



Adsorption of divalent heavy metal ions from water using carbon nanotube sheets

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ABSTRACT

Removal of some divalent heavy metal ions (Cu^{2+} , Zn^{2+} , Pb^{2+} , Cd^{2+} , Co^{2+}) from aqueous solutions using carbon nanotube (CNT) sheets was performed. CNT sheets were synthesized by chemical vapor deposition of cyclohexanol and ferrocene in nitrogen atmosphere at 750°C , and oxidized with concentrated nitric acid at room temperature and then employed as adsorbent for water treatment. Langmuir and Freundlich isotherms were used to describe the adsorption behavior of heavy metal ions by oxidized CNT sheets. The obtained results demonstrated that the oxidized CNT sheets can be used as an effective adsorbent for heavy metal ions removal from water. It was found out that kinetics of adsorption varies with initial concentration of heavy metal ions. Preference of adsorption onto the oxidized CNT sheets can be ordered as $\text{Pb}^{2+} > \text{Cd}^{2+} > \text{Co}^{2+} > \text{Zn}^{2+} > \text{Cu}^{2+}$. Using the oxidized CNT sheets, waste water treatment without CNT leakage into water is economically feasible. Therefore, CNT sheets have good potential application in environmental protection.

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1. Introduction

Heavy metal ions in water have been a major preoccupation for many years because of their toxicity toward aquatic-life, plants, animals, human beings and the environment. As they do not degrade biologically like organic pollutants, their presence in water is a public health problem due to their absorption and therefore possible accumulation in organisms. Water contaminated by heavy metal ions had become much more serious with a rapid development of industries and competitive use of fresh water in many parts of words. Therefore, heavy metal ions removal from water has become an important subject today [1,2].

Waste waters from many industries such as metallurgical, tannery, chemical manufacturing, mining, battery manufacturing industries, etc. contain one or more toxic heavy metal ions. It is necessary to remove these ions from the waste waters before releasing them into the environment. There has been increasing concern and more stringent regulation standards pertaining to the discharge of heavy metal ions into the aquatic environment [3,4].

Many technologies and methods for heavy metal ions removal from waste waters have been developed, such as ion-exchange, evaporation and concentration, chemical precipitation, reverse osmosis, adsorption, and electrodialysis. Considering from econ-

omy and efficiency point of view, adsorption is regarded as one of the most promising and widely used methods [1–4].

A number of materials, including activated carbon (AC) [5,6], fly ash [7,8], peat [9], sewage sludge ash [10], zeolites [11], biomaterials [12,13], recycled alum sludge [14], manganese oxides [15], peanut hulls [16], kaolinite [17] and resins [18], have been reported to be capable of adsorbing heavy metal ions from aqueous solutions. However, these adsorbents suffer from low adsorption capacities or removal efficiencies of heavy metal ions. Therefore, research for new and more effective materials to be used as adsorbents is a continuous effort for many researchers.

Carbon materials are a class of significant and widely used engineering adsorbent. As a new member of the carbon family, carbon nanotubes (CNTs) have exhibited great potentials as an attractive adsorbent in waste water treatment [19–30].

In 2004 the US Environmental Protection Agency (EPA) expressed a need for the environmental applications of CNTs to be explored and remediation or treatment was identified as one of the key areas that needed to be investigated. Since then CNTs have been gaining increasing recognition for their adsorption capabilities. This is due mainly to their extremely small size, uniform pore distribution and large specific surface area. The comparison of CNTs with other adsorbents suggests that the CNTs have great potential applications in environmental protection [31].

Recently, powder of CNTs has been used as adsorbent in adsorption processes very often. In industrial scale, when powder of CNTs is used as adsorbent, mixing of the CNTs with waste water with ultrasonic agitation is not economically and technically possible.

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Also, after adsorption process, it is difficult to completely remove powder of CNTs from treated water without centrifuging process. Also, separation of the CNTs from treated water by filtration is difficult because the filter may be quickly blocked by the CNTs. With the accumulating evidence of the toxicity of CNTs, there are serious concerns over their health and environmental risks once released to the environment. Also, adsorption of toxic substances by CNTs may enhance the toxicity of CNTs and further affect the transfer of toxic substances in the environment. Therefore, economical waste water treatment without CNT leakage into water is preferable [32].

In our previous study [32], CNT sheets were synthesized by chemical vapor deposition method and oxidized with concentrated nitric acid and then employed as a practical adsorbent for sodium chloride removal from water. In the present work, capability of the oxidized CNT sheets for various divalent heavy metal ions (Cu^{2+} , Zn^{2+} , Pb^{2+} , Cd^{2+} , Co^{2+}) removal from water was investigated. Also, Langmuir and Freundlich isotherms and three kinetic models were applied to fit the experimental data.

2. Experimental procedure

2.1. Synthesis of the CNT sheets

As described earlier [32], CNT sheets were synthesized by chemical vapor deposition (CVD) method at 750°C . The CVD reactor consisted of a horizontal stainless steel tube (70 cm long, 3.2 cm in diameter) was housed in a one stage cylindrical furnace, in which nitrogen was used to carry a gas mixture of precursors toward the center of the reactor, where pyrolysis of the gases took place and CNT sheets were deposited on the reactor walls. The precursor solution was a mixture of catalyst (ferrocene; purity $\geq 98\%$, B.D.H.) and carbon source (cyclohexanol; purity $\geq 98\%$, Fluka) with mass ratio of 1:10, brought to its boiling point in a flask (steel container) connected to the reactor. Evaporating the reagents was performed using an oil bath (details of the synthesis process were presented elsewhere [32,33]). The as-synthesized CNT sheets were immersed in concentrated nitric acid (65%, Merck) for 20 h and then washed using deionized water several times until pH of the washing water showed no change, then dried at 110°C for 24 h. This oxidized CNT sheets were used as adsorbent for heavy metal ions removal from water.

Scanning electron microscope (SEM, Philips: XL30) was used for analysis of the oxidized CNT sheets morphology, and nanostructure of the CNTs was determined by transmission electron microscope (TEM, Philips: CM200).

2.2. Adsorption procedure

Analytical grade of nitrate salts (Merck) and deionized water were used to prepare stock solutions of the metal ions. In the all experiments 50 mg of the oxidized CNT sheets were soaked into 25 ml solutions with initial concentrations of 100, 300, 600, 900 and 1200 mg/l. All the experiments were carried out at initial pH of about 7, at 25°C . A conductometer (CRISON, GLP 32) was used to measure the salt concentration of the solutions. Water conductivity directly depends on the salt concentration. These dependencies (calibration curves of the conductometer) are shown in Fig. 1. Equation and R -squared value on calibration curves of conductometer are shown in Table 1. After removing the oxidized CNT sheets from solutions, the amount of adsorbed salt can be obtained using the following equation:

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

where q_e is the equilibrium adsorption uptake (mg/g), C_0 is the initial salt concentration (mg/l), C_e is the equilibrium salt concen-

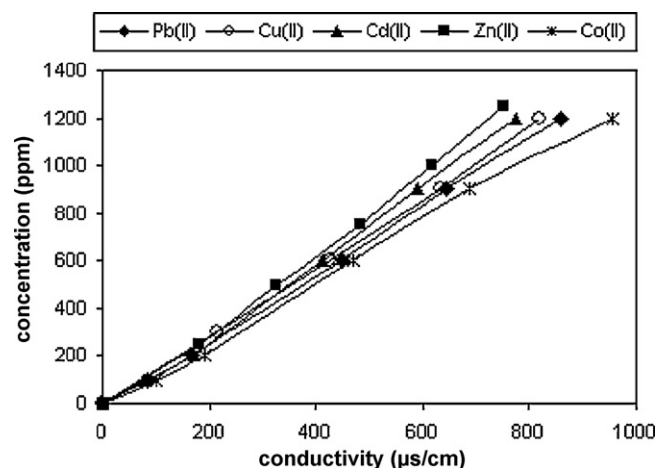


Fig. 1. Calibration curves of the conductometer for heavy metal ions.

tration (mg/l), V is the volume of the solution (l) and w is the mass of the adsorbent (g).

Kinetics studies were carried out at initial concentrations of 100 and 1200 mg/l.

3. Results and discussion

3.1. Characterization of CNT sheets

Fig. 2 shows the oxidized CNT sheets: (a) an overview image and (b) a surface SEM image (inset: a TEM image of a typical CNT with inner tube diameter of about 10 nm and outer tube diameter of about 30–40 nm) and (c) a high magnification SEM image. From the SEM images, the CNT sheet is regarded as an entangled CNT network. The CNT sheets have high flexibility and are not easily broken during oxidation, washing and drying processes.

Fig. 3a and b show the adsorption behavior of heavy metal ions onto the as-synthesized and the oxidized CNT sheets as a function of adsorption time. As can be observed, the oxidized CNT sheets exhibit greater heavy metal ions adsorption capacity than the as-synthesized CNT sheets. This can be explained by the fact that the metal ion adsorption capacity of CNTs does not directly related to their specific surface area, pore specific volume and mean pore diameter but strongly depends upon their surface total acidity including functional groups [3]. As reported in the literature, different acidic functional groups such as carboxyl, lactones and phenols can be formed by nitric acid oxidation [1,24]. These functional groups induce negative charge on the CNTs surface and oxygen atoms of these functional groups donate their single pair of electrons to the metal ions, and this consequently increases cation exchange capacity of the CNTs [3,20]. Protons in the functional groups of the CNTs are exchanged with the metal ions [3]. Chemical interaction (bond) between the metal ions and the surface acidic functional groups of the CNTs is mainly responsible for adsorption [3,22,23,34]. The surface total acidity of the as-synthesized and

Table 1

Equations and R -squared values on calibration curves of conductometer for heavy metal ions.

Ions	Equation	R -squared value
Pb^{2+}	$y = 1.3842x$	0.9982
Cu^{2+}	$y = 1.4393x$	0.9991
Cd^{2+}	$y = 1.5167x$	0.9954
Zn^{2+}	$y = 1.6155x$	0.9955
Co^{2+}	$y = 1.2660x$	0.9967

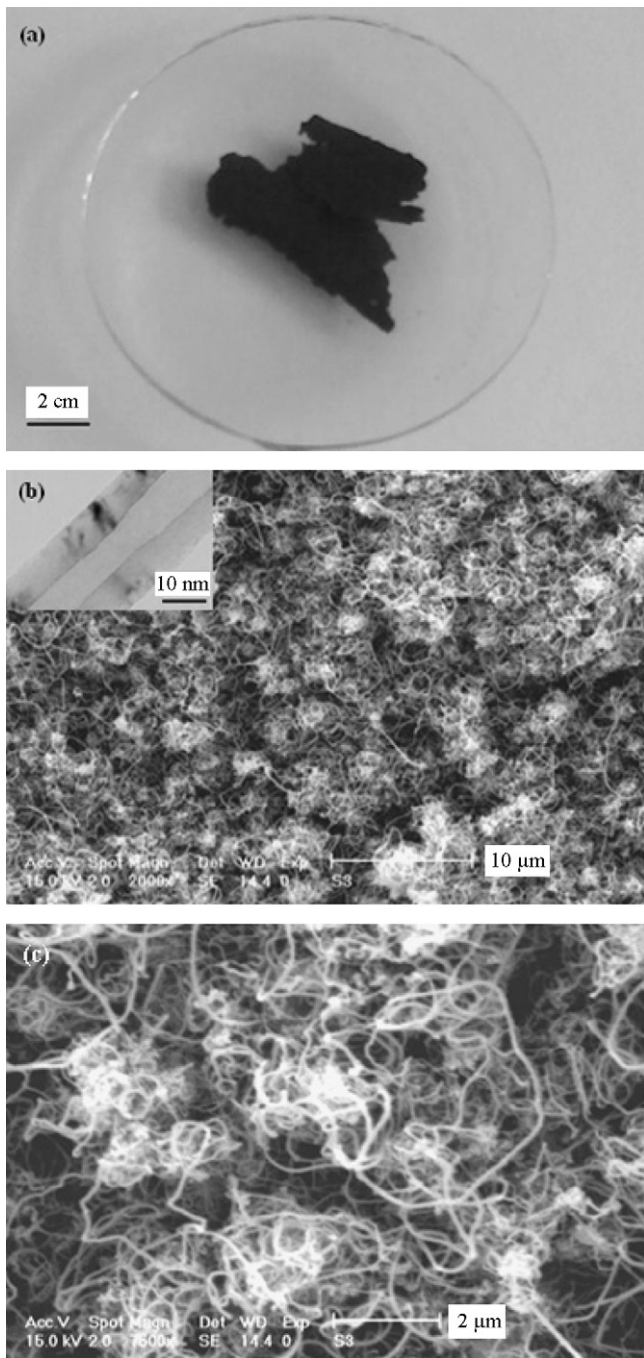


Fig. 2. Synthesized oxidized CNT sheets, (a) an overview image, (b) a surface SEM image (inset: a TEM image of a CNT) and (c) a high magnification SEM image.

oxidized CNT sheets were quantified by Boehm method [24] and presented in Table 2.

The surface charge depends on pH of the surrounding electrolyte. There is a pH value, called ‘point of zero charge’ (PZC), at which the net surface charge is zero. The pH_{PZC} of the as-synthesized and oxidized CNT sheets were quantified by mass

Table 2
Surface acidity and pH_{PZC} of the as-synthesized and the oxidized CNT sheets.

	Surface acidity (mmol/g)	pH_{PZC}
As-synthesized CNT sheets	1.6	6.8
Oxidized CNT sheets	3.6	3.9

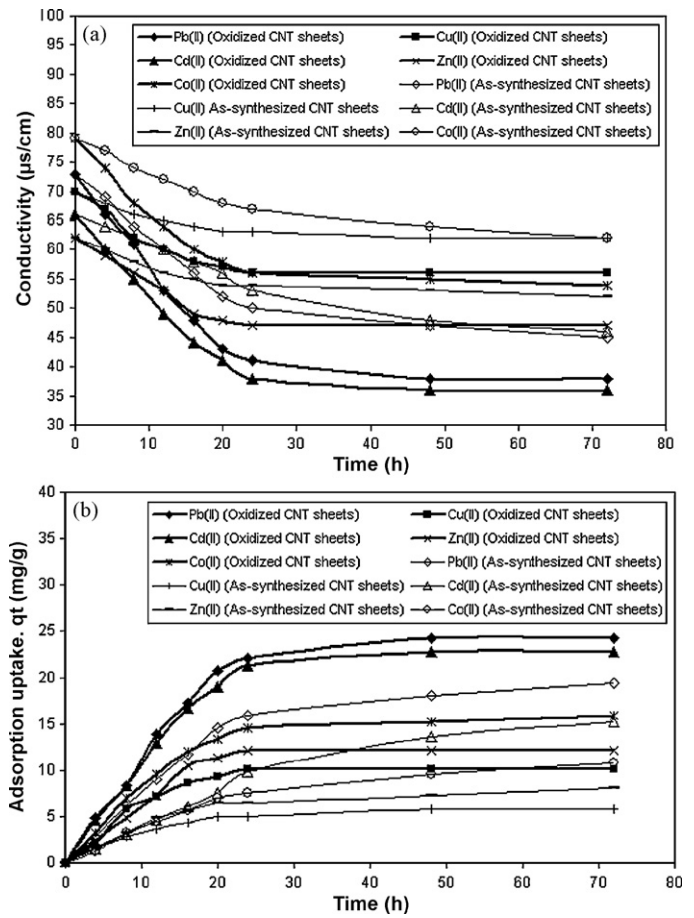


Fig. 3. Effect of adsorption time on (a) conductivity and (b) adsorption uptake of heavy metal ions (solutions with concentration of 100 mg/l) for the as-synthesized and the oxidized CNT sheets.

titration [25] and presented in Table 2. As observed, the pH_{PZC} shifts to lower pH values after nitric acid oxidation. These results confirmed our observations (Fig. 3) and the data obtained from Boehm’s titration.

The adsorption behavior of heavy metal ions onto the oxidized CNT sheets at different initial heavy metal ions concentration was investigated. Fig. 4 shows the equilibrium adsorption uptake of the oxidized CNT sheets at different initial heavy metal ions concentration. As can be observed, increasing initial heavy metal ions

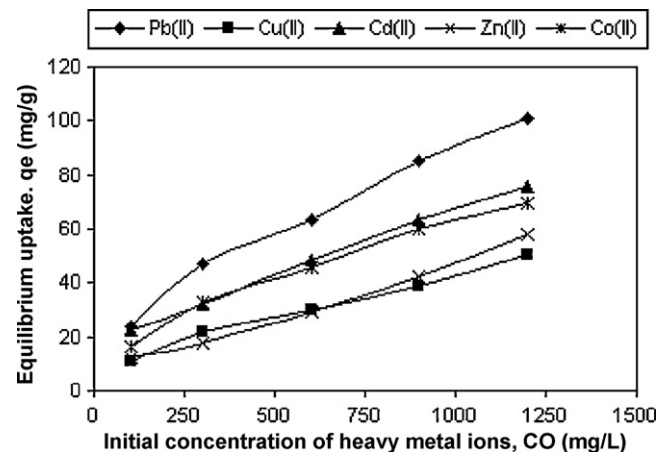


Fig. 4. Effect of initial heavy metal ions concentration on equilibrium adsorption uptake.

concentration increases significantly the equilibrium adsorption uptake of the CNT sheets. It can be due to the fact that adsorption onto the oxidized CNT sheets is a diffusion based process. At higher initial concentration, the mass transfer driving force is larger, and hence, this results in more adsorption of heavy metal ions.

The equilibrium adsorption uptake (adsorption capacity) is an important factor because it determines how much adsorbent is required quantitatively for enrichment of an analyte from a given solution. As can be observed in Fig. 4, lead ions were more favorably adsorbed onto the oxidized CNT sheets. The adsorption capacity of Pb^{2+} attained 101.05 mg/g at initial concentration of 1200 mg/l, while the adsorption capacity of Cd^{2+} , Co^{2+} , Zn^{2+} and Cu^{2+} were 75.84, 69.63, 58.00 and 50.37 mg/g, respectively. The adsorption capability of CNT sheets for these heavy metal ions can be ordered as $Pb^{2+} > Cd^{2+} > Co^{2+} > Zn^{2+} > Cu^{2+}$. The obtained results do not confirm the affinity order of $Pb^{2+} > Cu^{2+} > Cd^{2+}$ found by Li et al. [4], and $Cu^{2+} > Pb^{2+} > Co^{2+}$ found by Stafiej and Pyrzynska et al. [1]. However, their carbon nanotubes were oxidized with different methods. As mentioned, the metal ion adsorption capacity of CNTs strongly depends upon their surface total acidity including functional groups [3]. Also, it is evidence that some metal ions tend to more interact with some functional groups. The nature and concentration of functional groups are related to oxidant nature (HNO_3 , HF , H_2O_2 , $KMnO_4$ and etc.), oxidation technique (soaking, refluxing, heating in various temperature and etc.) and CNTs morphologies (the extent of CNTs surface defects) which is mainly attributed to their preparation process and their precursors (carbon source and catalyst) [1,35–37]. CNTs with more surface defects can be easily introduced more functional groups on their surface during oxidation process [37]. Therefore, different orders reported in the literature ($Pb^{2+} > Cu^{2+} > Cd^{2+}$ [4] and $Cu^{2+} > Pb^{2+} > Co^{2+}$ [1]) and in this work $Pb^{2+} > Cd^{2+} > Co^{2+} > Zn^{2+} > Cu^{2+}$, directly relates to the nature and concentration of acidic functional groups. Chemistry of the functional groups must be further investigated.

3.2. Adsorption isotherms

The experimental data for heavy metal ions adsorption onto the oxidized CNT sheets were analyzed using Freundlich and Langmuir isotherms.

The Langmuir isotherm was used successfully to characterize the monolayer adsorption process. It can be represented by the following equation:

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

Eq. (2) can be expressed in a linear form:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (3)$$

where q_e is the equilibrium adsorption uptake of heavy metal ions, in mg/g, C_e is the equilibrium concentration of heavy metal ions, in mg/l, q_m is the maximum adsorption capacity corresponding to the complete monolayer coverage, in mg/g, and K_L is the Langmuir constant which is related to the energy of adsorption.

An essential characteristic of Langmuir isotherm can be expressed by a dimensionless constant called equilibrium parameter:

$$R_L = \frac{1}{1 + K_L C_0} \quad (4)$$

where K_L is the Langmuir constant and C_0 is the highest initial heavy metal ions concentration, in mg/l. The value of R_L indicates the type of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

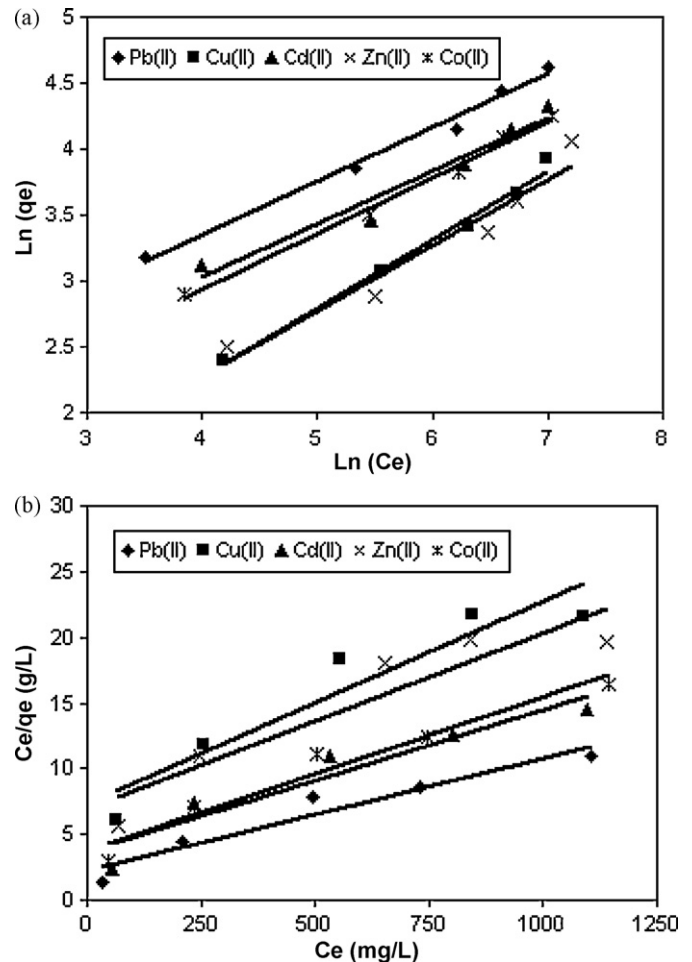


Fig. 5. (a) Freundlich and (b) Langmuir isotherms for adsorption of heavy metal ions onto the oxidized CNT sheets.

The Freundlich isotherm is a semi-empirical equation based on the adsorption occurred on heterogeneous surface. It can be presented by the following form:

$$q_e = K_F C_e^n \quad (5)$$

Eq. (5) can be expressed in a linear form:

$$\log q_e = n \log C_e + \log K_F \quad (6)$$

where q_e is the equilibrium adsorption uptake of heavy metal ions, in mg/g, C_e is the equilibrium concentration of heavy metal ions, in mg/l, and K_F and n are the Freundlich parameters related to adsorption capacity and adsorption intensity, respectively.

The slope and the intercept of each linear plot in Fig. 5 are used to calculate Langmuir and Freundlich parameters. The calculated Langmuir and Freundlich parameters are listed in Table 3. As can be observed, the dimensionless constants R_L lie within the favorable limit between 0 and 1. The q_m values calculated using the Langmuir isotherm are 117.65, 92.59, 85.74, 74.63 and 64.93 mg/g for Pb^{2+} , Cd^{2+} , Co^{2+} , Zn^{2+} and Cu^{2+} , respectively. The values of K_F calculated using the Freundlich model are large indicating that the oxidized CNT sheets have high affinity toward heavy metal ions. The constant value of K_F is higher for adsorption of Pb^{2+} onto the oxidized CNT sheets which is consistent with the experimental observations (Fig. 4). Also, not much difference among the adsorption intensities (n) of heavy metal ions is observed. Deviation of the n values from unity indicates a non-linear adsorption that takes place on heterogeneous surfaces. The n values are smaller than 1, which indicates favorable adsorption of heavy metal ions onto the oxidized

Table 3
Parameters of Langmuir and Freundlich isotherms for adsorption of heavy metal ions onto the oxidized CNT sheets.

Ions	Langmuir isotherm				Freundlich isotherm		
	q_m (mg/g)	K_L (l/mg)	R_L	R^2	n	K_F (l/mg)	R^2
Pb ²⁺	117.6470	0.0038	0.1798	0.9333	0.4071	5.4938	0.9888
Cu ²⁺	64.9350	0.0021	0.2840	0.8930	0.5170	1.2356	0.9889
Cd ²⁺	92.5925	0.0029	0.2232	0.9069	0.4017	4.1192	0.9506
Zn ²⁺	74.6268	0.0019	0.3048	0.8870	0.5024	1.2962	0.9424
Co ²⁺	85.7400	0.0031	0.2118	0.9552	0.4244	3.4051	0.9909

CNT sheets. These results demonstrate that both Langmuir and Freundlich isotherms agree well with the obtained experimental data [1,20,23,24,30,38].

3.3. Adsorption kinetics

In order to analyze the adsorption mechanism of heavy metal ions onto the oxidized CNT sheets, three kinetic models including the pseudo-first-order, the pseudo-second-order and the intra-particle diffusion models were applied to fit the experimental data obtained at lower (100 mg/l) and higher (1200 mg/l) initial concentrations of heavy metal ions.

The pseudo-first-order kinetic model [39] can be expressed by:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (7)$$

Eq. (1) can be expressed in linear form:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (8)$$

The pseudo-second-order kinetic model [40] is expressed by:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (9)$$

Eq. (3) can be expressed in linear form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (10)$$

where k_1 and k_2 are the adsorption rate constants of first and second order kinetic models, in min^{-1} and l/mg min , respectively; q_e and q_t , in mg/g , are equilibrium adsorption uptake (at time $t = \infty$) and adsorption uptake (at time t), respectively.

The slope and the intercept of each linear plot in Figs. 6 and 7 are used to calculate the adsorption rate constants (k_1 and k_2) and the amount of adsorption in equilibrium (q_e). The calculated kinetics parameters for adsorption of heavy metal ions onto the oxidized CNT sheets at two initial concentrations of heavy metal ions (low and high) are listed in Table 4. As can be observed, at low initial concentration (100 mg/l) of heavy metal ions, the correlation coefficients (R^2) of the pseudo-second-order kinetics model are higher than those of the pseudo-first-order kinetics model. Also, the experimental q_e values are closer to q_e values calculated from the pseudo-second-order kinetic model. The consistency of the experimental data with the pseudo-second-order kinetic model indicates that the adsorption of heavy metal ions onto the oxidized CNT sheets at low initial concentration is controlled by chemical adsorption (chemisorption) involving valence forces through sharing or exchange electrons between sorbent and sorbate. In chemical adsorption, it is assumed that the adsorption capacity is proportional to the number of active sites occupied on the adsorbent surface [40–42]. As can be observed in Table 4, the experimental data agree with the pseudo-first-order kinetic model especially at higher initial concentration (1200 mg/l) of heavy metal ions, which indicates that adsorption of heavy metal ions onto the oxidized CNT sheets is a diffusion based process [43].

The kinetic results were analyzed by the intra-particle diffusion model [44] in order to elucidate the diffusion mechanism. The intra-particle diffusion model is expressed by:

$$q_t = k_p t^{1/2} + C \quad (11)$$

where k_p is the intra-particle diffusion rate constant, in $\text{mg/g h}^{1/2}$, and C , in mg/g , is a constant related to the thickness of the boundary layer. The intra-particle diffusion model parameters for adsorption of heavy metal ions onto the oxidized CNT sheets at two initial heavy metal ions concentrations (100 and 1200 mg/l) were calculated as listed in Table 5. According to this model, if the plot of q_t versus $t^{1/2}$ gives a straight line, then intra-particle diffusion is involved in the adsorption process and if this line passes through the origin then intra-particle diffusion is the rate-controlling step [45]. However, if the data present multi-linear plots, then two or more steps influence the adsorption process such as external diffusion, intra-particle diffusion and etc. [42].

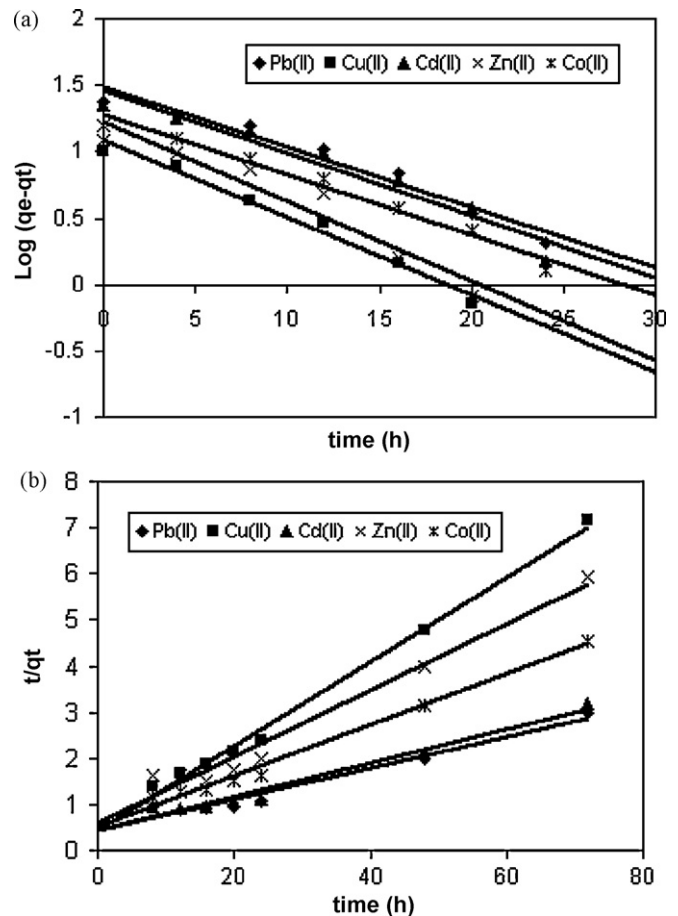


Fig. 6. (a) Pseudo-first-order and (b) pseudo-second-order kinetic models for adsorption of heavy metal ions (solutions with initial concentration of 100 mg/l) onto the oxidized CNT sheets.

Table 4

Parameters of pseudo-first-order and pseudo-second-order kinetic models for adsorption of heavy metal ions onto the oxidized CNT sheets.

Ions	C_0 (mg/l)	$q_{e,exp}$	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
			q_e	k_1	R^2	q_e	$k_2 \times 10^{-3}$	R^2
Pb ²⁺	100	24.2235	30.4018	0.1041	0.9613	26.9597	2.5604	0.9845
Cu ²⁺	100	10.0751	12.0920	0.1338	0.9808	10.6953	12.1569	0.9956
Cd ²⁺	100	22.7458	29.2280	0.1082	0.9453	25.0186	3.1088	0.9796
Zn ²⁺	100	12.1163	16.6494	0.1379	0.9336	13.8805	5.6352	0.9849
Co ²⁺	100	15.8254	18.8581	0.1038	0.9773	16.1938	5.8192	0.9968
Pb ²⁺	1200	101.046	108.331	0.0403	0.9888	243.9024	0.0430	0.9203
Cu ²⁺	1200	50.3755	52.5174	0.0396	0.9960	128.2051	0.0772	0.7800
Cd ²⁺	1200	75.8350	88.719	0.0502	0.9743	181.8181	0.0611	0.8852
Zn ²⁺	1200	58.0000	63.7823	0.0343	0.9967	144.9275	0.0672	0.9244
Co ²⁺	1200	69.6300	79.701	0.0442	0.9729	294.1176	0.0165	0.6917

Table 5

Parameters of intra-particle diffusion model for adsorption of heavy metal ions onto the oxidized CNT sheets.

Ions	C_0 (mg/l)	k_{p1} (mg/g h ^{1/2})	C_1	R^2	k_{p2} (mg/g h ^{1/2})	C_2	R^2
Cu ²⁺	100	5.9560	7.7299	0.9965	0.4387	19.2640	0.8126
Cd ²⁺	100	3.9712	4.4215	0.9922	0.3510	12.8160	0.9743
Zn ²⁺	100	3.9527	5.8872	0.9725	0.2713	10.0700	0.7849
Co ²⁺	100	3.1898	3.8654	0.9761	0.2417	8.2520	0.8056

Ions	C_0 (mg/l)	k_p (mg/g h ^{1/2})	C	R^2
Cu ²⁺	1200	7.4377	10.7990	0.9907
Cd ²⁺	1200	11.4210	16.5780	0.9846
Zn ²⁺	1200	8.4333	12.9600	0.9967
Co ²⁺	1200	10.774	19.2310	0.9875

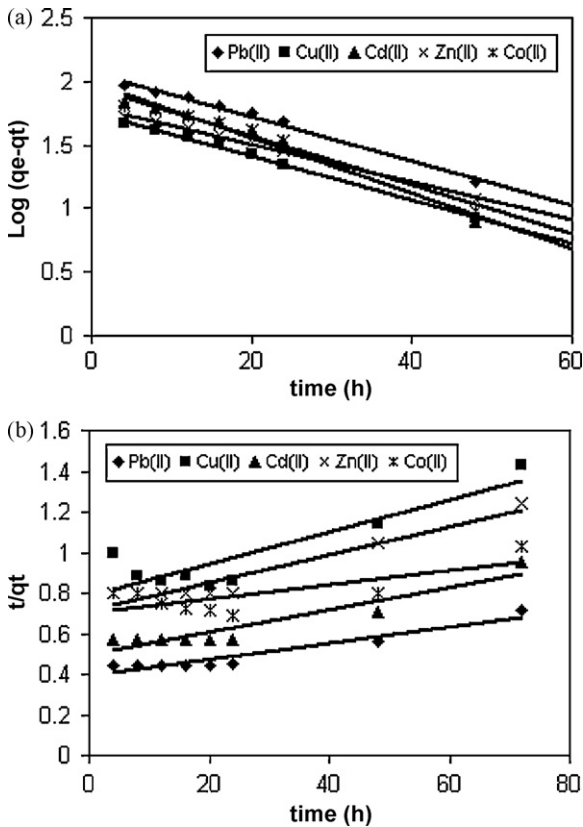


Fig. 7. (a) Pseudo-first-order and (b) pseudo-second-order kinetic models for adsorption of heavy metal ions (solutions with initial concentration of 1200 mg/l) onto the oxidized CNT sheets.

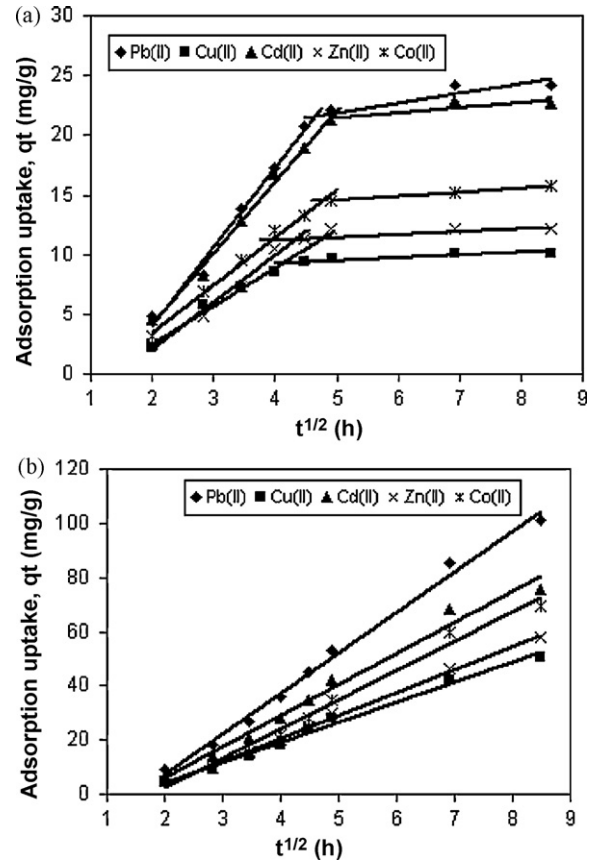


Fig. 8. Intra-particle diffusion model for adsorption of heavy metal ions onto the oxidized CNT sheets (a) solutions with initial concentration of 100 mg/l, (b) solutions with initial concentration of 1200 mg/l.

As can be observed in Fig. 8, at low initial concentration of heavy metal ions (100 mg/l), the data points are related by two straight lines (Fig. 8a). The first sharper portion is attributed to the diffusion of adsorbate through the solution to the external surface of the adsorbent (external diffusion) and the second portion describes the gradual adsorption stage, corresponding to diffusion of adsorbate molecules inside the pores of the adsorbent (intra-particle diffusion) [42]. At high initial concentration (1200 mg/l), the data points are related by one straight line (Fig. 8b), indicating that intra-particle diffusion is mainly involved in the adsorption process. The deviation of straight lines from the origin indicates that the intra-particle diffusion is not the sole rate-controlling mechanism.

The obtained results demonstrate that kinetics of adsorption varies with initial concentration of heavy metal ions. At lower initial concentration of heavy metal ions, adsorption is controlled by chemical adsorption, external diffusion and to some extent intra-particle diffusion (low R^2 values), while at higher initial concentration, desorption process is mainly involved intra-particle diffusion. This can be explained by the fact that at higher initial concentration, the mass transfer driving force is larger, and hence this results in higher diffusion rates of heavy metal ions within the pores of CNT sheets. As can be observed in Table 5, the intra-particle diffusion rate constant values increase significantly with increasing initial concentration of heavy metal ions due to the greater driving force.

Using the oxidized CNT sheets as adsorbent eliminates problems of agitating and removing of the CNTs with and from water before and after adsorption process, respectively. Also, using the oxidized CNT sheets as adsorbent, economical waste water treatment without CNT leakage into water is feasible. As a result, the oxidized CNT sheets with high practical potential can be recommended as an economical and effective adsorbent for heavy metal ions removal from waste water in industrial scale.

4. Conclusion

Chemical vapor deposition was used for synthesis of CNT sheets. The CNT sheets were then oxidized with concentrated nitric acid at room temperature. The results demonstrate that the adsorption capacity of the CNT sheets increases significantly after oxidation process. Also, increasing initial salts concentration increases the adsorption capacity of the CNT sheets. The adsorption behaviors of heavy metal ions onto the oxidized CNT sheets match well with Langmuir and Freundlich isotherms. The results demonstrated that kinetics of adsorption varies with initial concentration of heavy metal ions. The preference order of adsorption on the oxidized CNT sheets is $Pb^{2+} > Cd^{2+} > Co^{2+} > Zn^{2+} > Cu^{2+}$. Using the oxidized CNT sheets as adsorbent, economical waste water treatment without CNT leakage into water is feasible. The oxidized CNT sheets are promising materials for pre-concentration and solidification of heavy metal ions from large volume of solutions.

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