EVALUATION OF L-CYSTEINE FUNCTIONALIZED MULTI-WALLED CARBON NANOTUBES AS ADSORBENT FORCD (II) IONS FROM AQUEOUS SOLUTIONS

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ABSTRACT

This study demonstrates the adsorption process of Cd (II) ions onto L-Cysteine functionalized multi-walled carbon nanotubes. The adsorption behavior of Cd (II) was studied by varying the parameters such as pH, L-MWCNT dosage, contact time and initial cadmium concentration. The adsorption rate increased with increasing adsorbent dosage and contact time. The optimum condition of the Cd (II) removal process was found at the pH=7.0, 15 mg/l L-MWCNT dosage, 6 mg/l cadmium concentration and the contact time of 60 min. The removal percent was equal to 89.56% at optimum condition. Equilibrium adsorption isotherms and kinetics were also investigated based on Cd adsorption tests. The experimental data were analyzed by the Langmuir and Freundlich models of adsorption, and the results fitted well to the Langmuir isotherm. The kinetic data have been analyzed using pseudo-first-order and pseudo-second-order equations. The experimental data fitted very well with pseudo-second-order kinetic model with correlation coefficients (R^2) equal to 0.998, 0.992 and 0.998 for 3, 6 and 9 mg/l of Cd concentration, respectively. The experimental data were fitted well to the Langmuir isotherm model (R^2=0.994) and the maximum capacity of L-MWCNT was 43.47 mg/g. Overall, L-MWCNT is an effective adsorbent for Cd (II) removal from aqueous solutions.

Keywords: Adsorption, Cadmium, Carbon nanotube, L-MWCNT, Water treatment

1. Introduction

Heavy metal ions in water are toxic toward aquatic-life, plants, animals, human beings and the environment. They do not degrade biologically like organic pollutants. Therefore, they can be absorbed and possibly that accumulated in the living organisms, so their presence in water are a public health problem (FouladiFard *et al.* 2011; Maleki *et al.* 2011; Tofighy & Mohammadi 2011). The removal of toxic heavy metals such as cadmium from aqueous environment has received substantial attention due to its supreme toxicity to human health in small concentration (Li *et al.* 2003; Boparai *et al.* 2010; MamdouhAllawzi & Al-Asheh 2010). The maximum contaminant level of cadmium in drinking water was determined less than 0.003 mg/L by World Health Organization (WHO) guidelines (Boparai *et al.* 2010). The long period exposure by drinking water containing cadmium higher than this level can cause nausea, salivation, diarrhea, muscular cramps, renal degradation, lung insufficiency, bone lesions, cancer and hypertension in humans (Li *et al.* 2003; Sarangi *et al.* 2012; Shadborestan *et al.* 2013). IARC has classified cadmium and cadmium compounds in Group 2A because there is some evidence that cadmium is carcinogenic.

Among the many methods which were proposed for heavy metals removal, CNTs have been used due to their unique hollow tube structure and many remarkable and outstanding mechanical, electronic, chemical and optical properties (Rao *et al.* 2007; Gao *et al.* 2009). The previous studies

have revealed that CNTs possess higher adsorption capacity and show better reversibility through many cycles of water treatment and regeneration than the commercial adsorbents toward heavy metal ions. So, CNTs have been suggested as promising adsorbents for the removal of heavy metal ions or organic contaminants from large volumes of aqueous solutions regardless of their high unit cost at present time (Sheng *et al.* 2010). Liu *et al.* (Liu *et al.* 2008) reported high selectivity potential of biomolecule L-cysteine functionalized MWCNTs towards cadmium ions. Thus, this study was carried out to evaluate the applicability of L-Cysteine functionalized Multi-walled Carbon Nanotube (LMWCNT) as an effective adsorbent for cadmium removal from aqueous solutions.

2. Experimental
2.1. Materials
All chemical used in the study, including Cadmium stock solution (1000 mg/L), Nitric acid, Sulfuric acid, Hydrochloric acid, sodium hydroxide, Dimethylformamide, Triethylamine, Thionyl chloride, L-Cysteine, with analytical grade were purchased from Merck (Germany). MWCNT was purchased from Plasma Chem GmbH, Germany.

2.2. Preparation and characterization of adsorbent
The characteristics of MWCNT are shown in table 1. MWCNT fictionalization was performed by Liu's method (Liu *et al.* 2008) that is described as follows. At first, the MWCNT suspension was added to the mixture of concentrated sulfuric acid and nitric acid (3:1 v/v), then sonicated for 1 h in an ultrasonic bath. The suspension was stirred at 55 $^{\circ}$C for 8h and cooled to room temperature. The oxidized MWCNTs (MWCNT-COOH) were washed repeatedly with DDW until the residual acid was completely removed, and dried under vacuum. The MWCNT-COOH was dispersed in a solution of $SOCl_2$ and stirred at 70 $^{\circ}$C for 24 h. The resultant MWCNT-COCl was separated and dried under vacuum. L-Cysteine methyl ester hydrochloride, triethylamine in anhydrous DMF, and the MWCNT-COCl were mixed and stirred under Ar atmosphere at 50 $^{\circ}$C for 48 h. The resultant solid was separated, washed with DDW and DMF sequentially, and reacted with 2 mol/L HCl under Ar atmosphere at 50 $^{\circ}$C for 10 h. The prepared MWCNTs-cysteine was washed with DDW and dried under vacuum.

Nanostructure of the CNTs was determined by transmission electron microscope (TEM, Philips: CM120). The infrared spectra were obtained by using the conventional KBr pellet technique in a Fourier Transform Infrared Spectrometer (FTIR 8000 Series, Shimadzu, Japan), operating in the transmission mode between 4000 and 400 cm^{-1}.

2.3. Adsorption experiments
Bach experiments were performed to evaluate the effect of some parameters, such as pH, L-MWCNT dosage, contact time and initial Cd concentration on adsorption of Cd by L-MWCNT. The effect of each parameter was separately studied in a step. All experiments were conducted at room temperature (20±1°C). At the first of each step, some 100 mL glass flasks containing 50 mL of a Cd solution with desired concentration were prepared. The pH of the solutions was adjusted in a desired value. The pH measurements were made using a pH meter (Hach, pH tester 30). Then, the desired amount of L-MWCNT was added to the each glass flask. The flasks were placed on a shaker and were shaken for equilibrium time and 200 rpm. At the end of each step, the supernatant liquids were filtered through 0.45 µm membrane filters (Gao *et al.* 2009) and the cadmium concentrations were determined by using atomic adsorption spectrophotometer (PerkinElmer AAS 100, Wellesley, MA).

2.4. Kinetic study
To determine the adsorption kinetics of cadmium ions on L-MWCNT, the adsorption process parameters for contact time ranging from 5 to 120 min for the different initial cadmium concentrations were studied. The pseudo-first order and pseudo-second order models were used to study the kinetics of adsorption.

2.5. Adsorption isotherm

Adsorption isotherm was studied by adsorption of 6 mg/L cadmium ion on different L-MWCNT dosage ranging from 2 to 40 mg for 24 h. Langmuir and Freundlich models are two isotherm models that describe the equilibrium sorption.

3.   Results and discussion
3.1. Characterization of L-MWCNT

The characteristics of used MWCNT are presented in table1. The specific surface area of MWCNT was 240 m^2/g. Also, its length and inner diameter were 1-10 μm and 2-6 nm, respectively.

Table 1: The characteristics of MWCNT used as adsorbent in this study

Number of walls	3-15
Specific surface area (BET, N_2)	Ca. 240 m^2/g
Outer diameter/ inner diameter/ length	5-20 nm/ 2-6 nm/ 1-10 μm
Purity (Carbon)	> 95%
Apparent density	150-350 g/cm^3

3.2. FTIR analysis

The FTIR analysis in solid phase was performed on MWCNT and L-MWCNT in a KBr disk in order to determine which functional groups were responsible for metal uptake. Fig. 1 shows the infrared spectra of MWCNT and L-MWCNT. FTIR spectrums of MWCNT and L-MWCNT have the characteristic stretching vibration band of hydrogen bonded alcohol, O–H, around 3348 cm^{-1}, also possess absorption band in 2923 cm^{-1} due to stretching vibration of C–H bond. L-MWCNT has the characteristic stretching of amide carbonyl (C=O), amide II and υ (NH) stretching vibrations absorption bands at 1635 and 1573, 2337 cm^{-1}, respectively.
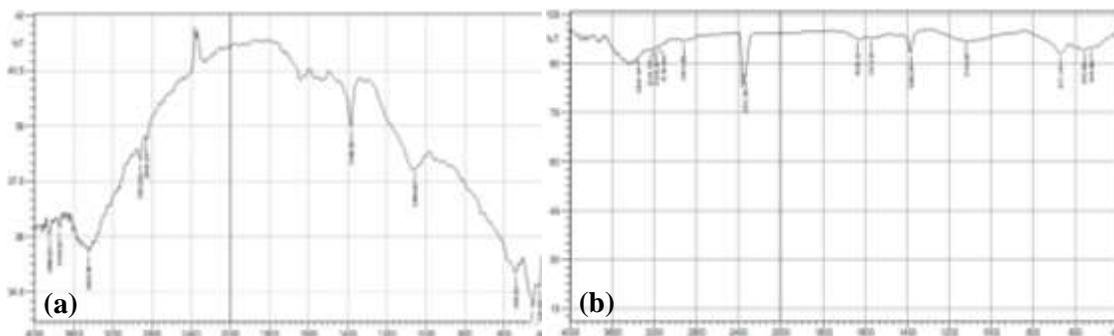
Figure 1: FTIR spectra of (a) MWCNT and (b) L-MWCNT

3.3. Effect of pH

The pH of solution is the most important parameter that can affect the adsorption process(Al-Anber & Matouq 2008). The effect of initial over a pH range of 2-12 on the adsorption of cadmium ions by L-MWCNT is shown in Fig. 2. It is obvious from Fig. 2 that an increase in pH resulted in the increase of the amount of adsorbed cadmium and it reached to 9.35 mg/g at pH =7.0.

The increase of cadmium removal efficiency was negligible and it could be assumed almost constant over the range of pH>7.0. The maximum removal efficiency of cadmium ions was 96.1 % at pH 12. Many researchers have reported that adsorption capacity of adsorbents raises with an increase in pH value (Fouladi Tajar *et al.* 2009; Wang *et al.* 2010). At the pH >6.0, the positive surface charge on the surface of L-MWCNT caused a significant electrostatic repulsion between surface of L-MWCNT, and the cationic cadmium ions and high concentration of H^+ in the solution compete with

cadmium ions for the adsorption sites which resulted in the reduced uptake (Fouladi Tajar *et al.* 2009; Wang *et al.* 2010). The number of positively charged sites decreases and the number of negatively charged sites increases on the surface of L-MWCNT as the pH of the solution increases (Wang *et al.* 2010). The optimum pH adsorption of Cd(II) ions by Titanate nanotube was found to be in the pH range of 5-6 (Xiong *et al.* 2011). While, White *et al* reported that the optimal pH binding of Cd(II) on Magnetic γ-Fe$_2$O$_3$ nanoparticles coated with poly-L-Cysteine is at the pH value of 8.0 (White *et al.* 2009).
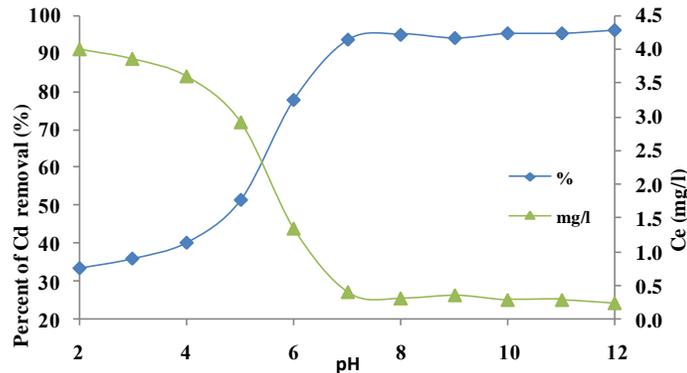
Figure 2: Effect of the pH on the adsorption of Cd (II) ions on L-MWCNT.

3.4. Effect of L-MWCNT dosage

To examine the effect of L-MWCNT dosage on the cadmium ions removal efficiency, several experiments were performed at different L-MWCNT dosages over the range 2 to 40 mg/50 mL as shown in Fig.3. This figure is evident that the removal efficiency of cadmium ions rapidly accelerates (from 20.56 to 89.56 %) with an increasing of L-MWCNT dosage from 0.002 to 0.15 g. This increase was expected because the increase of adsorbent results in the greater availability of exchangeable sites for the cadmium ions (Al-Anber & Matouq 2008). After this point, the increase of removal efficiency continues with the increase of L-MWCNT dosage, but this increase is less than the initial increase that can be ignored. The percentage of removal reached to 96.68% at L-MWCNT dosage of 0.04 g.
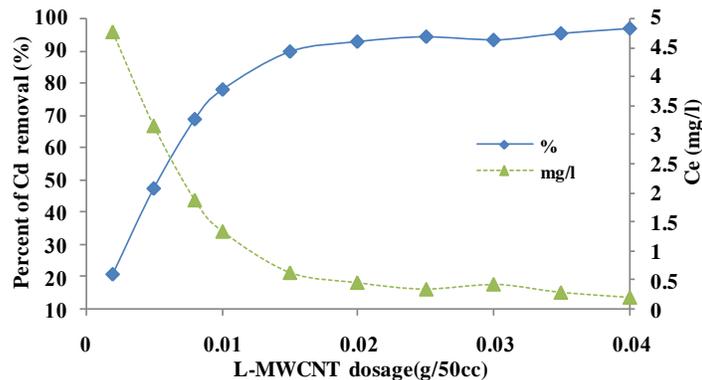
Figure 3: Effect of the L-MWCNT dosage on the adsorption of Cd(II) ions on L-MWCNT.

3.5. Effect of contact time

The effect of contact time on the adsorption of cadmium at 6 mg/L and pH 7 by 0.15 g L-MWCNT is shown in Fig.4. It is obvious that the uptake rate of cadmium ion is very fast at first 40 minutes of the

process as the cadmium removal efficiency reaches from 21.6 to 83% with an increase of contact time from 5 to 40 min. The fast adsorption velocity indicates that strong chemisorption or strong surface complexion contributes to the adsorption of Cd(II) ions on L-MWCNTs(Xu *et al.* 2008). The maximum removal of cadmium (88.9 %) occurred at 60min, after which there were no significant changes. This may contribute to this fact that more active sites and more functional groups are available at the initial contact time that participate in the cadmium ions uptake (Saif *et al.* 2012). Thus, a decrease of the availability of active sites and functional groups with an increase of contact time brings about the slowly adsorption of cadmium ions at the later contact time. Similar phenomena were observed in the literature (White *et al.* 2009; Xiong *et al.* 2011). The optimum contact time for removal of cadmium ions was found to be 60 min.
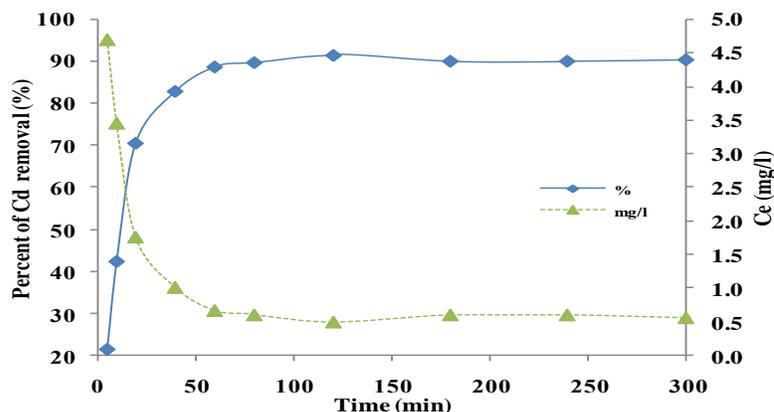
Figure 4: Effect of the contact time on the adsorption of Cd (II) ions on L-MWCNT.

3.6. Effect of initial cadmium concentration

the removal efficiency of cadmium ions decrease with an increase of initial cadmium concentration. The removal efficiency decreased from 95.4 to 63.1 % when initial cadmium concentration increased from 0.5 to 12 mg/L. This might be due to saturation of active adsorption sites on L-MWCNT at higher initial cadmium concentration (Saif *et al.* 2012). On the other hand, the total amount of cadmium adsorbed accelerated with an increase in the amount of initial cadmium concentrations. This phenomenon can be explained that the high available Cd^{2+} concentration at the higher initial cadmium concentrations caused a higher driving force for the cadmium ions from the solution to the adsorbent(Tofighy & Mohammadi 2011; Gupta & Nayak 2012). So, more collision occurred between cadmium ions and active sites on adsorbent. Therefore, the amount of adsorbed cadmium ions on L-MWCNT increased at the higher initial cadmium concentration.

3.7. Kinetic of adsorption

The parameters of two kinetic models are calculated and listed in table 2. The pseudo-first order model showed poor fitting to the experimental data with very low correlation coefficients. In contrast, the fitting of experimental data to the pseudo-second order model was good and this model provided excellent correlation coefficients. So, it can be concluded that the adsorption of Cd (II) onto L-MWCNT perfectly complied with the pseudo-second order kinetic model. Hence, the rate-controlling step might be chemisorptions (Samarghandy *et al.* 2011; Xiong *et al.* 2011). Based on the pseudo-second order kinetic model, that each metal ion binds to the active sites on the surface in a 1:2 stoichiometric ratio (Copello *et al.* 2012). Similar kinetics were observed in the adsorption of Cd (II) onto ethylenediamine-functionalized Fe_3O_4 magnetic polymers (Zhao *et al.* 2010), carbon nanotube sheets (Tofighy & Mohammadi 2011), MW/H_2SO_4 and MW/H_2SO_4/$KMnO_4$ process modified CNTs (Kuo & Lin 2009).

Table 2: The kinetic parameters of Cd (II) adsorption on L-MWCNTs.

kinetic model	parameter	cadmium concentration (mg/l)		
		3	6	9
pseudo-first-order	q_e(mg/g)	19.45	15.83	15.68
	k_1(1/h)	0.002	0.008	0.028
	R^2	0.607	0.716	0.947
pseudo-second-order	q_e(mg/g)	10.20	20.83	27.77
	k_2(g/mg.h)	0.013	0.003	0.002
	R^2	0.998	0.992	0.998

3.8. Adsorption isotherm

The equilibrium distribution of cadmium ions between the L-MWCNT and the solution is important in determining the maximum sorption capacity (Al-Anber & Matouq 2008). Table 3 lists the constants and correlation coefficients involved in the two isotherm models. The Langmuir model showed best fit to the adsorption data with high correlation coefficient (R^2=0.994). Based on the assumptions of Langmuir model, surface of L-MWCNT is homogeneous and there is no interaction between the adsorbed species on adjacent active sites (Xiong *et al.* 2011). The dimensionless constant, R_L, was 0.098, so the adsorption for Cd (II) by L-MWCNT can be considered to be favorable. Values of the adsorption capacity of other adsorbents from the literature are given in Table 4 for comparison.

Table 3: The parameters for Langmuir and Freundlich isotherm models of Cd (II) adsorption on L-MWCNTs.

Isotherm model	parameter	L-MWCNT
Langmuir	q_m(mg/g)	43.47
	b (L/mol)	1.53
	R^2	0.994
	R_L	0.098
Freundlich	K_f (mg/g (L/mg)$^{1/n}$)	21.78
	n	2.14
	R^2	0.965

This study was carried out to assess the applicability of the L-Cysteine functionalized multi-walled carbon nanotubes for Cd (II) ions removal from aqueous solutions. The results showed that the adsorption of Cd (II) ions on L-MWCNT is strongly dependent on pH values and it increased with an increase in solution pH and the optimum pH value was around neutral range. With an increase of L-MWCNT dosage, the removal efficiency of Cd (II) ions increased. Based on the results, the optimum dosage of L-MWCNT was 15 mg/50 ml. The adsorption process was rapid and the equilibrium was achieved within 60 min. An increase of initial cadmium ions concentration resulted in the increase and decrease of the amount of cadmium ions adsorbed per unit of weight of adsorbent (q_e) and the removal efficiency of cadmium ions, respectively. The pseudo-second-order model well described the adsorption kinetic of Cd (II) onto the L-MWCNT. Thus, chemisorption was determined as the rate-controlling step in this process. The experimental data were fitted to the Freundlich and Langmuir models. The Langmuir model provided the best fit of the equilibrium data. According to this model, the maximum cadmium uptake was 43.47 mg/g which it is evident for high affinity of L-MWCNT towards Cd (II) in comparison to the other CNTs. Consequently, L-MWCNT can efficiently remove Cd (II) ions from aqueous solutions.

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