Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2015.1072738

57 (2016) 15384–15396
July

Taylor & Francis
Taylor & Francis Group

Copper ions removal from aqueous solutions using acid-chitosan functionalized carbon nanotubes sheets

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Received 30 September 2014; Accepted 5 July 2015

ABSTRACT

Copper ions (Cu^{2+}) removal from aqueous solutions using carbon nanotubes (CNTs) sheets was performed. CNTs sheets were synthesized via chemical vapor deposition of cyclohexanol and ferrocene in nitrogen atmosphere at 750°C, and functionalized with concentrated nitric acid and chitosan. The as-synthesized and functionalized CNTs sheets were used as adsorbents for copper ions removal from water. The results demonstrated that functionalization with concentrated nitric acid and chitosan improves copper ions adsorption capacity of CNTs sheets from 23.32 to 57.34 mg/g at initial copper ions concentration of 800 mg/l. Therefore, the acid–chitosan-functionalized CNTs sheets can be used as an effective adsorbent for copper ions removal from water and have a good potential application in the environmental protection. Langmuir and Freundlich isotherm models were used to describe the adsorption behavior of copper ions by CNTs sheets. Two kinetics models including the pseudo-first-order and the pseudo-second-order equations were applied to fit the experimental data.

Keywords: Carbon nanotubes sheets; Copper ions; Adsorption; Isotherm; Kinetics

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1. Introduction

Heavy metal ions as the main components of industrial wastewater have caused more environmental problems today. As a result of poisonous effects of heavy metal ions in water on human beings and their accumulation in organisms, their presence in water is a general health concern. Thus, research relating to heavy metal ions removal from water is essential for the environmental health [1–3].

Copper as one of the most important toxic heavy metals has many applications in industries. Copper contamination in water occurs mainly from metal cleaning and plating bath, paper and pulp, fertilizer, refineries, and wood preservatives. Copper can cause serious problems to human beings such as stomach intestinal distress, kidney damage, anemia and even coma, and eventual death. Therefore, it is important to develop technologies that can be industrially used for copper ions removal from water. Several conventional methods such as ion exchange, evaporation and concentration, chemical precipitation, reverse osmosis, adsorption, and electrodialysis have been applied for heavy metal ions removal from effluents. Considering from economy and efficiency point of view, adsorption is regarded as one of the most promising and

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widely used methods [3–5]. The most common adsorbent materials are activated carbon [6], alumina silica [7], metal hydroxides [8], and biosorption materials [9]. However, low adsorption capacities or removal efficiencies of heavy metal ions are the main problem of these adsorbents. Therefore, research for finding new and more effective materials to be used as adsorbents is very important subject [10–14].

Carbon nanotubes (CNTs) have captured much attention worldwide since discovery of CNTs in 1991 [15]. Significant work has been done to reveal the unique structural, mechanical, electrical, electromechanical, and chemical properties of CNTs and to explore the key applications of these novel materials. CNTs have unique size distributions, novel hollow tube structures, high specific surface area, electrical conductivity and semiconductivity, and functionalization capability by various surface functional groups [16]. Different diameters and chiralities of CNTs offer various chemical, physical, and mechanical properties [17–19]. These characteristics allow applications of CNTs in many fields such as photocatalysis [20], medicine [21], nanoscale electronics [22], hydrogen storage [23,24], mechanical systems [25], SEM probes [26], and electron field emission tips [27].

Several research studies have shown capability of CNTs in adsorption and removal of different pollutants such as virus from water [28], dichlorodiphenyltrichloroethane and its metabolites at trace level in water samples [29], organophosphorus pesticides in wastewater sludge [30], nicosulfuron, thifensulfuron-methyl and metsulfuron-methyl in water samples [31], atrazine from aqueous solution [32–34], polyhalogenated organic pollutants in environmental water samples [35–39], tetrabromobisphenol A [40], pharmaceuticals in spiked water samples [41], drugs in urine [42], ionizable organic compounds [43], poly aromatic hydrocarbons [44], thiamethoxam, imidacloprid, acetamiprid [45], polycyclic aromatic hydrocarbons in environmental water [46], different pesticides, [47] and heavy metal ions [1,3,48–64] from different environments. As reported in literatures [65], CNTs have demonstrated superior affinity toward copper ions, compared to other divalent heavy metal ions.

CNTs sheet is an entangled CNTs network. Using CNTs sheets as new adsorbent eliminates, problems of agitating and removing CNTs with and from water before and after adsorption process, respectively. Because, in industrial scale, when powder of CNTs is used as adsorbent, mixing of CNTs with wastewater with ultrasonic agitation is not economically and technically possible. Also with accumulating evidence of their toxicity, there are serious concerns over CNTs health and environmental risks once released to the environment. Also, adsorption of toxic substances by CNTs may enhance their toxicity and further affect transfer of toxic substances to the environment. Using CNTs sheets as adsorbent, economical wastewater treatment without CNTs leakage into water is feasible [3,66–68].

Recently, modification of CNTs with polymers has been of significant interest due to their exceptional properties and applications. One of the common polymers that are used for CNTs modification is chitosan (CS). Chitosan, a natural aminopolysacharide polymer, with excellent properties, such as high hydrophilicity, good film and fiber-forming ability, normal chemical resistance, wide availability and biocompatibility, and its abundant amino and hydroxyl functional groups (as reactive sites), has great importance for heavy metal ions adsorption [69–73].

In the present work, CNTs sheets were synthesized via chemical vapor deposition (CVD) method and then functionalized using acid treatment and chitosan as a good functionalizing agent and used as a novel adsorbent for copper ions removal from wastewater. Also, the Langmuir and the Freundlich isotherm models and the pseudo-first-order and the pseudo-second-order kinetic models were applied to fit the experimental data.

2. Experimental procedure

2.1. Synthesis of CNTs sheets

CNTs sheets were synthesized via 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 reactor center (at temperature of 750°C), where pyrolysis of the gases took place and CNTs sheets were deposited on the reactor walls. The precursors solution was a mixture of catalyst (ferrocene; purity ≥ 98%, B.D.H) and carbon source (cyclohexanol; purity ≥ 98%, Fluka) with mass ratio of 1:10, brought to its boiling point in a flask (a steel container) connected to the reactor. Evaporating the reagents was performed using an oil bath (details of the synthesis process were presented elsewhere [3,66–68]).

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

2.2. Functionalization of CNTs sheets

The as-synthesized CNTs 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.

Chitosan (CS) (Mw_{ave} = 190,000–310,000, Aldrich) polymeric solution (2 wt.%) was prepared by dissolving distinct amount of chitosan powder in 1% (v/v) acetic acid solution with stirring at room temperature for 24 h. The as-synthesized and the acid-treated CNTs sheets were dipped in the polymer solution for 15 min and then removed and placed on a glass plate. The excess solution and air bubbles were gently squeezed out by a roller. Samples were dried at ambient temperature for 1 d and then annealed at 90˚C for 1 h.

The as-synthesized, acid-treated, chitosan-treated, and acid–chitosan-treated CNTs sheets were used as adsorbent for copper ions removal from wastewater.

2.3. Adsorption procedure

Analytical grade of $Cu(NO_3)_2{\cdot}3H_2O$ (Merck) and deionized water was used to prepare stock solutions of the copper ions. In all the experiments, 50 mg of the as-synthesized and the functionalized (acid treated, chitosan treated and acid–chitosan treated) CNTs sheets were soaked into 50 ml solutions with initial concentrations of 100, 200, 400, 600, and 800 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 ion concentration of the solutions. Water conductivity directly depends on the ion concentration. These dependencies (calibration curves of the conductometer) are shown in Fig. 1. After removing the adsorbents from the solutions, the amount of adsorbed ion can be obtained using the following equation:

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

where q_e is the equilibrium adsorption uptake (mg/g), C_0 is the initial copper ions concentration (mg/l), C_e is the equilibrium copper ions concentration (mg/l), V is the volume of the solution (l), and w is the mass of the adsorbent (g).

All adsorption experiments were performed twice and the average values were reported. The maximum error was less than 3%.

2.4. Batch kinetics studies

Kinetics studies were carried out at initial copper ions concentration of 200 and 800 mg/l, and the procedure was identical to that of adsorption experiments. The aqueous samples were taken at preset time intervals and the copper ions concentration was similarly measured. The adsorption amount at time (t), q_t (mg/g), was calculated using the following equation:

$$q_t = \frac{(C_0 - C_t)V}{w} \tag{2}$$

where C_t (mg/l) is copper ions concentration at time (t).

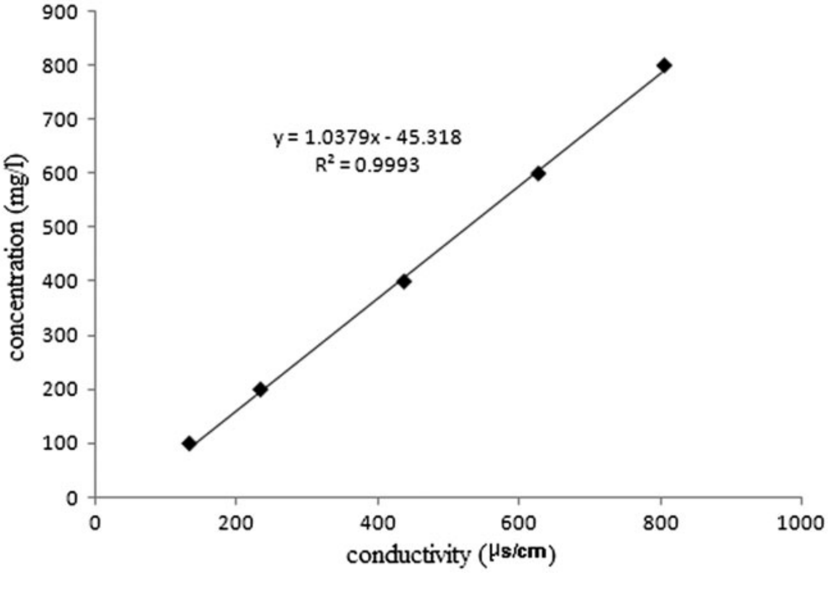

Fig. 1. Calibration curve of the conductometer for copper ions.

All kinetics experiments were performed twice and the average values were reported. The maximum error was less than 3%.

3. Results and discussion

3.1. Characterization of CNTs sheets

Fig. 2 shows CNTs 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 SEM images, CNTs sheets are regarded as an entangled CNTs network. CNTs sheets have high flexibility and are not easily broken during functionalization, washing, and drying processes.

Fig. 3 shows FTIR spectra of the functionalized CNTs sheets. As observed, the peak at 1,527 cm^{-1} is assigned to the C=C bond of CNTs. The characteristic peaks at approximately 1,730 and 3,440 cm^{-1} are attributed to the C=O and O–H bonds which indicate the formation of carboxyl groups (–COOH) and hydroxyl groups (–OH) on the surface of CNTs. These functional groups provide a large number of chemical adsorption sites and thereby increase adsorption capacity of CNTs sheets.

The adsorption behavior of copper ions onto the as-synthesized and the functionalized CNTs sheets at different initial copper ions concentrations was investigated. Fig. 4 shows the equilibrium adsorption uptake of the as-synthesized and the functionalized CNTs sheets at different initial copper ions concentrations. As can be observed, increasing initial copper ions concentration increases significantly equilibrium adsorption uptake of CNTs sheets. It can be due to the fact that adsorption onto the as-synthesized and the functionalized CNTs sheets is a diffusion-based process [3].

As can be observed in Figs. 4 and 5, the functionalized CNTs sheets exhibit greater copper ions adsorption capacity than the as-synthesized CNTs sheets. This can be explained by the fact that copper ions adsorption capacity of CNTs strongly depends upon their surface total acidity including functional groups [74]. As can be observed in Figs. 4 and 5, copper ions are more favorably adsorbed onto the acid–chitosan-treated CNTs sheets. Adsorption capacity of copper ions for acid–chitosan CNTs sheets attains 56.46 mg/g at initial copper ions concentration of 800 mg/L, while those for the as-synthesized, the acid-treated and the chitosan-treated CNTs sheets are 24.08, 28.23, and 49.82 mg/g at initial copper ions concentration of 800 mg/L, respectively. Adsorption capability of copper ions for the used adsorbents can be ordered as acid–chitosan-treated > chitosan-treated > acid-treated > as-synthesized CNTs sheets. As reported in the literature, different acidic functional groups like –COOH and –OH can be formed on surface of the CNTs by nitric acid oxidation [58]. Also, chitosan has both amino and hydroxyl functional groups, and functionalizaion with chitosan increases the amount of functional groups on the surface of CNTs [58–62]. These functional groups (react with and) adsorb copper ions from wastewater. Since adsorption is mainly performed by functional groups of CNTs, increasing the number of functional groups improves adsorption capacity of copper ions. Chemical interaction (bond) between the metal ions and the surface functional groups of CNTs sheets is mainly responsible for adsorption [54,56,57,74,75].

The surface total acidity of the as-synthesized and the functionalized CNTs sheets were quantified via Boehm method [58] as presented in Table 1. As observed, functionalization with concentrated nitric acid and chitosan improves surface total acidity and therefore copper ions adsorption capacity of CNTs sheets, significantly. The preference order of the surface total acidity is acid–chitosan-treated > chitosan-treated > acid-treated > as-synthesized CNTs sheets. The acid–chitosan-treated CNTs sheets have higher surface total acidity.

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 $\mathrm{pH_{PZC}}$ of the as-synthesized and the functionalized CNTs sheets were quantified by mass titration [59] as presented in Table 1. As observed, the $\mathrm{pH_{PZC}}$ shifts to lower pH values after functionalization and the acid–chitosan-treated CNTs sheets have lower value. These results confirm our observations (Fig. 5) and the data obtained from the Boehm's titration.

3.2. Adsorption isotherms

The obtained experimental data for copper ions adsorption onto the as-synthesized and the functionalized CNTs sheets were analyzed using the Freundlich and the Langmuir isotherms.

The Langmuir isotherm model assumes that equilibrium is attained when a monolayer of the adsorbate molecules saturates the adsorbent. Its linear form can be represented by the following equation:

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

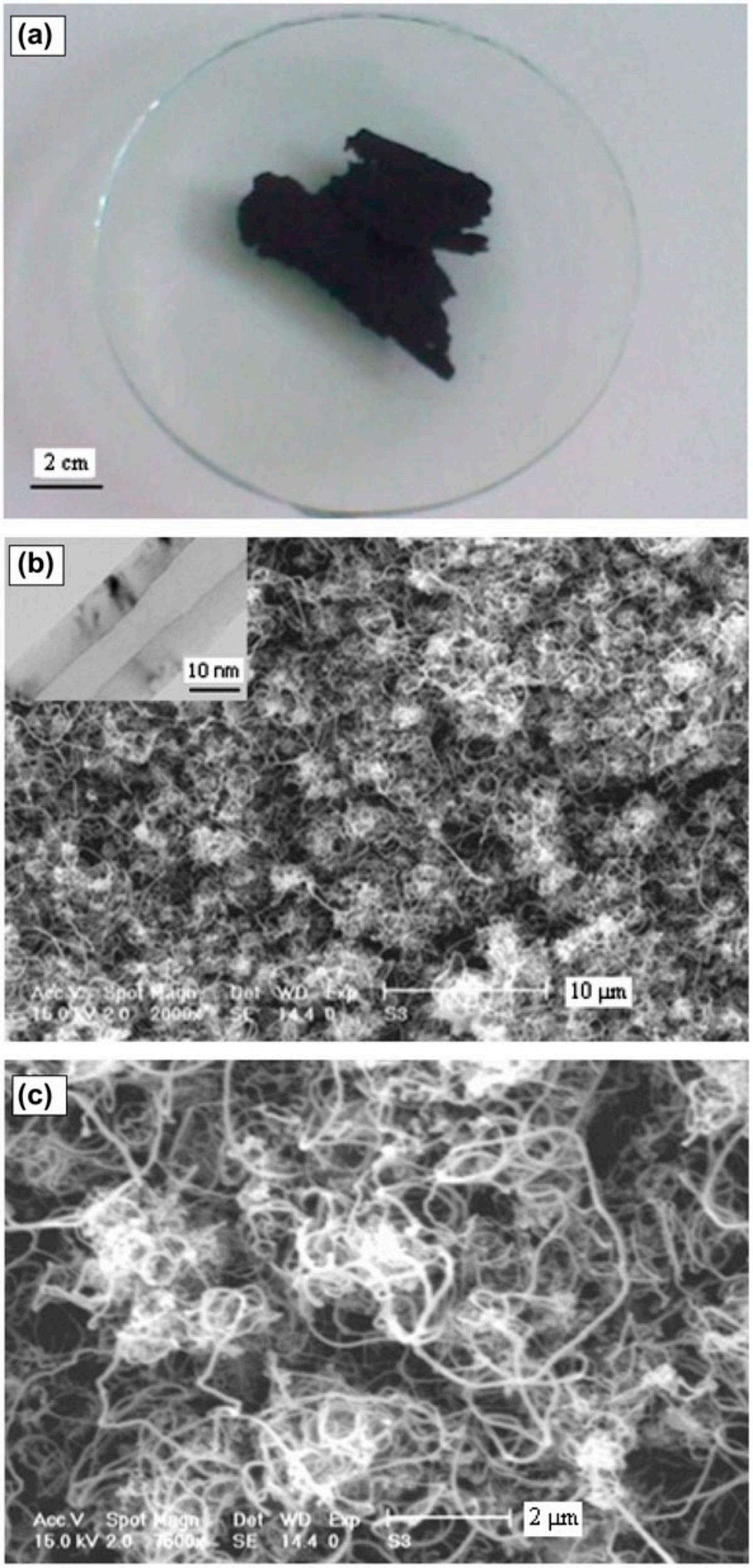

Fig. 2. CNTs sheets, (a) an overview image, (b) a surface SEM image (inset: a TEM image of a CNT), and (c) a high magnification SEM image.

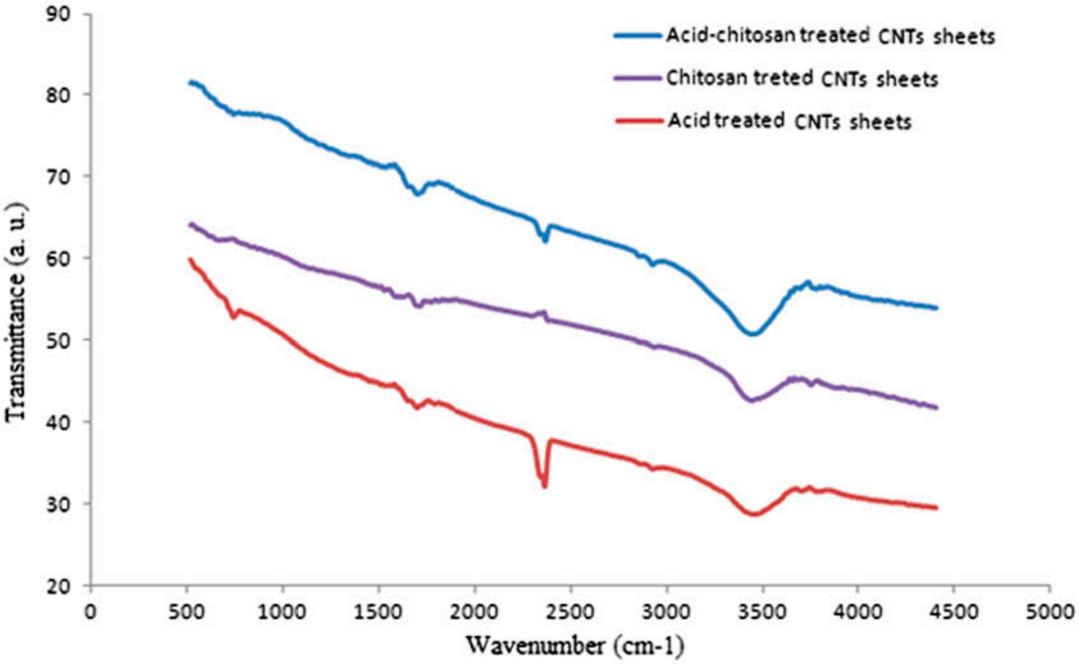

Fig. 3. FTIR spectra of the prepared adsorbents.

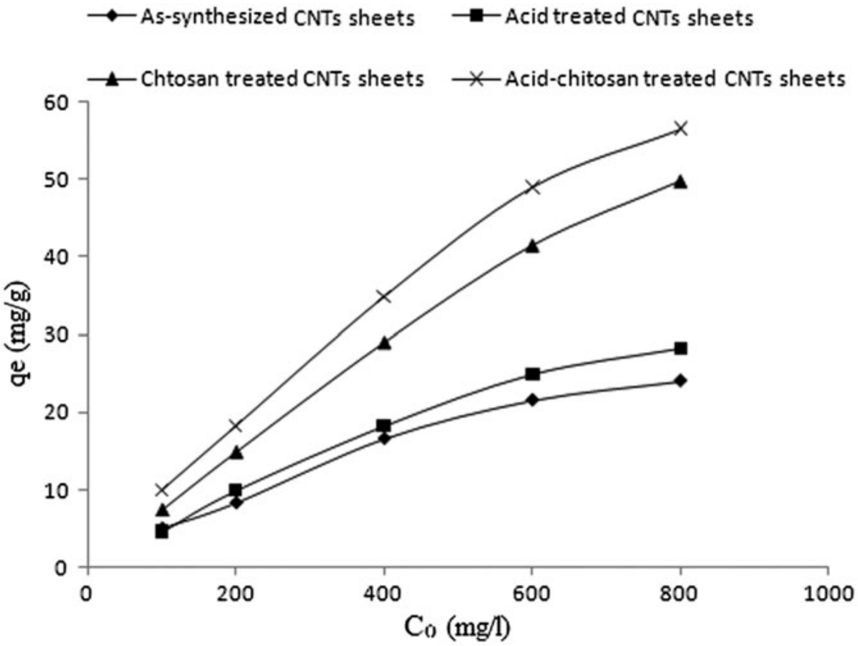

Fig. 4. Effect of initial copper ions concentration on equilibrium adsorption uptake (initial pH of about 7 and temperature of 25˚C).

where 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.

The Freundlich isotherm is a semiempirical equation employs to describe the multilayer adsorption with a heterogeneous energetic distribution of active sites, performed by interactions between

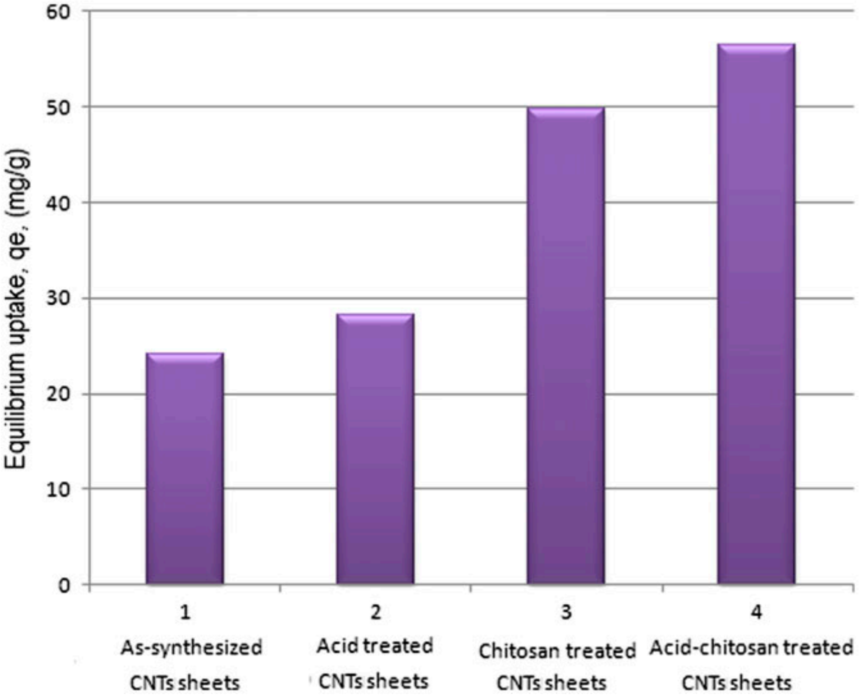

Fig. 5. Equilibrium adsorption uptake of the prepared adsorbents (initial pH of about 7, temperature of 25℃, and initial copper ions concentration of 800 mg/l).

Table 1
Surface total acidity and pH_{PZC} of the as-synthesized and the functionalized CNTs sheets

Adsorbents	Surface total acidity (mmol/g)	pH_{PZC}
As-synthesized CNTs sheets	1.6	6.8
Acid-treated CNTs sheets	3.6	3.9
Chitosan-treated CNTs sheets	4.3	3.6
Acid–chitosan-treated CNTs sheets	4.8	3.2

adsorbed molecules. Its linear form can be presented by the following form:

$$\log q_e = n \log C_e + \log K_F \quad (4)$$

where K_F and n are the Freundlich parameters related to adsorption capacity and adsorption intensity, respectively. Value of $n < 1$ represents a favorable adsorption condition.

The slope and the intercept of each linear plot in Fig. 6(a) and (b) are used to calculate the Langmuir and the Freundlich parameters. The calculated Langmuir and Freundlich parameters are listed in Table 2. As can be observed, the q_m values calculated using the Langmuir isotherm are 158.73, 120.48, 82.64, and 55.25 mg/g for the acid–chitosan-treated, chitosan-treated, acid-treated, and as-synthesized CNTs sheets, respectively. As observed, this order is consistent with the experimental observations. The K_F values calculated using the Freundlich model are large indicating that the functionalized CNTs sheets have high affinity toward copper ions. Also, no significant difference among the adsorption intensities (n) of copper ions onto the different adsorbents is observed. Deviation of the n values from unity indicates a non-linear adsorption that takes place on heterogeneous surfaces [1,64,76].

Applicability of isotherm models to describe the adsorption process was also judged using the correlation coefficient (R^2) values. As observed in Table 2, based on the correlation coefficient (R^2) values, both the Langmuir and the Freundlich isotherm models match well the experimental data. Several researchers reported that the metal ions sorption onto CNTs can

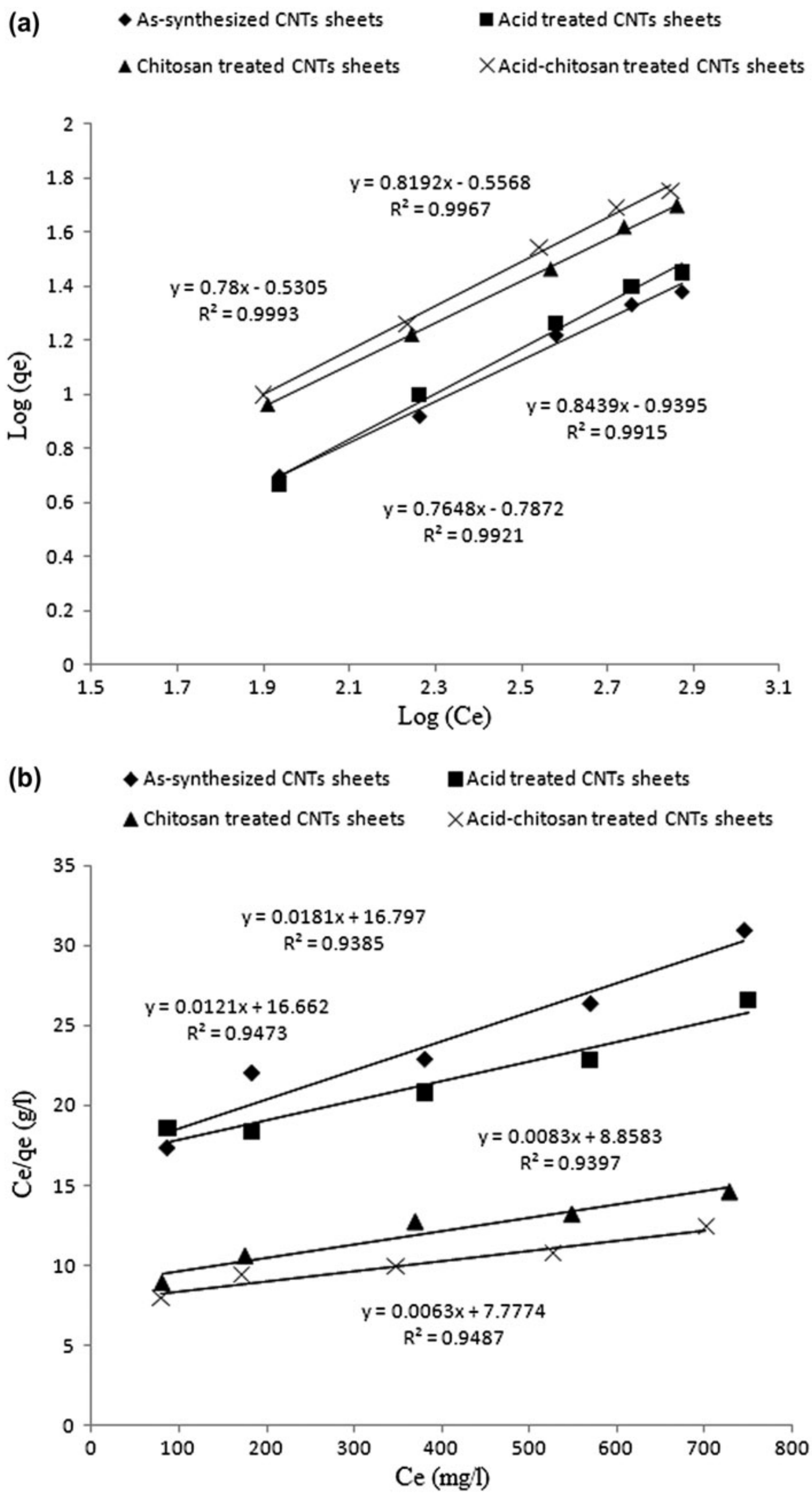

Fig. 6. (a) Freundlich and (b) Langmuir isotherms for adsorption of copper ions onto the prepared adsorbents.

Table 2
Parameters of Langmuir and Freundlich isotherms for adsorption of copper ions onto the prepared adsorbents

	Langmuir isotherm			Freundlich isotherm		
Adsorbents	q_m (mg/g)	K_L (L/mg)	R^2	n	K_F (L/mg)	R^2
As-synthesized CNTs sheets	55.248	0.00107	0.9385	0.8190	0.2774	0.9967
Acid-treated CNTs sheets	82.640	0.000726	0.9473	0.7810	0.2947	0.9987
Chitosan-treated CNTs sheets	120.482	0.000930	0.9724	0.8439	0.1149	0.9915
Acid–chitosan-treated CNTs sheets	158.732	0.000814	0.9487	0.7648	0.1632	0.9921

be described by both the Langmuir and the Freundlich isotherms [54,57,77].

3.3. Adsorption kinetics

In order to analyze the adsorption kinetics of copper ions, two kinetics models including the pseudo-first-order and the pseudo-second-order equations were applied to fit the experimental data obtained at 200 and 800 mg/l initial concentration of copper ions.

The linear form of pseudo-first-order and pseudo-second-order kinetic models can be expressed by the following equations, respectively:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \tag{5}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{6}$$

where k_1 and k_2 are adsorption rate constants of the first- and the second-order kinetic models, in min^{-1} and l/mg min, respectively.

The calculated kinetics parameters for adsorption of copper ions onto the as-synthesized and the functionalized CNTs sheets at initial copper ions concentrations of 200 and 800 mg/l are listed in Table 3.

As can be observed, at lower initial concentration (200 mg/l) of copper 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 the q_e values calculated using the pseudo-second-order kinetics model. The consistency of the experimental data with the pseudo-second-order kinetics model indicates that the rate-limiting step may be chemical adsorption (chemisorption) involving valence forces through sharing or exchanging electrons between sorbent and sorbate. In chemical adsorption, it is assumed that the adsorption capacity is proportional to the number of active sites (functional groups) incorporated on the adsorbent surface [78–81]. As can also be observed in Table 3, the experimental data agree with the pseudo-first-order kinetic model at higher initial concentration (800 mg/l) of copper ions, which indicates that adsorption of copper ions onto CNTs sheets is a diffusion-based process [82]. The

Table 3
Parameters of pseudo-first-order and pseudo-second-order kinetics models for adsorption of copper ions onto the prepared adsorbents

			Pseudo-fist-order kinetics model			Pseudo-second-order kinetics model		
Adsorbents	Initial Cons. (mg/l)	$q_{e,exp}$	q_e	k_1	R^2	q_e	$k_2 \times 10^{-3}$	R^2
As-synthesized CNTs sheets	200	8.3032	12.4018	0.1054	0.9813	9.9597	2.6540	0.9855
Acid-treated CNTs sheets	200	9.9638	13.0920	0.1327	0.9609	10.6953	12.9845	0.9976
Chitosan-treated CNTs sheets	200	16.6034	20.2280	0.1091	0.9445	17.0186	3.4323	0.9953
Acid–chitosan-treated CNTs sheets	200	18.2670	22.8581	0.1105	0.9783	19.1938	5.3454	0.9951
As-synthesized CNTs sheets	800	23.3256	24.4312	0.0234	0.9921	26.7643	0.0231	0.9345
Acid-treated CNTs sheets	800	28.5421	30.0987	0.0123	0.9843	34.5423	0.0986	0.9523
Chitosan-treated CNTs sheets	800	49.0934	49.8907	0.0321	0.9912	54.1223	0.08743	0.9412
Acid–chitosan-treated CNTs sheets	800	57.3412	58.4312	0.0154	0.9854	64.2365	004,589	0.9534

Table 4
Comparison of the maximum monolayer heavy metal ions adsorption capacities of the acid–chitosan-treated CNT sheets (this work) with other adsorbents documented in the literature [74]

	Maximum monolayer adsorption capacity, q_m (mg/g)					
Adsorbents	Cd^{2+}	Cu^{2+}	Ni^{2+}	Pb^{2+}	Zn^{2+}	Conditions
Acid–chitosan-treated CNTs sheets (This work)		158.732				pH: 7, $T = 25$°C, $C_0 = 100–800$ mg/l
CNTs				1.00		pH: 7, T = room, $C_0 = 2–14$ mg/l
CNTs (HNO_3)				49.95		pH: 7, T = room, $C_0 = 2–14$ mg/l
CNTs	1.1					pH: 5.5, $T = 25$°C, $C_0 = 9–50$ mg/l
CNTs (H_2O_2)	2.6					pH: 5.5, $T = 25$°C, $C_0 = 9–50$ mg/l
CNTs ($KMnO_4$)	11.0					pH: 5.5, $T = 25$°C, $C_0 = 9–50$ mg/l
CNTs (HNO_3)	5.1					pH: 5.5, $T = 25$°C, $C_0 = 9–50$ mg/l
SWCNTs					11.23	pH: 7, $T = 25$°C, $C_0 = 10–80$ mg/l
SWCNTs (NaOCl)					43.66	pH: 7, $T = 25$°C, $C_0 = 10–80$ mg/l
MWCNTs					10.21	pH: 7, $T = 25$°C, $C_0 = 10–80$ mg/l
MWCNTs (NaOCl)					32.68	pH: 7, $T = 25$°C, $C_0 = 10–80$ mg/l
MWCNTs (HNO_3)	1,086	24.49		97.08		pH: 5, T = room, $C_0 = 2–15$ mg/l (Cd^{2+}), $C_0 = 5–30$ mg/l (Cu^{2+}), $C_0 = 10–80$ mg/l (Pb^{2+})
MWCNTs (HNO_3)			9.80			pH: 6.55, $T = 60$°C, $C_0 = 6–20$ mg/l
Fly ash	8.00	8.10				pH: 5.0, T = room, $C_0 = 335$ mg/l (Cu^{2+}), 320 mg/l (Cd^{2+})
Granular activated carbon			20.55			pH: 7.0, $T = 25$°C, $C_0 = 60$ mg/l
Iron slug		88.50		95.24		pH: 5.5, $C_0 = 200$ mg/l
Sugar beet pulp	24.39	21.16	11.86	73.76	17.79	pH: 4.7, $T = 20$, $C_0 = 2.5 \times 10^{-3}$ M

obtained results are in agreement with our previous results [3].

Table 4 presents a comparison of the maximum monolayer heavy metal ions adsorption capacities of the acid–chitosan-treated CNTs sheets (this work) with other adsorbents documented in the literature [74]. As can be observed, the acid–chitosan-treated CNTs sheets have larger adsorption capacity compared with the others based on the data obtained from the literature.

It must be mentioned that the CNT release from the functionalized CNTs sheets into the solution after adsorption process was investigated using optical microscopy. The results demonstrated that after adsorption process, there is no CNT release from the acid–chitosan-treated CNTs sheets into the water. Acid–chitosan treatment increases the mechanical resistance of CNTs sheets and decreases the CNTs leakage from CNTs sheets into the solution, significantly. Therefore, using the functionalized CNTs sheets as adsorbent, economical copper ions removal from water without CNT leakage into water is feasible.

Also, based on our primary results, the functionalized CNTs sheets can be reused several times [67]. As a result, the functionalized CNTs sheets with high practical potential can be recommended as an economical and effective adsorbent for wastewater treatment in industrial scale.

4. Conclusion

CVD was used for synthesis of CNTs sheets. CNTs sheets were then functionalized with concentrated nitric acid and chitosan at room temperature. The results demonstrated that adsorption capacity of CNTs sheets increases significantly after the functionalization process. Also, increasing initial copper ions concentration increases the adsorption capacity of CNTs sheets. The adsorption behavior of copper ions onto the functionalized CNTs sheets does match well both with the Langmuir and the Freundlich isotherm models. The results demonstrated that kinetics of adsorption does match well with the pseudo-second-order kinetics model. The preference order of copper ions adsorption on CNTs sheets is acid–chitosan-treated > chitosan-treated > acid-treated > as-synthesized CNTs sheets. Using the functionalized CNTs sheets as adsorbent, economical wastewater treatment without CNTs leakage into treated wastewater is feasible. The functionalized CNTs sheets are promising materials for the removal of copper ions from large volumes of contaminated aqueous solutions.

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