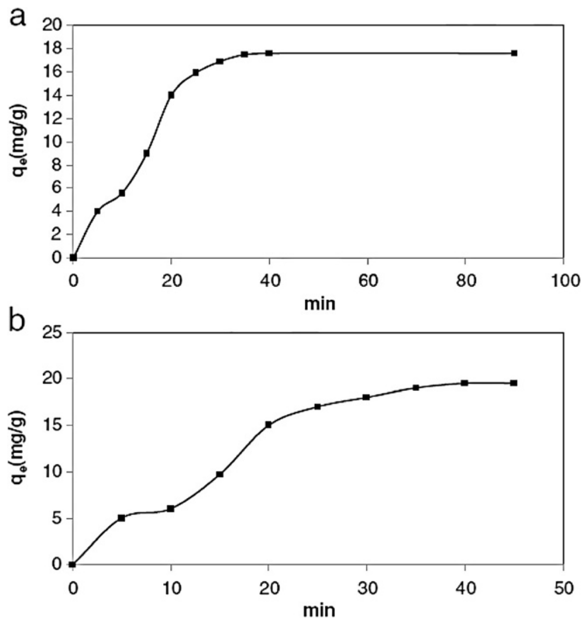

Figure 2 **Effect of contact time on adsorption of Pb(II) ions by (a) MWCNT and (b) MWCNT-COOH surfaces.** **(a)** Initial concentration, 100 mg/L; adsorbent dosage, 50 mg/L, and T = 298 K. **(b)** Initial concentration, 100 mg/L; adsorbent dosage, 50 mg/L and T = 298 K.

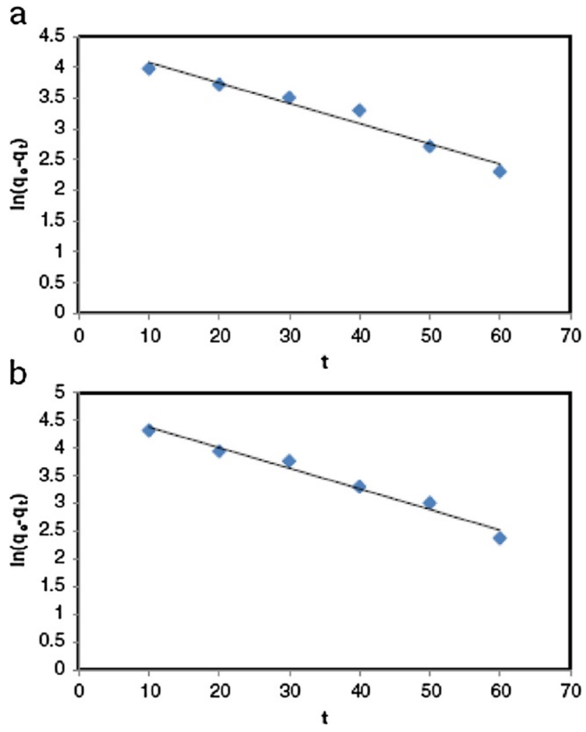

Figure 3 **Pseudo-first-order kinetics for removal of lead ions by (a) MWCNT and (b) MWCNT-COOH surfaces.**

Table 1 Fitted pseudo-first-order-model kinetic parameters for the removal of lead ions by MWCNTs at 25°C

C_0 (mg/L)	k_1	R^2	Equation
10	0.044	0.9869	2
50	0.046	0.9890	2
75	0.047	0.9901	2
100	0.048	0.9901	2

manufacturing method, catalytic chemical vapor deposition) and MWCNT-COOH (content of COOH: 1 to 6 wt.%; purity, >95%; average diameter 1 to 2 nm; length 5 to 30 nm, and SSA, 400 m^2/g) were purchased from NanoAmor, Nanostructured & Amorphous Materials, Inc, Houston, TX, USA. Doubly distilled water was used and all adsorbents were washed before using. Figure 1 presents SEM images of MWCNTs and MWCNT-COOH. $Pb(NO_3)_2$ (molecular weight, 331.20 g/mol) were supplied by Merck, Darmstadt, Germany (maximum purity available). All solutions were prepared with deviations of less than ±0.1% from the desired concentrations.

Adsorption studies

In this research, the 1,000 mg/L stock solution of Pb(II) was prepared by dissolving $Pb(NO_3)_2$ in deionized water and adding water to 1,000 mL. The experimental solutions were prepared by diluting the stock solution with deionized water when necessary. To evaluate the equilibrium properties, we first prepared various solutions with initial lead ion concentration from 10 to 100 mg/L and then added 0.05 g MWCNTs and MWCNT-COOH for each, as adsorbent to the solution. These samples were then mounted on a shaker (HZQ-C, Hangzhou Chincan Trading Co., Ltd, Hangzhou, China) and shaken continuously for 5 to 45 min at 298 K. Ultrasonic bath (71020-DTH-E; Model 1510 DTH, 220V; EMS Company,) was used to prevent the particles to aggregate and form a bulk. Then, the samples were centrifuged at 450 rpm, and the supernatant was filtered by 0.2-μm filtered papers for subsequent analysis of lead ion concentration. The filtrates were then immediately examined using atomic absorption spectrophotometry (Perkin-Elmer AAnalyst 700, Waltham, MA, USA) in order to measure the ion concentration. The difference between the initial and the equilibrium ion concentration determines the amount of ion adsorbed onto MWCNT-COOH and MWCNT surfaces. All the experiments were performed in triplicate, and only the mean values are reported. As shown previously, the adsorption of ion on the bottle wall is ignorable. The amount of lead adsorbed was calculated using the following equation:

$$q_e = \frac{(C_0 - C_e)V}{m}, \tag{1}$$

where C_0 and C_e (mg/L) are the liquid-phase concentrations of lead at initial and equilibrium concentrations, respectively. V is the volume of the solution (L) and m is the mass of adsorbent used (g). All the experiments were performed in triplicate, and the mean values have been used in calculations.

Table 2 Fitted pseudo-first-order-model kinetic parameters for the removal of lead ions by MWCNT-COOH at 25°C

C_0 (mg/L)	k_1	R^2	Equation
10	0.045	0.98695	2
50	0.047	0.9869	2
75	0.049	0.9900	2
100	0.050	0.9909	2

Table 3 Pseudo-second-order kinetic model in linearized forms

Type	Linearized form	Plot	Equation
Linear 1	$\frac{t}{q_e} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$	t/q vs. t	3
Linear 2	$\frac{1}{q_e} = \frac{1}{q} + \left(\frac{1}{k_2 q_e^2}\right) \frac{1}{t}$	$1/q$ vs. $1/t$	4
Linear 3	$q_e = q_t - \left(\frac{1}{k q_t}\right) \frac{q}{t}$	q vs. q/t	5
Linear 4	$\frac{q_e}{t} = k q_t^2 - k q_e q_t$	q/t vs. q	6

Results and discussion

Effect of contact time

In order to determine the time required for removal of lead ions by MWCNT-COOH and MWCNT surfaces, 10 mL of 100 mg/L solution was shaken with 0.05 g MWCNTs. The equilibrium studies were performed at the selected interval of time ranging from 5 to 60 min. As shown in Figure 2, after 35 min of stirring the solution, the removal efficiency did not increase. Therefore, the optimum value of stirring time was found to be 35 min. The change in the rate of lead ion removal might be due to the fact that initially all adsorbent sites were vacant and the solute concentration gradient is high. Afterwards, the lead ion uptake rate by the MWCNT-

Table 4 Fitted pseudo-second-order-model kinetic parameters for removal of lead ions by MWCNTs at 25°C

C_0 (mg/L)	k_2	R^2	Equation
75	0.0016	0.9948	3
75	0.0017	0.9970	4
75	0.0019	0.9960	5
75	0.0020	0.9960	6

Table 5 Fitted pseudo-second-order-model kinetic parameters for removal of lead ions by MWCNT-COOH at 25°C

C_0 (mg/L)	k_2	R^2	Equation
75	0.0018	0.9948	3
75	0.0019	0.9970	4
75	0.0020	0.9960	5
75	0.0021	0.9960	6

COOH and MWCNT surfaces decreased significantly due to the decrease in adsorption sites. On the basis of these results, a 35-min shaking period was selected for all further studies.

Adsorption kinetics

Kinetic modeling not only allows estimation of sorption rates but also leads to suitable rate expressions characteristic of possible reaction mechanisms. In this respect, several kinetic models including the pseudo-first-order kinetics model, pseudo-second-order kinetics models (four linear forms), and the intraparticle diffusion model were investigated.

Pseudo-first-order model

A pseudo-first-order kinetic equation is given as [15]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t, \tag{2}$$

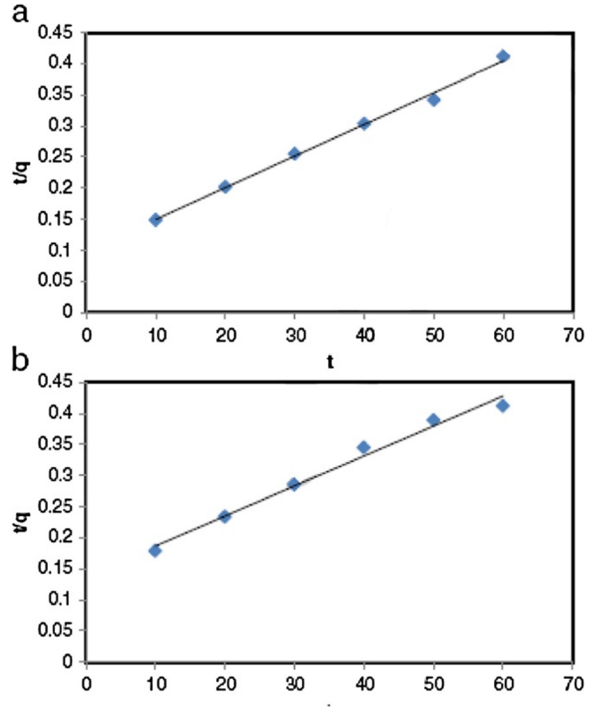

Figure 4 **Pseudo-second-order kinetic model for removal of lead ions by MWCNTs (a) and MWCNT-COOH surfaces (b).** (for Equation 2).

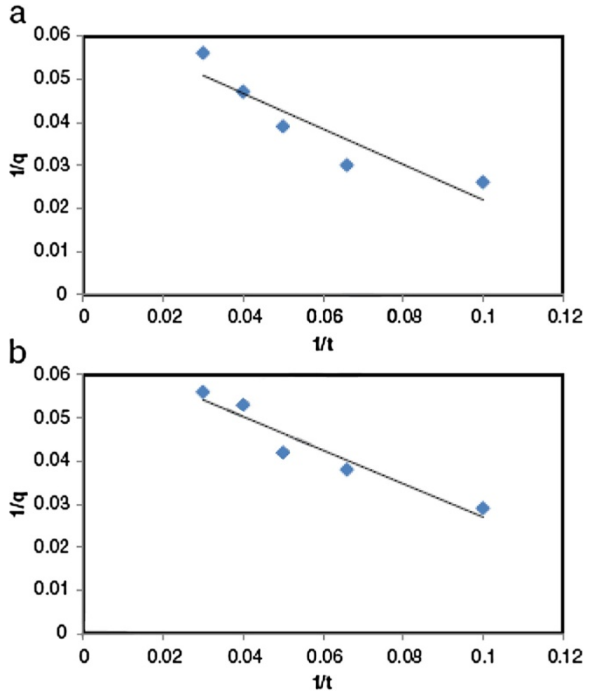

Figure 5 **Pseudo-second-order kinetic model for removal of lead ions by MWCNTs (a) and MWCNT-COOH surfaces (b).** (for Equation 3).

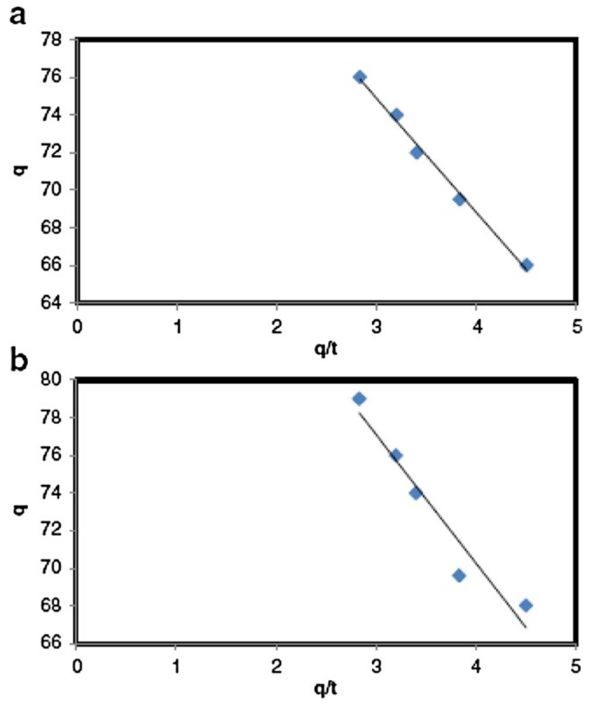

Figure 6 **Pseudo-second-order kinetic model for removal of lead ions by MWCNTs (a) and MWCNT-COOH surfaces (b).** (for Equation 4).

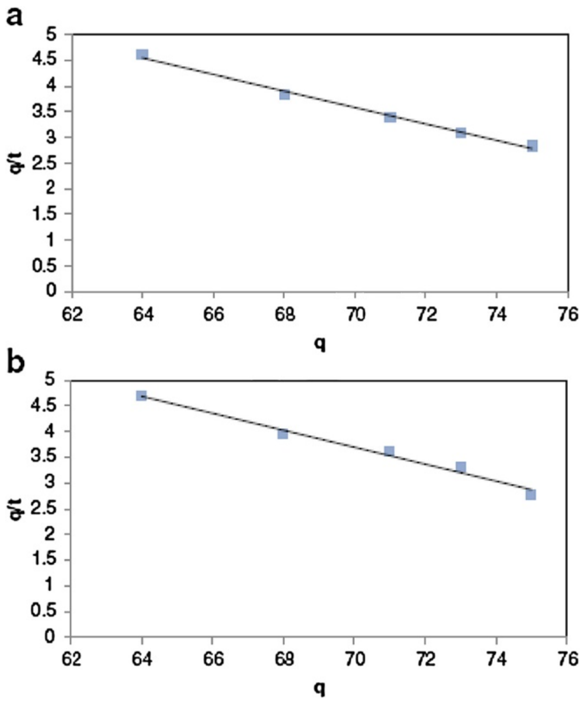

Figure 7 **Pseudo-second-order kinetic model for removal of lead ions by MWCNTs (a) and MWCNT-COOH surfaces (b).** (for Equation 5).

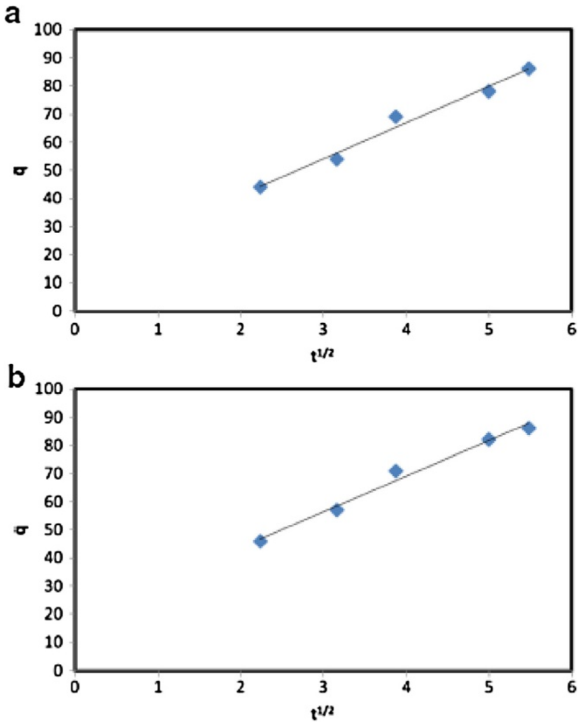

Figure 8 **Intraparticle diffusion model kinetics for removal of lead by (a) MWCNT surfaces and (b) MWCNT-COOH surfaces.**

Table 6 Fitted intraparticle diffusion model kinetic parameters for removal of lead ions by MWCNT surfaces at 25°C

C_0 (mg/L)	k_3	R^2	Equation
75	11.312	0.9881	7
75	11.433	0.9849	7
75	11.566	0.9899	7
75	11.877	0.9877	7

where q_t is the amount of lead ions removed at time t (mg/g), q_e is the adsorption capacity at equilibrium (mg/g), k_1 is the pseudo-first-order rate constant (1/min), and t is the contact time (min). Using Equation 2, $ln\ (q_e - q_t)$ versus t was plotted as shown in Figure 3. The pseudo-first-order rate constant (k_1) determined from the model is presented. Results are presented in Tables 1 and 2 for the removal of lead ions by MWCNTs and MWCNT-COOH, respectively, at 25°C.

Pseudo-second-order model

In this model, the rate-limiting step is the surface adsorption that involves chemisorption, where the removal from a solution is due to physicochemical interactions between the two phases [16]. The model is usually represented by its linear form as shown in Figure 2 and Table 3. Fitted pseudo-second-order-model kinetic parameters for the removal of lead ions by MWCNTs and MWCNT-COOH at 25°C are presented in Tables 4 and 5, respectively.

Where k_2 (g/mg/min) is the pseudo-second-order rate constant of adsorption. The plot is shown in Figures 4,5,6 and 7.

Intraparticle diffusion model

The intraparticle diffusion model describes adsorption processes, where the rate of adsorption depends on the speed at which adsorbate diffuses towards adsorbent (i.e., the process is diffusion-controlled), which is presented by Equation 7.

$$q_e = k_3 t^{1/2} + c, \tag{7}$$

Table 7 Fitted intraparticle diffusion model kinetic parameters for removal of lead ions by MWCNT-COOH surfaces at 25°C

C_0 (mg/L)	k_3	R^2	Equation
75	11.432	0.9890	7
75	11.489	0.9868	7
75	11.601	0.9900	7
75	11.890	0.9900	7

where, k_3 is the rate constant of the intraparticle transport (g/mg/min) and c is the intercept [17-20]. The intraparticle diffusion model as fitted with the experimental data is presented in the plot of q_t versus $t^{1/2}$ depicted in Figure 8a,b, and the values of k_i and correlation coefficients are given in Tables 6 and 7.

Comparing the results of the kinetics models reveals that the pseudo-second-order model has the best agreement with the experimental data.

Conclusions

The present investigation showed that the MWCNTs and MWCNT-COOH surfaces were effective in the removal of lead ions from the aqueous solution. The surface area of the MWCNT-COOH was relatively high with large-pore-volume MWCNT surfaces as adsorbents The adsorption of Pb(II) ion amount increased with increasing time by both surfaces. Kinetics for the removal of lead ions were obtained and fitted to different kinetics models. Kinetics data were best fitted by the pseudo-second-order model and the result indicated that this adsorbent is excellent in the removal of lead from aqueous solution at variable concentrations.

Competing interests

The author declares that he has no competing interests.

Acknowledgements
The author would like to thank the Islamic Azad, Islamshahr Branch for their financial support.

Received: 29 May 2013 Accepted: 29 May 2013
Published: 15 July 2013

References

1. Cho, HH, Wepasnick, K, Smith, BA, Bangash, FK, Fairbrother, DH, Ball, WP, Ball, WP: Sorption of aqueous Zn[II] and Cd[II] by multiwall carbon nanotubes: the relative roles of oxygen-containing functional groups and graphenic carbon. Langmuir **26**, 967–981 (2010)
2. Hyung, H, Kim, JH: Natural organic matter (NOM) adsorption to multi walled carbon nanotubes: effect of NOM characteristics and water quality parameters. Environ. Sci. Technol. **42**, 4416–4421 (2008)
3. Xu, D, Tan, X, Chen, CL, Wang, XK: Removal of Pb(II) from aqueous solution by oxidized multiwalled carbon nanotubes. J. Hazard. Mater. **154**, 407–416 (2008)
4. Sheng, GD, Li, JX, Shao, DD, Hu, J, Chen, CL, Chen, Y, Wang, X: Adsorption of copper(II) on multiwalled carbon nanotubes in the absence and presence of humic or fulvic acids. J. Hazard. Mater. **178**, 333–340 (2010)
5. Schierz, A, Zaenker, H: Aqueous suspensions of carbon nanotubes: surface oxidation, colloidal stability and uranium sorption. Environ. Pollut. **157**, 1088–1094 (2009)
6. Giannakopoulos, E, Christoforidis, KC, Tsipis, A, Jerzykiewicz, M, Deligiannakis, Y: Influence of Pb(II) on the radical properties of humic substances and model compounds. J. Phys. Chem. A. **109**, 2223–2232 (2005)
7. Sadeghian, Z: Large-scale production of multi-walled carbon nanotubes by low cost spray pyrolysis of hexane. New. Carbon. Mater. **24**, 33–38 (2009)
8. Shao, D, Hu, J, Wang, X: Plasma induced grafting multiwalled carbon nanotube with chitosan and its application for removal of $UO_2{}^{2+}$, Cu^{2+}, and Pb^{2+} from aqueous solutions. Plasma. Process. Polym. **7**, 977–985 (2010)
9. Wang, P, Shi, QH, Liang, HJ, Steuerman, DW, Stucky, GD, Keller, AA: Enhanced environmental mobility of carbon nanotubes in the presence of humic acid and their removal from aqueous solution. Small **4**, 2166–2170 (2008)
10. Ren, XM, Chen, CL, Nagatsu, M, Wang, XK: Carbon nanotubes as adsorbents in environmental pollution management: a review. Chem. Eng. J. **170**, 395–410 (2011)
11. Petersen, EJ, Zhang, LW, Mattison, NT, O'Carroll, DM, Whelton, AJ, Uddin, N, Nguyen, T, Huang, QG, Henry, TB, Holbrook, RD, Chen, KL: Potential release pathways, environmental fate, and ecological risks of carbon nanotubes. Environ. Sci. Technol. **45**, 9837–9856 (2011)
12. Zhang, D, Pan, B, Zhang, H, Ning, P, Xing, BS: Contribution of different sulfamethoxazole species to their overall adsorption on functionalized carbon nanotubes. Environ. Sci. Technol. **44**, 3806–3811 (2010)
13. Mauter, MS, Elimelech, M: Environmental applications of carbon-based nanomaterials. Environ. Sci. Technol. **42**, 5843–5859 (2008)
14. Tian, Y, Gao, B, Wang, Y, Morales, VL, Carpena, RM, Huang, Q, Yang, L: Deposition and transport of functionalized carbon nanotubes in water saturated sand columns. J. Hazard. Mater. **213–214**, 265–272 (2012)
15. Li, YH, Wang, S, Luan, Z, Ding, J, Xu, C, Wu, D: Adsorption of Cadmium(II) from aqueous solution by surface oxidized carbon nanotubes. Carbon **41**, 1057–1062 (2003)
16. Wang, H, Zhou, A, Peng, F, Yu, H, Yang, J: Mechanism study on adsorption of acidified multi-walled carbon nanotubes to Pb(II). J. Colloid Interface Sci. **316**, 277–283 (2007)
17. Schierz, A, Zanker, H: Aqueous suspensions of carbon nanotubes: Surface oxidation, colloidal stability and uranium sorption. Envi. Pollution **157**, 1088–1094 (2009)
18. Hameed, BH, Daud, FBM: Adsorption studies of basic dye on activated carbon derived from agricultural waste: *Hevea brasiliensis* seed coat. Chem. Eng. J. **139**, 48–55 (2008)
19. Ho, YS, McKay, G: Pseudo-second order model for sorption processes. Process. Biochem. **34**, 451–465 (1999)
20. Weber, TW, Chakkravorti, RK: Pore and solid diffusion models for fixed-bed adsorbers. AICHE J. **20**, 228–232 (1974)

doi:10.1186/2193-8865-3-55
Cite this article as: Robati: Pseudo-second-order kinetic equations for modeling adsorption systems for removal of lead ions using multi-walled carbon nanotube. *Journal Of Nanostructure in Chemistry* 2013 **3**:55.

Submit your manuscript to a SpringerOpen journal and benefit from:

- ► Convenient online submission
- ► Rigorous peer review
- ► Immediate publication on acceptance
- ► Open access: articles freely available online
- ► High visibility within the field
- ► Retaining the copyright to your article

Submit your next manuscript at ► springeropen.com