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Preparation of triethanolamine functionalized carbon nanotube for aqueous removal of Pb(II)

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ABSTRACT

Triethanolamine functionalized multi-walled carbon nanotube (MWCNT-TEA) was prepared and utilized for the removal of Pb(II) from aqueous solutions. The characterization of MWCNT-TEA composite was validated by Fourier transform infrared spectroscopy, Raman spectroscopy, thermogravimetric analysis, Brunauer–Emmett–Teller surface area analysis, scanning electron microscopy, high-resolution transmission electron microscopy and energy-dispersive X-ray spectroscopy. The adsorption conditions, such as contact time, temperature, pH and initial concentration, of Pb(II) were optimized, and contrast experiments were also carried out. The kinetics and mechanism of Pb(II) removal by MWCNT-TEA were investigated using different kinetic models, isotherm models and thermodynamic equations, and the results showed that the adsorption process best fitted the pseudo-second-order model and the Langmuir model, and the adsorption is a spontaneous and endothermic process. The experimental data also indicated that MWCNT-TEA composite exhibited superior adsorption capability for Pb(II) than that of oxidized MWCNT. In addition, MWCNT-TEA composite can be readily separated from aqueous solution by filtration or centrifugation after the adsorption. Therefore, MWCNT-TEA composite could be used as a novel adsorbent for the aqueous removal of heavy metal ions in the future due to its advantages such as easy preparation, high adsorption capacities and excellent environmental stability.

Keywords: Carbon nanotube; Triethanolamine; Composites; Adsorption; Lead

1. Introduction

It is well known that the increasing amounts of anthropogenic pollutants in the aqueous environment impose serious risks (both acute and delayed) to human beings. Heavy metal is a common type of pollutant among accidental pollutions. In recent years, the frequency and intensity of accidental heavy metal pollution events tend to increase in China [1–3]. As one of the most important aspects in the aqueous pollution, water pollution by heavy metals is a worldwide issue. Because of their extreme toxicities even at low concentration, tendency to bioaccumulate in the tissues of organisms, and not easy to degrade, heavy metal contamination need to be considered with urgency and great concern [4,5].

Among these various toxic heavy metals such as lead (Pb), cadmium (Ca), copper (Cu), chromium (Cr), selenium (Se) and mercury (Hg). Pb(II) is considered to cause many health problems to humans and animals because it can be accumulated in living tissues throughout the food chains and it has nonbiodegradable properties [6,7]. Thus, it is urgently necessary to remove Pb(II) from aqueous solutions [8]. To eliminate or lessen heavy ions from aquatic environments,

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various technologies such as adsorption [9–11], chemical complexation [12], membrane filtration [13], precipitation [14], alkali kneading [15], flocculation [16] and so on have been developed and widely used. However, most of these processes have showed distinct disadvantages such as incomplete removal, high energy consumption, high cost of treatment, production of toxic sludge and so on [17]. Until now, adsorption is considered as one of the most practical methods because heavy metal ions could be removed more facilely and relatively recovered more easily [18].

The exploitation of carbon nanomaterials including carbon nanotubes (CNTs), fullerene and graphene for industrial applications has been shown to improve promptly in the recent years [19–23]. It is well known that these carbon nanomaterials could be used as effective adsorbents for heavy metal ions removal [24–28]. As a new form of carbon, CNTs have attracted great interest in research due to their exceptional mechanical properties and unique electrical properties [29,30], high chemical stability and large specific surface area since their discovery [31]. Specially, the large specific surface area, and small, hollow and layered nanosized structures may make CNTs a good candidate as useful adsorbents for removal of heavy metals and organic contaminants. In addition, the adsorption capacities and dispersibility of CNTs could be regulated by introducing diverse functional groups on their surface [32]. For instance, thiol or amino functional groups functionalized CNTs have been developed and used to effectively remove heavy metal ions from aqueous solution [33,34]. As reported previously, the attachment of oxygen containing functional groups such as hydroxyl and carboxyl groups on the surface of CNTs would form additional chelating ligands with heavy metal ions, highly enhancing their adsorption capacities [35,36]. The oxidized multi-walled CNTs (ox-MWCNT) has better adsorption performance for heavy metal ions, such as Cu(II), Pb(II), and Cr(II), than pristine MWCNTs, which has been reported in many literature published in the past few years [37]. To improve its adsorption properties, the surface modification of CNTs using various organic/inorganic species has been widely studied [23,38].

Triethanolamine (TEA), a kind of hydroxyl tertiary amine, is an important and effective heavy metal chelator, with four chelating binding sites, which can form the chelate-metal complex with several kinds of heavy metal ion in normal temperature and a wide range of pH conditions [39]. Herein, TEA was chosen as a modifier to modify MWCNTs). And the TEA-modified MWCNT (MWCNT-TEA) composite was fully characterized by Fourier transform infrared (FTIR) spectroscopy, Raman spectroscopy, thermogravimetric analysis (TGA), Brunauer–Emmett–Teller (BET) surface area analysis, scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS) and high-resolution transmission electron microscopy (HRTEM). The MWCNT-TEA composite was used as a novel adsorbent to remove Pb(II) from aqueous solutions. The adsorption behavior of Pb(II) on MWCNT-TEA composite was carried out by batch experiments. The effects of solution pH, contact time, initial concentration of Pb(II) ion and solution temperature were investigated. To compare its adsorption properties with ox-MWCNT, a series of contrast experiments were also conducted. To reveal the adsorption mechanism, the adsorption thermodynamic, adsorption kinetics and adsorption isotherms of Pb(II) by MWCNT-TEA were further discussed.

2. Experimental

2.1. Reagents and chemicals

MWCNTs with the main diameters in the range of 20–40 nm, a purity by weight of more than 97% and specific surface area of 80–140 m^2/g were bought from Shenzhen Nanotech Port Co., Ltd., China. TEA (98 wt%) was supplied by Tianjin Hengxing Chemical Reagent Co., Ltd., China. Lead nitrate ($Pb(NO_3)_2$) was purchased from Guangdong Xi Long Chemical Co., Ltd., China. Other reagents such as nitric acid (HNO_3, 63%), dimethyl sulfoxide (DMSO, 99%), N1-((ethylimino)methylene)-N3,N3-dimethylpropane-1,3-diamine (EDC, 99%), 4-dimethylaminopyridine (DMAP, 99%), ethanol (EtOH, 99.8%), acetone and ethyl ether were used as received without any further purification.

2.2. Oxidation of MWCNT

MWCNT (400 mg) was dispersed in 50.0 mL of HNO_3, and the mixture was stirred at 120°C for 24 h to introduce oxygen groups onto its surface. The mixture was then cooled to room temperature, and it was diluted using deionized (DI) water (300.0 mL) and vacuum-filtered through a polytetrafluoroethylene (PTFE) membrane (pore size = 0.45 μm). The solid residue was washed repeatedly with DI water until the pH of the filtrate was neutral. The solid residue was then washed thoroughly using ethanol, acetone and ether. Finally, the black solid on the filter membrane was collected and dried at 80°C for 24 h to obtain 293.0 mg of ox-MWCNT.

2.3. Preparation of MWCNT-TEA

The functionalization of MWCNT using TEA is illustrated in Fig. 1 [40,41]. Ox-MWCNT (290.0 mg) was dispersed in TEA (50.0 mL) by sonication, and the coupling agents for the esterification, EDC (1 g) and DMAP (0.5 g) were added into the mixture. The reaction was heated to 80°C and stirred for 12 h. After that, the mixture was cooled to room temperature, then filtered and rinsed successively and thoroughly using DI water and ethanol for several times. Finally, the obtained product was dispersed in DI water under sonication and then vacuum freeze-dried at –55°C for 48 h to obtain 250 mg of MWCNT-TEA composite.

2.4. Characterization methods

The samples were characterized by FTIR spectroscopy, Raman spectroscopy, SEM, HRTEM, TGA and BET method.

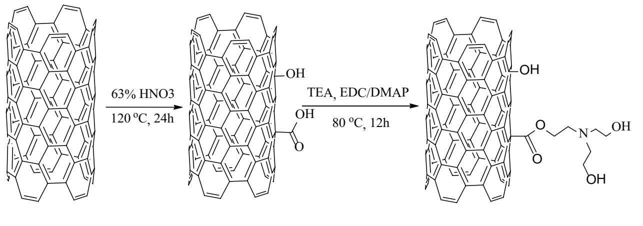

Fig. 1. Schematic diagram of the functionalization of MWCNT using TEA.

2.5. Batch adsorption experiments

Analytical-grade lead nitrate ($Pb(NO_3)_2$) was employed to prepare a stock solution containing 1 g/L of lead ions (Pb(II)), which was further diluted with DI water to the required concentration and used for the adsorption experiments. MWCNT-TEA composite was used as the adsorbent, and its adsorption behavior toward Pb(II) in aqueous solutions was investigated. In order to evaluate its adsorptive properties, the factors including reaction time (5–240 min), adsorption temperature (15°C–35°C), the initial concentrations of Pb(II) (10–100 mg/L) and pH (1.2–6.0) were studied. And 1.0 mol/L of HNO_3 and 1.0 mol/L of NaOH were used to adjust pH of the solutions.

Batch adsorption experiments were implemented by addition of 10.0 mg of MWCNT-TEA composite and 20.0 mL of Pb(II) aqueous solution with the requested concentrations in 50.0 mL polyethylene bottles. And the bottles were then placed in a water-bathing constant temperature vibrator, which operated at fixed temperatures and frequencies. The adsorption kinetics was investigated using an initial Pb(II) concentration 50 mg/L and 10.0 mg of MWCNT-TEA composite, and the mixture was oscillated at 25°C with contact time ranging from 5 to 240 min at an oscillation frequency of 220 rpm. The adsorption isotherms was studied using 10.0 mg of MWCNT-TEA composite with 20.0 mL of Pb(II) solutions with initial concentrations ranging from 10 to 100 mg/L, and the mixtures were oscillated at pH 5.5 at 15°C, 25°C and 35°C, respectively. The pH values of the solutions were adjusted between 1.2 and 6 by adding aqueous solution of NaOH (1 mol/L) and HNO_3 (1 mol/L) at room temperature. A contrast experiment was also carried out to compare the adsorption capacities of MWCNT-TEA composite and ox-MWCNT for Pb(II) solutions with different initial concentrations at 25°C. All of the Pb(II) solutions before and after adsorption were filtered through a 0.45-μm PTFE membrane and Pb(II) concentrations in the filtrate were analyzed using an inductively coupled plasma optical emission spectroscopy. The amount of Pb(II) adsorbed onto the adsorbents could be calculated by the difference of the initial concentration and the equilibrium concentration. The sorption capacity and percentage of Pb(II) from the aqueous solutions could be calculated by the following equations [42–44]:

$$R(\%) = \frac{C_0 - C_e}{C_0} \times 100 \tag{1}$$

$$q_e = \frac{(C_0 - C_e)}{C_0} \times V \tag{2}$$

where q_e (mg/g) is the amount of Pb(II) ion adsorbed onto adsorbents; C_0 (mg/L) is the initial Pb(II) concentration; C_e (mg/L) is the final metal-ion concentration after a certain period of contact time; V (mL) is the volume of the Pb(II) solution; m (g) is the adsorbent dosage; and R(%) is the removal percentage of Pb(II).

3. Results and discussion

3.1. Characterization of MWCNT-TEA

FTIR spectra of pristine MWCNT, ox-MWCNTs and MWCNT-TA are shown in Fig. 2. The samples were scanned in the range of 400–4,000 cm^{-1} with a resolution of 8 cm^{-1} using a Nicolet Avatar 360 FTIR spectrometer. The peak at 1,078 cm^{-1} could be assigned to stretching vibration of C–O group, and the peaks at 1,621 cm^{-1} (or 1,634 cm^{-1}) and 1,568 cm^{-1} correspond to aromatic ring structure of MWCNT. The peak at around 3,460 cm^{-1} corresponds to stretching vibration of O–H group. The emerging new peak at 1,730 cm^{-1} corresponds to the vibration of C=O group of MWCNT-TEA. The formation of ester bond between TEA and MWCNT was confirmed through the FTIR curves.

Raman spectra analysis was implemented using a Renishaw Micro-Raman System 2000 spectrometer, which was operated at a laser wavelength of 514.5 nm. The Raman spectra of MWCNT contains two typical peaks that are located in the range of 1,200–1,800 cm^{-1}. As shown in Fig. 3, the peak at around 1,356 cm^{-1}, named the "D-band", can be assigned to the existence of disorder in MWCNT. Another peak at 1,571 cm^{-1}, called the "G-band", that corresponds to the tangential vibrations of the carbon atoms and originates from a defect induced double resonance scattering process [45]. The intensity ratio of the D-band to the G-band (I_D/I_G) is commonly used to evaluate the degree of defects on carbon nanomaterials. The I_D/I_G of MWCNT-TEA (0.81) was decreased a little compared with that of pristine MWCNT (1.02), indicating that the CNT's sidewall was damaged due to the covalent functionalization treatments including the oxidization and the esterification. The results also reflected the conversion of some sp^2 carbons on the sidewall of MWCNT to sp^3 hybridization.

TGA was carried out on a TA Instruments 2100/2910 differential scanning calorimeter in the temperature range of 25°C–650°C with a heating rate of 10°C /min in an atmosphere of argon. By comparing the temperatures of onset of active pyrolysis, pristine MWCNT was stable and hardly decomposed (Fig. 4). Additionally, MWCNT-TEA exhibits a weight loss of about 11.85 wt% at 200°C–650°C, which could be attributed to the thermal decomposition of grafted TEA groups, indicating TEA was successfully attached onto the surface of ox-MWCNT.

Morphological observations of the samples were made with an MIRA3 TESCAN SEM and a JEM-2100 HRTEM.

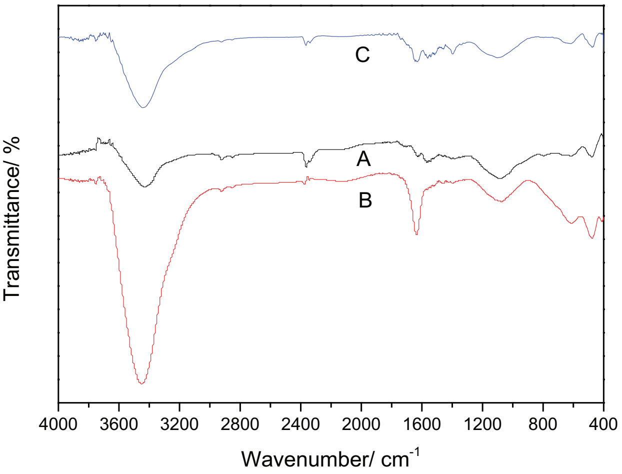

Fig. 2. FTIR spectrum of the samples: (A) MWCNT-TEA; (B) pristine MWCNT and (C) ox-MWCNTs.

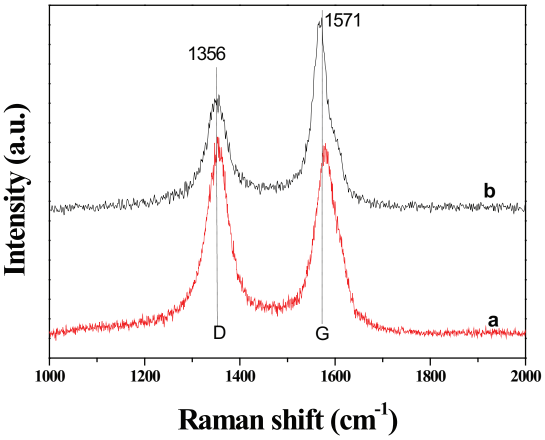

Fig. 3. Raman spectrum of the samples: (a) pristine MWCNT and (b) MWCNT-TEA.

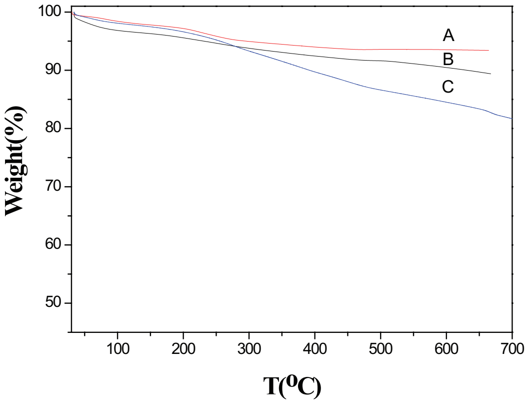

Fig. 4. TGA curves of the samples: (A) pristine MWCNT; (B) ox-MWCNT and (C) MWCNT-TA.

No obvious difference between pristine MWCNT and MWCNT-TEA could be observed. MWCNTs usually are curved and highly tangled tubes with rope-like structure, and aggregates are formed among the tubes due to intermolecular forces (Fig. 5(A)). In contrast with pristine MWCNTs, MWCNT-TEA has many defects on the surface and both ends of the tubes, facilitating the possible interactions between metal ions and the modified tubes (Figs. 5(B) and 6).

Specific surface area measurements of pristine MWCNT and MWCNT-TEA were done using a BET method on a JW-BK132F apparatus at 77 K by N_2 adsorption–desorption isotherms. By argon multi-layer adsorption measurement, the BET specific surface test results show that the specific surface areas of pristine MWCNT and MWCNT-TEA are about 90.749 and 133.919 m^2/g, respectively (Table 1). According to the measurements, the specific surface area of MWCNT-TEA was found to increase a little by the chemical functionalization. Usually, nanoparticles tend to be composed of agglomerates due to agglomeration. Depending on the interaction forces involved, the nanoparticles will agglomerate and cause large losses of its specific surface. The surface modification of the nanoparticles was considered as one of the most effective methods to reduce the agglomeration [46,47].

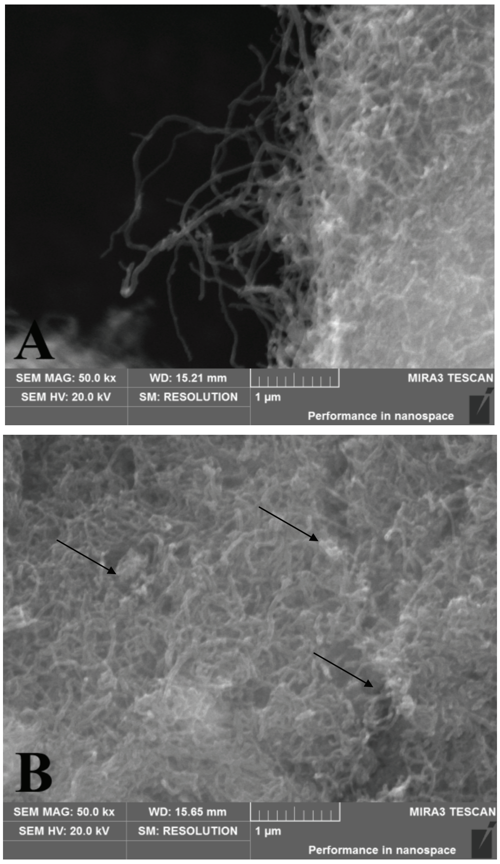

Fig. 5. SEM images of the samples: (A) pristine MWCNTs and (B) MWCNT-TEA. The defects are obvious on both the surface and ends of the tubes (as indicated by the arrows).

EDS analysis of pristine MWCNT and MWCNT-TEA shows that the atomic ratio of C:O:N for pristine MWCNT is 100:0:0, and the atomic ratio of C:O:N for MWCNT-TEA is 86.17:7.17:6.39, indicating that TEA was successfully attached onto MWCNT (Table 2).

3.2. Adsorption experiments

3.2.1. Effects of contact time

The adsorption capacity increased with an increasing contact time, and the effects of contact time on the adsorption of Pb(II) by MWCNT-TEA were investigated. As shown in Fig. 7, the adsorption of Pb(II) by MWCNT-TEA reached equilibrium in about 1 h. To ensure equilibrium could be reached, 120 min was chosen as the contact time in all subsequent experiments.

3.2.2. Effects of pH

It is well known that the pH of the aqueous solution is an important parameter that controls the adsorption of heavy metal ions. The existence of metal ion species depends on the pH of the solutions. Pb(II) ions would start to precipitate as

$Pb(OH)_2$ above pH of 5.7, and adsorption experiments were carried out in the pH range of 1–6 at 26°C. The pH values of the solutions were adjusted using 1 mol/L of NaOH or 1 mol/L of HNO_3.

As shown in Fig. 8, it can be seen that the capacities of MWCNT-TEA toward Pb(II) are largely depended on the pH of the solutions. The adsorption capacities of MWCNT-TEA toward Pb(II) increased when the pH increased from 1.2 to 5.5, but decreased at pH of 6 when Pb(II) began to form precipitate [48]. At low initial pH values, the surface of sorbent was surrounded by the hydronium ion (H_3O^+), which prevented Pb(II) ion from approaching the binding sites of the adsorbents. Therefore, Pb(II) ion solution with an initial concentration of 50 mg/L and pH of 5.5 was prepared for the subsequent experiments.

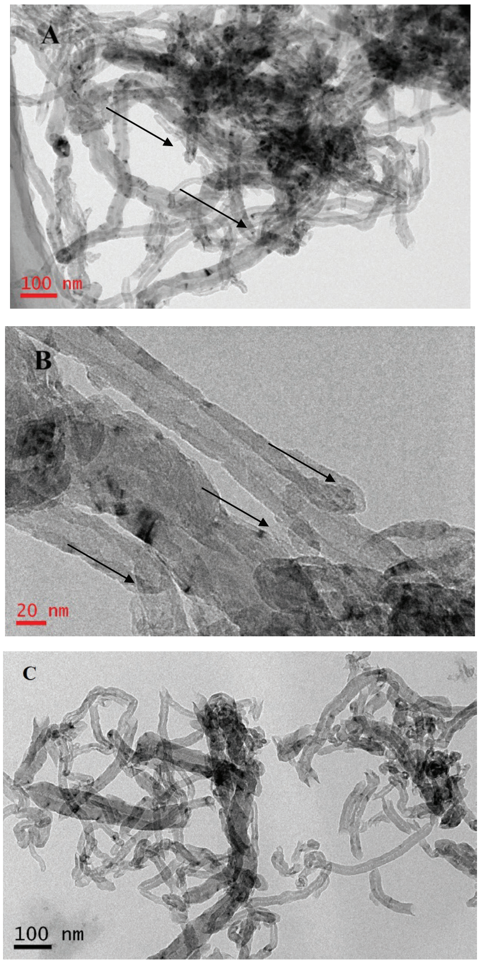

Fig. 6. TEM images of the samples: (A) MWCNT-TEA of low-resolution; (B) MWCNT-TEA of high-resolution and (C) pristine MWCNT. The defects are obvious on both the surface and ends of the tubes (as indicated by the arrows).

3.2.3. Adsorption isotherms

The adsorption isotherm is an important factor to explain the adsorption mechanism between adsorbent and adsorbate. Adsorption isotherm could be carried out by varying the initial concentration of Pb(II) and at different reaction temperature. And many adsorption isotherms could be employed to describe the interaction between adsorbents and adsorbates [49,50]. In this study, the adsorption results were analyzed using Langmuir isotherm equation and Freundlich isotherm model in Eqs. (3) and (4), respectively:

$$\frac{C_e}{q_e} = \frac{1}{K_c q_m} + \frac{C_e}{q_m} \tag{3}$$

$$\ln q_e = \ln K_d + \frac{1}{n} \ln C_e \tag{4}$$

where q_e (mg/g) and C_e (mg/L) are the equilibrium adsorption capacity and the equilibrium concentration, respectively; q_m (mg/g) is the maximum adsorption capacity; and K_c is Langmuir constant related to affinity of binding site and a measure of the adsorption energy. Values of Langmuir parameters of q_m and K_c could be calculated from the slope and intercept of the linear plot C_e/q_e vs. C_e, respectively. K_d and n are empirical constants of Freundlich that indicate the relative adsorption capacity and adsorption intensity, respectively. The values of K_d and n could be got from slope of linear plot $\ln q_e$ vs. $\ln C_e$, respectively. If the value of n is between 1 and 10, the adsorption process is considered to be favorable. Generally, the Langmuir isotherm assumes monolayer adsorption on a uniform surface with a finite number of adsorption sites, and Freundlich isotherm model describes the relationship between nonideal and reversible adsorption.

The adsorption isotherms for the Pb(II) removal by MWCNT-TEA at 298, 308 and 318 K with the initial Pb(II) concentrations in the range of 10–100 mg/L were investigated (Fig. 9). The correlation coefficients values (R^2) indicate that the adsorption of Pb(II) onto MWCNT-TEA fits better by the Langmuir isotherm equation (R^2 = 0.996–0.998) than the Freundlich isotherm model (R^2 = 0.272–0.748). Furthermore, the values of q_m (103.734–118.483 mg/g) calculated from Langmuir isotherm equation are logical and approximated to the experimental value (Table 3). Therefore, the adsorption could be mainly considered as monolayer adsorption on a uniform surface with a finite number of adsorption sites.

Table 1
BET surface areas, pore volumes and pore diameters of pristine MWCNT and MWCNT-TEA

Sorbents	BET specific surface area (m^2 g^{-1})	DR method of micro-pore volume (cm^3 g^{-1})	Total pore volume (cm^3 g^{-1})	Average pore diameter (nm)
MWCNT	90.749	0.032	0.32254	10.14108
MWCNT-TEA	133.919	11.689	0.36593	6.77070

3.2.4. Adsorption kinetics

To investigate the adsorption rate and the rate-controlling step, the adsorption data were also determined quantitatively and compared by two different kinetic models of the first-order kinetic model and second-order kinetic equation, respectively. And the two models are shown as follows [49,51]:

$$\log\left(q_e - q_t\right) = \log q_e - \frac{k_a}{2.303}t \tag{5}$$

Table 2
EDS analysis of pristine MWCNT and MWCNT-TEA

Element	Pristine MWCNT		MWCNT-TEA	
	Weight %	Atomic %	Weight %	Atomic %
C	100	100	82.85	86.17
O	0	0	9.18	7.17
N	0	0	7.16	6.39

$$\frac{t}{q_t} = \frac{1}{k_b q_e^2} + \frac{1}{q_e}t \tag{6}$$

where q_e and q_t are the amounts of metal ion adsorbed (mg/g) at equilibrium and at time *t*, respectively; $K_{a/b}$ (min^{-1}) is the rate constant of adsorption; and correlation coefficient (R^2) is used to evaluate the goodness of fit.

As shown in Fig. 10, it can be observed that the correlation coefficient of pseudo-second-order adsorption equation ($R^2 = 0.99998$) is higher than that of pseudo-first-order adsorption equation (R^2 = 0.47736). And the calculated parameters from the experimental data are summarized in Table 4. The calculated adsorption capacity ($q_{e,cal}$) was evaluated and compared with the experimental adsorption capacity ($q_{e,exp}$). It could be observed that the $q_{e,cal}$ of 5.82 mg/g from the pseudo-first-order kinetics was far away from the $q_{e,exp}$ of 98.17 mg/g. However, the $q_{e,cal}$ calculated from the pseudo-second-order was 98.23 mg/g, which was very close to the $q_{e,exp}$ of 98.17 mg/g. Therefore, the pseudo-second-order model gave a better description of the kinetic data of Pb(II) adsorption on MWCNT-TEA.

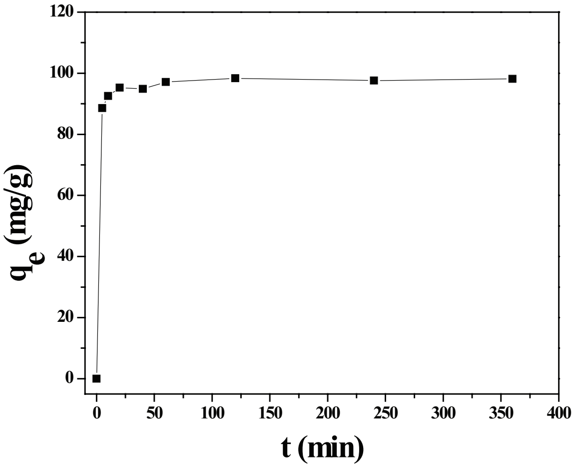

Fig. 7. Effects of contact time on the adsorption of Pb(II) by MWCNT-TEA at 26°C (V = 20.00 mL, C_0 = 50.00 mg L^{-1}, m = 0.0100 g).

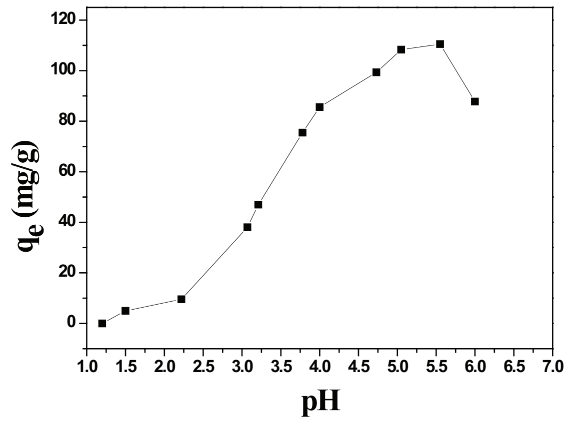

Fig. 8. Effects of pH on the adsorption of Pb(II) by MWCNT-TEA at 26°C (V = 20.00 mL, C_0 = 50.00 mg·L^{-1}, m = 0.0100 g).

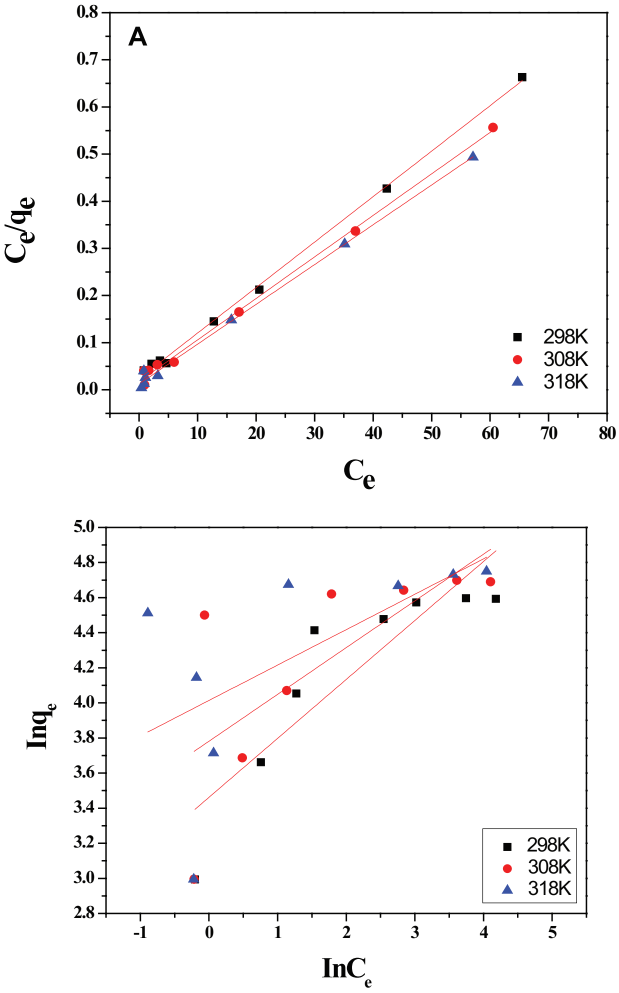

Fig. 9. Graphical representation of adsorption isotherms of Pb(II) on MWCNT-TEA at different temperatures (pH = 5.0, contact time = 1 h): (A) Langmuir isotherm model and (B) Freundlich isotherm equation.

3.2.5. Adsorption thermodynamics

The adsorption thermodynamic parameters can afford useful information on energy changes of the adsorption process. The thermodynamic parameters, including energy ($\Delta G°$), enthalpy ($\Delta H°$) and entropy ($\Delta S°$), were calculated using the following Van't Hoff thermodynamic equations as follows [52–54]:

$$\ln K_e = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \tag{7}$$

$$\Delta G° = \Delta H° - T\Delta S° \tag{8}$$

$$K_e = \frac{C_0 - C_e}{C_e} \tag{9}$$

where K_e is the equilibrium distribution coefficient for the adsorption process; C_0 and C_e (mg/L) are the initial and equilibrium concentrations of Pb(II) in the supernatant after separation, respectively; R (8.314 J/mol·K) is the gas constant. The adsorption experiments were conducted at T = 298, 308, and 318 K, respectively. The thermodynamic parameters of $\Delta H°$ and $\Delta S°$ can be acquired from the slope and intercept of the linear plot of lnk_e vs. $1/T$, respectively (Fig. 11).

As shown in Table 5, the negative value of $\Delta G°$ indicated that the adsorption reaction in nature is spontaneous at all the experimental temperatures. The positive value of $\Delta H°$ indicated that the adsorption is endothermic, and the increasing of temperature was beneficial to the adsorption. The positive value of $\Delta S°$ demonstrated that the adsorption on MWCNT-TEA is driven by an increase of entropy [49].

3.2.6. Contrast experiments

To contrast the adsorption capacity of MWCNT-TEA with initial raw materials, the adsorption of Pb(II) onto ox-MWCNT was also carried out in the initial Pb(II) concentrations of 10–100 mg·L^{-1}. As shown in Fig. 12, the adsorption capacities of MWCNT-based adsorbents toward Pb(II) increased accordingly with an increasing initial concentrations of Pb(II), and the adsorption capacities of the adsorbents were increasing along with the increasing temperature. And the adsorption performance of MWCNT-TEA toward Pb(II) was better than those of ox-MWCNT and pristine MWCNT, indicating the introducing TEA onto ox-MWCNT was beneficial to its adsorption capacity.

Table 3
Langmuir and Freundlich isotherm parameters for Pb(II) adsorption on MWCNT-TEA

Temperature (K)	Langmuir isotherm			Freundlich isotherm		
	q_m (mg/g)	K_c	R^2	n	K_d	R^2
298	103.734	0.400	0.998	2.976	1.399	0.748
308	113.636	0.493	0.996	3.750	1.306	0.432
318	118.483	0.067	0.996	4.955	1.224	0.272

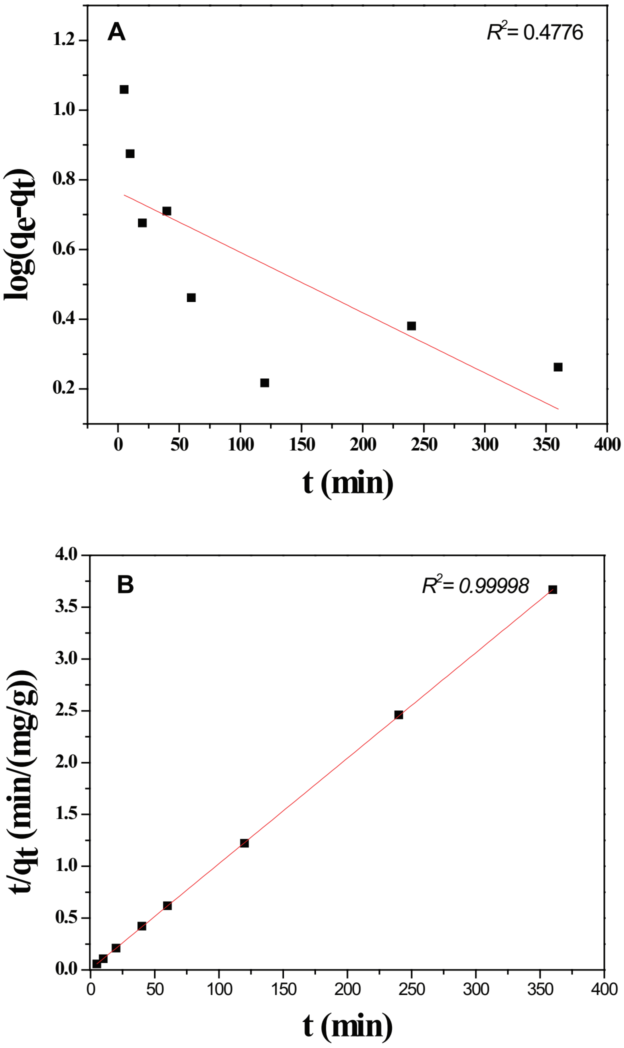

Fig. 10. Graphical representation of adsorption kinetics of Pb(II) on MWCNT-TEA: (A) pseudo-first-order kinetic model and (B) pseudo-second-order kinetic model.

Table 4
Constants for the kinetic sorption data using pseudo-first-order and pseudo-second-order kinetic models

Pseudo-first-order kinetic model				Pseudo-second-order kinetic model			
K_a (min^{-1})	R^2	$q_{e,cal}$ (mg/g)	$q_{e,exp}$ (mg/g)	K_b (min^{-1})	R^2	$q_{e,cal}$ (mg/g)	$q_{e,exp}$ (mg/g)
0.00398	0.47736	5.82063	98.17	0.01402	0.99998	98.23180	98.17

In addition, by means of the maximum adsorption capacities, the adsorption ability of MWCNT-TEA toward Pd(II) was quantitatively compared with the previously reported adsorbents. As shown in Table 6, although the adsorption capacity of MWCNT-TEA is lower than that of tartaric acid modified graphene oxide (GO-TA) [17], however, it is still much higher than those of other adsorbents such as Terminalia arjuna fruit powder [55], arborvitae leaves [56], mistletoe leaves [57], carboxylate functionalized wool fibers [58] and several other carbon-based materials such as diiodocarbene modified graphene [26] or dibromocarbene modified graphene [27], indicating that MWCNT-TEA possesses potential applications in adsorption of heavy metal ions.

4. Conclusions

Herein a novel adsorbent, MWCNT-TEA, was prepared by a convenient method. MWCNT-TEA was fully characterized and subsequently used for efficiently removing Pb(II) from aqueous solutions. The adsorption kinetics, isotherms and thermodynamics were investigated in detail. The results indicated that the adsorption data can be well described by pseudo-second-order kinetic model and Langmuir isotherm equation, and the adsorption is a spontaneous and endothermic process. The high adsorption capacity of MWCNT-TEA toward Pb(II) might make it possible to be used as a promising candidate for removing heavy metal from aqueous solutions.

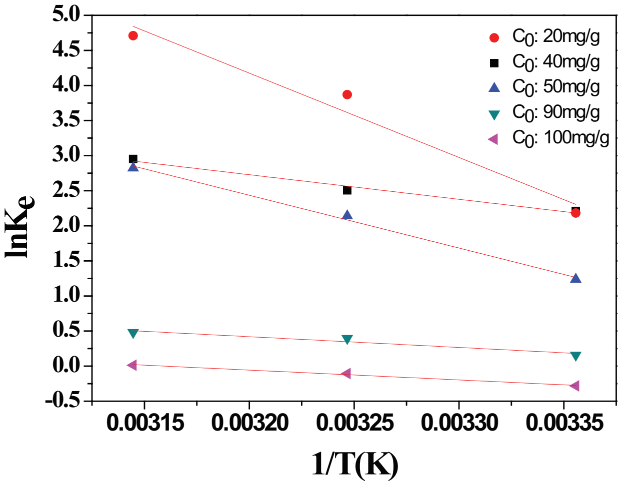

Fig. 11. The linear plot of lnk_e vs. 1/T for the adsorption of Pb(II) on MWCNT-TEA.

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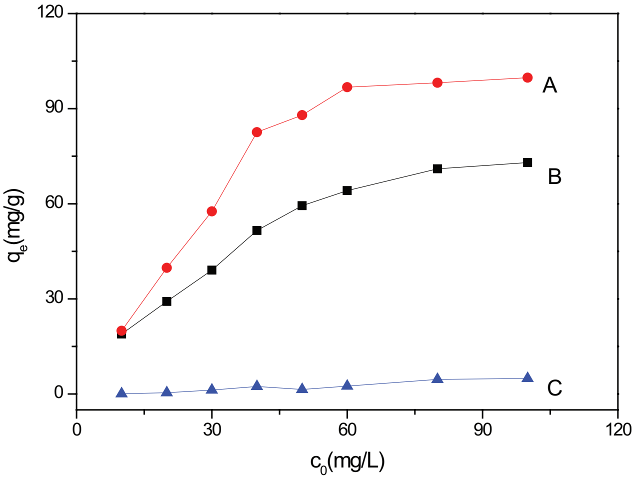

Fig. 12. Adsorption of Pb(II) onto different adsorbents at 298 K: (A) MWCNT-TEA; (B) ox-MWCNT and (C) MWCNT.

Table 6
The adsorption capacities of various adsorbents for Pd(II)

Adsorbent	Q_m (mg/g)	Reference
GO-TA	125.63	[17]
Terminalia arjuna fruit powder	15.0	[55]
Arborvitae leaves	35.84	[56]
Mistletoe leaves	68.53	[57]
Carboxylate functionalized wool fibers	66.67	[58]
Diiodocarbene modified graphene	49.36	[26]
Dibromocarbene modified graphene	49.46	[27]
MWCNT-TEA	98.17	This work

Table 5
The thermodynamic parameters of adsorption of Pb(II) onto MWCNT-TEA

C_0 (mg/L)	$\Delta S°$ (J/(K mol))	$\Delta H°$ (kJ/mol)	$\Delta G°$ (kJ/mol)		
			298 K	308 K	318 K
20	115.92	29.13	–34.51	–35.67	–36.83
40	354.51	99.93	–105.54	–109.09	–112.64
50	220.39	62.54	–65.61	–67.82	–70.02
90	44.24	12.74	–13.17	–13.61	–14.06
100	36.82	11.65	–10.96	–11.33	–11.70

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