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Preparation of engineered carbon nanotube materials and its application in water treatment for removal of hydrophobic natural organic matter (NOM)

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ABSTRACT

Organic matters in drinking water are composed of soluble and particulate fractions. Soluble organic matters generally originated from allochthonous, autochthonous, and synthetic organic. Silica sand filters, which are utilized in water treatment, have a low potential of removing the soluble organic matters. Traditional carbon-based media such as activated carbon and anthracite are among the choices for the removal of soluble organic. Carbon nanotubes (CNTs) have a higher potential in removing synthetic and natural organic materials than the other traditional carbon based media. Utilization of CNTs at the slurry state requires the removal of the nanotubes themselves at the end of the process which leads to yet another problem to take care of. The present study, therefore, aims at solving this problem. In so doing, oxidized CNTs (140˚C, 5 h, Nitric acid) were bound to the surface of silica sand through 3-(triethoxysilyl)propylamine to act as a bonding agent. Humic acid was used as the index of natural organic matters. The removal potential of humic acid with the new adsorbent (CNT_{sand}) was studied under various operational conditions (contact time, temperature, and initial concentration). According to the obtained data, CNT_{sand} has a good potential in the removal of humic acid ($q_{\max}$ = 81.96 mg/g CNT). Additionally, the kinetic, isotherm, and thermodynamic of adsorption were investigated, for which the data followed the pseudo-second-order kinetic model and Langmuir isotherm. Evaluation of enthalpy change (ΔH = 11.02 kJ/mol) and free energy change (ΔG = –7.32 to –9.20 kJ/mol) indicated that the reaction is spontaneous, endothermic, and thermodynamically favorable. Regeneration study showed that the desorption step of humic acid was faster than its adsorption step. It was observed that after five cycles, the adsorption capacity amounted to roughly 50% of the initial adsorption capacity. The above data depict that the new engineered material is a good reusable adsorbent in water treatment.

Keywords: Silica sand; Carbon nanotube; Removal; Water treatment; Organic matter

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1. Introduction

Natural organic matters (NOMs) are carbon-based compounds which are produced through metabolic reactions in water supply and its surrounding watershed. There are number of reasons to prove the negative impacts of the presence of NOMs in water. First, these compounds can react with disinfectants and form disinfectant byproducts such as trihalomethanes and haloacetic acids which are carcinogenic compounds [1–3]. Second, NOMs can affect the odor, taste, and color of water [3]. Third, these materials reduce the amount of dissolved oxygen in water. Finally, the presence of these compounds enhances the regrowth of bacteria and the formation of biofilms in drinking water distribution systems [4]. NOMs can be removed from drinking water through several treatment processes such as coagulation and flocculation, ion exchange, electrochemical processes, membrane, advance oxidation, and adsorption [5]. Adsorption with activated carbon is a simple and efficient process to remove organic compounds [4] in almost all molar masses [1], but the slow adsorption kinetics and difficulty of regeneration limit its extensive application [6]. Nowadays, advances in new technology have resulted in the production of other carbon structures such as carbon nanotubes (CNTs) [7]. CNTs with mesopore structures have a high potential in adsorption of organic matters. CNTs have previously been utilized in removing organic matters such as organic dyes, pharmaceutical, pesticides, phenol, aromatic amines, and NOMs [8]. Adsorption mechanisms of CNTs are hydrophobic effect, π–π interaction, π–π electron donor–acceptor interaction, electrostatic interaction, and hydrogen bonding [9]. Although CNTs have a good potential in organic matter removal, their application in the slurry state is somewhat problematic because they must be removed in the final treatment. This problem can be solved by binding CNTs to a fixed media.

A good option, therefore, is to use the silica sand in water treatment filters as the fixed media. Silica sand is a great natural resource that can be used in water treatment plant filters. Although rapid sand filters have proven effective in removing some pollutants, they cannot remove soluble organic matters. Coating silica sand with CNTs not only solves the problems at slurry state, but also enhances the capability of silica grains, and results in the production of a new adsorbent—CNT_{sand}. Although this technology has a long way to practical use, it can be an effective step in silica grain enhancement. In a study by Gao et al. Graphene oxide-coated silica gel was used as the adsorbent for mercury and rodamin B removal in the batch and continuous experiments [10]. In another study, Fujigaya et al. investigated the coating of silica sphere with pristine single-wall carbon nanotube and presented a method based on a non-covalent bonding [11]. Further, several studies have been carried out on adsorption of NOMs by CNTs. Lu and Su investigated the adsorption process of NOMs by CNTs and observed that in pH below the isoelectric point ($\text{pH} < 5$), adsorption of NOMs is better than in $\text{pH} > 5$. They also noted that the adsorption capacity increased [7] as a result of an increase in ionic strength. Moreover, Hyung and Kim found that the type of NOMs is an important parameter in the adsorption capacity and this capacity increases in compounds with a high molar weight [12]. Based on the recent studies, the maximum adsorption capacity of removing NOMs by CNTs has been 94.21 mg/g [14]. In the present study, CNTs are bound to the silica particles used in the rapid sand filters. The aim of this study is to improve the performance of conventional sand filters through innovative technology in order to increase the efficiency of the removal process of soluble organic matters.

2. Materials and methods

2.1. Materials

Pristine multi-wall CNTs were purchased from Nanosav Company (Tehran Province, Iran). According to the data obtained from the company, the length of multi-wall carbon nanotube (MWCNT) was <10 μm, the amount of amorphous carbon was <5%, and the outer diameter ranged from 10 to 30 nm which was synthesized by the special chemical vapor deposition (CVD) method using iron, cobalt, and molybdenum as the catalyst. HNO_3 (Synth, 65%), hydrochloric acid (Synth, 37%), toluene (Synth, 99.9%), 3-(triethoxysilyl) propylamine, and methanol (Synth, 99.9%) were purchased from Merck. Silica grains were a gift from Tehran pars water treatment plant (Tehran, Iran) and according to the information obtained from the producing company they have 97.5% SiO_2 plus other impurities such as Al_2O_3, Fe_2O_3, CaO, MgO, and K_2O. Moreover, humic acid (humic acid, sodium salt, tech. 50–60% (as humic acid), black in color, and in the form of solid powder in physical state) was obtained from Acros organic company (USA), and stock solution (1,000 mg/l TOC) was prepared by dissolving appropriate amount of the humic acid in deionized water.

2.2. Instruments

Ultrasound bath (HWASHIN, Power Sonic 420, 50HZ, 700 W, Seoul, Korea) and JAR TEST instrument

(PHIPPS & BIRD, Model 7790–402, USA) were used for solution dispersion and solution mixing, respectively. Scanning electron microscopy (KYKY EM3200, China) was used to investigate the morphology of oxidized MWCNT and the surface of CNT_{sand}. Fourier Transform Infrared Ray (RAYLEIGH, WQF 510A, China) was used to detect any functional groups of MWCNT. Elemental analysis of MWCNT and MWCNT–COOH was performed by CHNS analyzer (Flash EA1112, Thermo Electron S.p.A, Italy). Finally, for determination of remaining amount of TOC in aqueous solution, TOC analyzer (model–VCSH, Shimadzu, Japan) was utilized.

2.3. Preparation of engineered carbon nanotube materials

2.3.1. Acid treatment of silica sand

Five hundred grams of silica sand was added to 500 ml of hydrochloric acid (Synth, 37%). The mixture was then heated at 100˚C for 3 h, washed with deionized water, and dried under vacuum for 24 h.

2.3.2. Bonding amino groups to silica

One hundred grams of acid-treated silica sand and 1 ml of 3-(triethoxysilyl)propylamine were added to 100 ml of dried toluene (99.9%) and refluxed for 48 h. Silica was washed with methanol (99.9%) for several times and finally dried under vacuum for 48 h at room temperature.

2.3.3. Oxidation of pristine MWCNT

One gram of pristine MWCNT was dispersed in 75 ml of HNO_3 (Synth, 65%) for different periods of time (5, 8, 12, and 20 h) and at different temperatures (80, 100, 120, and 140˚C). Then, it was centrifuged for 10 min at 10,000 rpm. The solid residue was washed with deionized water to remove the excess nitric acid. Finally, it was dried under vacuum for 72 h.

2.3.4. Binding of oxidized CNT to amino silica sand

Ten grams of amino silica sand was poured in a 100 ml beaker. 0.01 gr of oxidized CNTs was dispersed in 25 ml of deionized water and placed in ultrasonic bath for 20 min. Next, 5 ml of dispersion was poured on silica sand and the mixture was heated and stirred until the dispersed oxidized CNTs dried on sand. This step was repeated for the remaining oxidized CNTs. At last, mixture was heated at 200˚C for 1 h in oven.

2.4. Batch adsorption experiments

In all experiments, a certain amount of CNT_{sand} (5–40 gr) was added to 200 ml of solution containing humic acid (TOC = 2–12 mg/l). JAR TEST was used for solution mixing (100–120 rpm) and only the solution above CNT_{sand} was stirred. The amount of the remaining TOC in aqueous solution was determined by TOC analyzer. All the experiments relating to the kinetic, isotherm, and thermodynamic were repeated three times and only the mean value was reported, for which the maximum variance coefficient was <10%. For determination of the pH_{zpc}, 20 gr of SiO_2, $SiO_2@NH_2$, and CNT_{sand} were added to 200 ml of solution with a pH in the range of 2–10. When equilibrium time (about 1 h) passed, the final pH was measured. The initial pH was plotted vs. the final pH and the pH_{zpc} is a point where the curve crossed the $y = x$ line [13,14].

2.5. Adsorption/desorption process

Adsorption/desorption study was performed in order to investigate the adsorbent recovery. For this purpose, 20 g of engineered adsorbent was added to a 200 ml solution of humic acid with the initial TOC of 10 mg/l. After equilibrium, the adsorption capacity was measured. Next, the saturated adsorbent was added to a 200 ml solution with a pH in the range of 10–13 and under 100 rpm solution mixing with JAR TEST to attain the optimum pH. Further, the effect of desorption time was investigated in the range of 10–50 min to evaluate the optimum time. Finally, the desorption process was repeated for five cycles. All the experiments on adsorption/desorption were repeated three times and only the mean value was reported. The maximum variance coefficient was <10%.

3. Results and discussions

3.1. CNT_{sand} chemical bonding

The chemical bonding of CNTs to silica sand is based on a covalent bonding between amino groups of silica grains and carboxylic groups of oxidized CNTs. The schematic image of the bonding process is shown in Fig. 1.

At the first stage, acid treatment of silica sand not only removed impurities of the silica grains but also activated OH groups. Then, at the second stage, the amino group was bound to silica sand. At the third stage, the pristine multi-wall CNTs were oxidized. Since impurities such as amorphous carbon, graphitic plates, and metal catalysts can reduce the adsorption

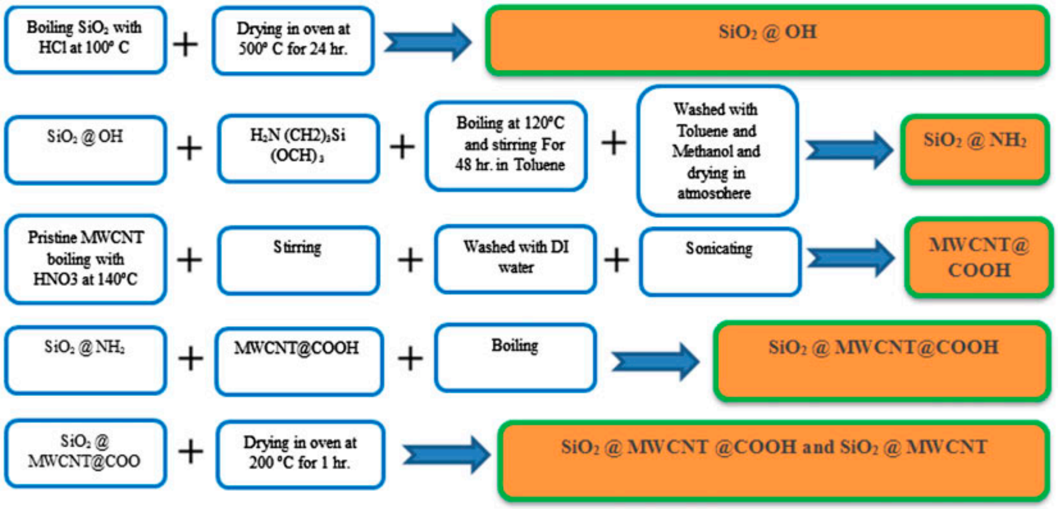

Fig. 1. Schematic diagram for production of CNT_{sand}.

effects of MWCNT, it is necessary to treat them with nitric acid [15–17]. Oxidation and acid treatment are common methods in this regard. The oxidation of CNTs not only purifies and enhances the chemical reactivity of graphitic network, but also increases the solubility in polar media [18,19]. Oxidation of CNTs introduced functional groups such as carboxyl, carbonyl, and hydroxyl that make the CNTs soluble in water [20,21]. Since temperature and contact time are important parameters in oxidation and solubility of CNTs [20], many various conditions were investigated. Based on Fig. 2, the best dispersibility of CNTs in deionized water was observed for oxidation at 140˚C for 5 h. At this state, it remained stable for four weeks and longer. Therefore, this procedure was selected as the method of carrying out the experiment.

After the preparation of the amino silica sand ($SiO_2@NH_2$) and oxidation of the CNTs (MWCNT@COOH), a new engineered adsorbent (SiO_2@MWCNT@COOH) is produced when the above-mentioned materials are combined through direct heating. This new engineered adsorbent is silica grains coated with a thin layer of CNTs to improve the capability of the raw silica in soluble organic matter removal. Images of each type of silica grains are presented in Fig. 3.

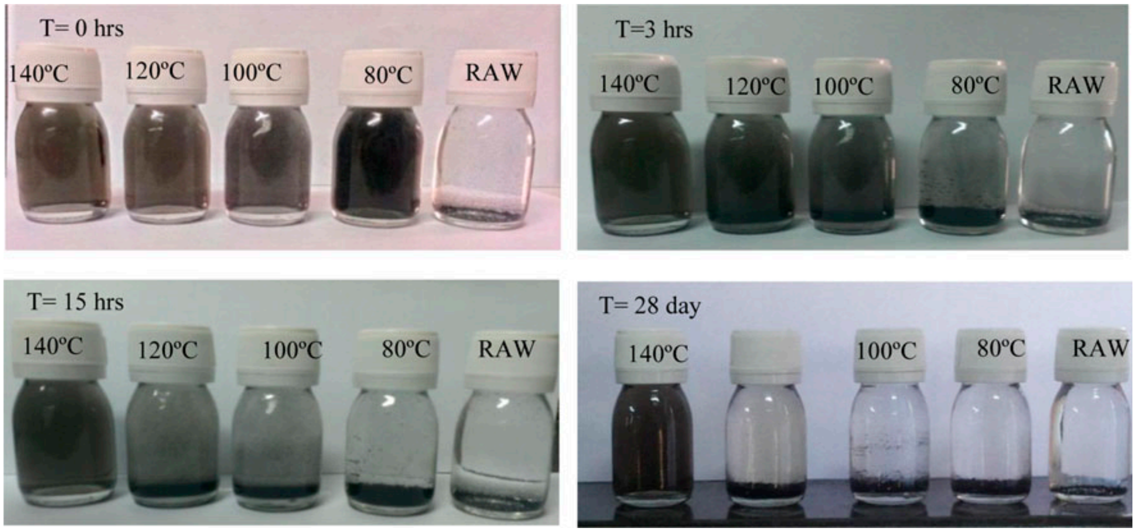

Fig. 2. Dispersibility of MWCNT in different times and temperatures.

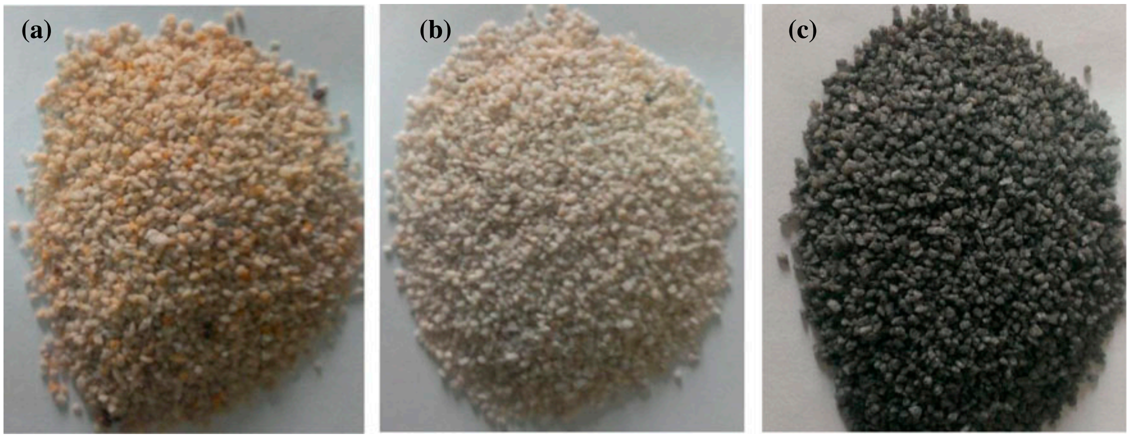

Fig. 3. Silica grains: (a) raw silica sand, (b) acid-washed silica sand, and (c) silica coated with CNT (CNT_{sand}).

3.2. Characterization of materials and new adsorbent

3.2.1. SEM analysis

SEM was used to detect possible morphological changes in pristine and oxidized MWCNTs and also to watch the surface of silica sand and the coated MWCNTs on silica. According to SEM images (Fig. 4), pristine MWCNTs have an irregular agglomeration of tubes and when they are oxidized with nitric acid, nanotubes become shortened and a significant change is observed in the structural integrity of MWCNTs. Furthermore, observation of CNT_{sand} illustrates a non-uniform coating of MWCNTs on silica grains that is different from the surface of the acid-treated silica.

3.2.2. CHNS analysis

CHNS analysis of pristine and oxidized CNTs is in agreement with images obtained from scanning electron microscopy. Based on CHNS analysis

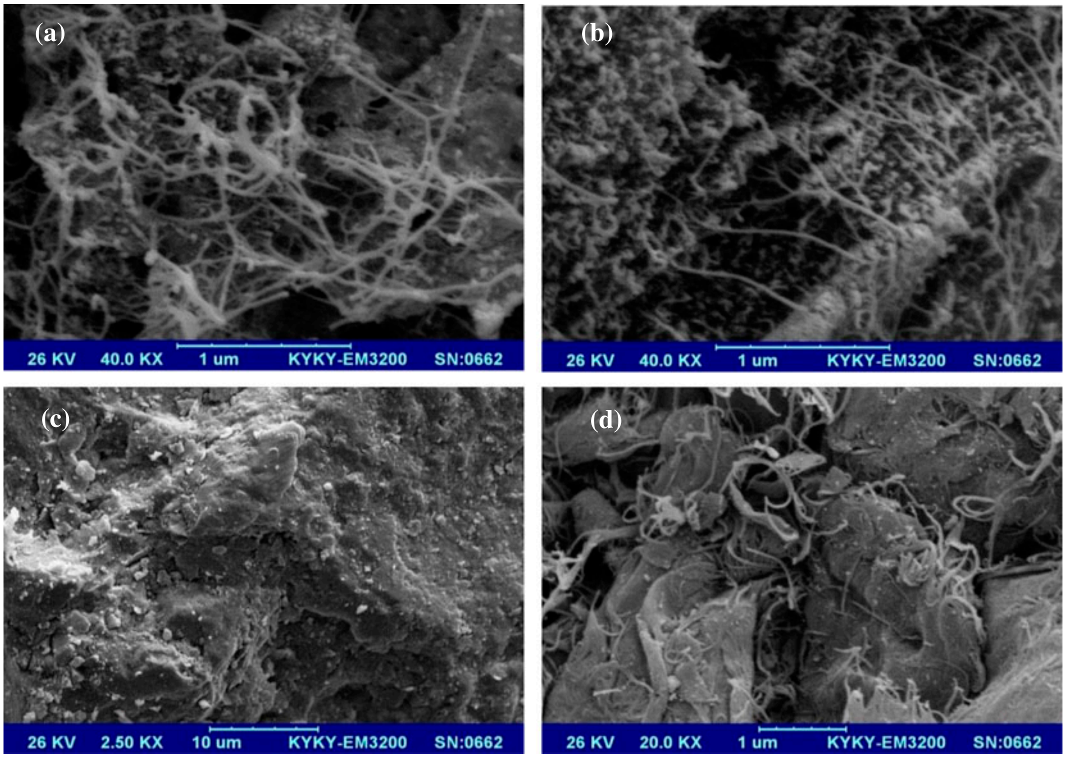

Fig. 4. SEM images: (a) pristine MWCNT, (b) oxidized MWCNT, (c) acid washed silica, and (d) CNT_{sand}.

Table 1
Atomic ratio of pristine and oxidized CNT with nitric acid

			Atomic ratio (%)				
Reaction condition	Temp. (℃)	Time (h)	C	O	N	H	S
Pristine CNT	–	–	95.7	3.85	0.1	0.1	0.25
Oxidized CNT	140	5	48.6	46.3	3.5	1.2	0.4

(Table 1), carbon and oxygen were seen in both pristine and oxidized CNTs, but in the oxidized CNTs, the ratio of oxygen has increased significantly. Presence of a high oxygen ratio in oxidized CNT is indicative of O–H and C=O functional groups on the CNT side wall. Likewise, the nitrogen atoms indicate that nitro groups exist on the side wall.

3.2.3. Fourier Transform Infrared (FTIR) analysis

Fourier transform infrared (FTIR) spectroscopy was used to investigate the chemical modification of CNTs (Fig. 5). Six occurrences of absorptions were spotted in the FTIR spectra of the oxidized sample at around 3,402, 2,924, 1,734, 1,637, 1,384, and 1,126 cm^{-1} which can be related to O–H, C–H, O–C=O, C=C, N=O, and C–O [15,22,23] stretching vibrations, respectively. Therefore, the FTIR spectroscopy demonstrates the presence of OH (3,402 cm^{-1}) and C=O (1,734 cm^{-1}) functional groups that cause increase in the amount of oxygen in the oxidized CNTs. This finding is in accordance with CHNS analysis.

3.2.4. Determination of pH_{zpc}

pH is an important parameter whose changes affect both CNTs and SiO_2. In environmental science, awareness of the pH_{zpc} (pH at which the surface has a net charge of zero) is important. According to previous studies, the amount of pH_{zpc} in pristine CNTs is equal to 5 [4], 6.1 [14], and 6.6 [24]. Similarly, the pH_{zpc} of oxidized CNT is 3.1 [14] and 3.7 [24]. In $pH < pH_{zpc}$, the surface of the CNT has positive charges. In this study, the pH_{zpc} of SiO_2, $SiO_2@NH_2$, and CNT_{sand} were investigated and based on Fig. 6, the values are roughly 3.4, 8.2, and 7.4, respectively. The pH_{zpc} of SiO_2 indicates that the surface of this material has negative charges at pH > 3.4 that can be due to OH groups the on surface of silica grains. On the other hand, the presence of NH_2 groups on the $SiO_2@NH_2$ induces a pH_{zpc} of about 8.2 for the surface of this material. Despite the presence of OH and CO groups on oxidized MWCNT, NH_2 remaining groups on silica surface, made the pH_{zpc} of CNT_{sand} about 7.4.

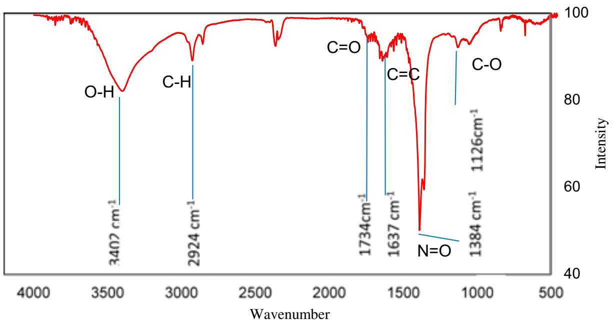

Fig. 5. FTIR spectra of oxidized CNT.

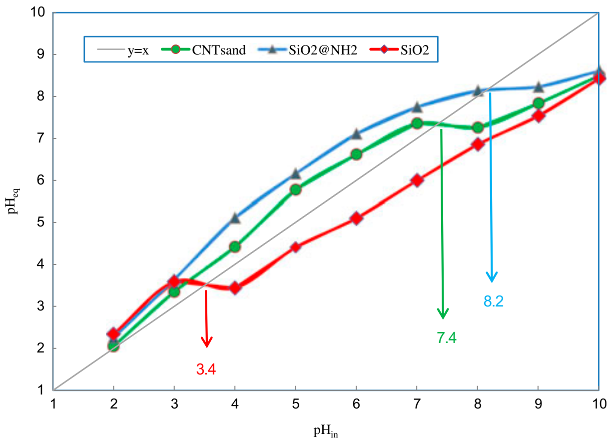

Fig. 6. pH_{zpc} of SiO_2, $SiO_2@NH_2$, and CNT_{sand}.

3.3. Batch adsorption experiments

3.3.1. Effect of pH_{in}

At the neutral pH, NOMs have negative charges due to the presence of phenolic, carboxylic, and hydroxyl groups, while CNT_{sand} has a positive charge. Therefore, at the neutral pH, humic acid can be adsorbed on the CNT_{sand} [5]. As a consequence, it is noteworthy to mention that in acidic pH, humic acids were flocculated and then precipitated which can cause a problem for adsorption studies because it is not clear which factor is responsible for the removal of humic acid. Thus, all experiments in this study were carried out at nearly neutral pH (in the range of 7–7.3). The obtained data indicate that equilibrium pH (pH_{eq}) has increased, which is probably the sign of the release of OH^- from the surface of the carbon nanotube in the solution. Therefore, ion exchange has a fundamental role in the adsorption process. A similar result was reported in a previous study [4].

3.3.2. Comparative analysis and effect of contact time and initial concentration

In order to determine the removal potential of humic acid, a comparative analysis was carried out among the initial silica, acid-washed silica, and CNT-coated silica. According to the data obtained from several experiments, neither the initial silica grains nor the acid-washed silica grains can remove humic acid. However, the silica grains that were coated with oxidized CNT have a good potential in humic acid removal (removal >70% in initial concentration of TOC = 10 mg/l and neural pH). After these experiments, it was demonstrated that the new adsorbent has a high potential in humic acid removal. Next, the effect of contact time (0–240 min) and initial TOC concentration (2–12 mg/l) were investigated. Based on Fig. 7, the adsorption of TOC onto CNT_{sand} (q_e) has a fast stage at first which is followed by a slow stage until reaching equilibrium. The initial fast stage is related to the quick adsorption of NOMs on available adsorption sites of CNT_{sand}. The adsorption rate decreases when these sites are occupied. Similar findings were reported in previous research [14]. According to this figure, the equilibrium time is about 40–60 min for CNT_{sand}. As it can be seen in Fig. 8, the dark brown solution changes into a relatively clear solution after about 40 min.

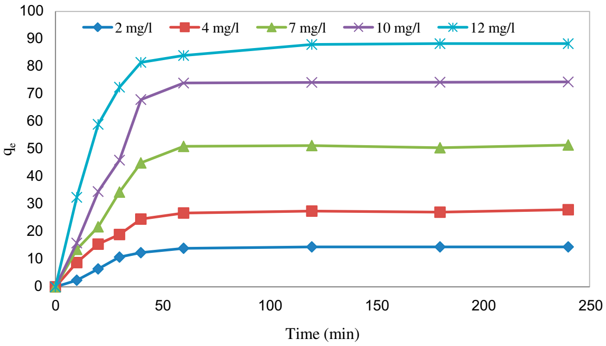

Fig. 7. Effect of adsorption time at different concentration of humic acid.

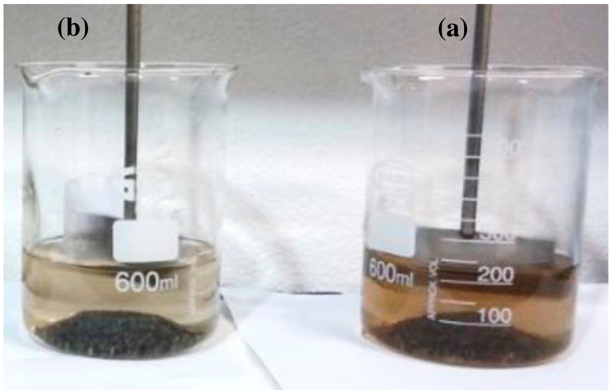

Fig. 8. (a) Color of solution containing humic acid and (b) color after 40 min of equilibrium.

Moreover, by increasing the initial TOC to a maximum of 12 mg/l, the adsorption rate increases which can be due to the increase in the collisions of adsorbate molecules with the adsorbent material. On the other hand, by increasing the initial concentration, the diffusion driving force of humic acid across the outer surface of CNT_{sand} would probably increase. As previously stated, several mechanisms can be considered for the adsorption of organic compounds onto CNT. The new adsorbent (CNT_{sand}), which has hydrophobic properties as well as hydrophilic functional groups, has a fairly available surface with a mesopore volume that can adsorb large groups of humic acid, especially those with high molecular weight. Besides, the hydrophobic interaction between humic acid and CNTs is an important factor for high adsorption. It must be noted that different sections of NOMs have different interactions with the surface of the adsorbent [7,25,26] and therefore, the π–π system enhances the interaction between the cross-linked aromatic network of humic molecules and the aromatic ring of CNT [27] in CNT_{sand}.

3.3.3. Adsorption isotherms

The adsorption isotherms are used to determine the adsorption capacity of an adsorbent [28]. In the present research, two equilibrium adsorption isotherms, namely Freundlich and Langmuir, have been studied. The linear forms of Freundlich and Langmuir equations can be obtained from the following equations, respectively [29].

$$\log q_e = \log K_f + \left(\frac{1}{n}\right)\log C_e \tag{1}$$

$$\frac{c_e}{q_e} = \frac{c_e}{q_m} + \frac{1}{bq_m} \tag{2}$$

where q_e (mg/g) is the amount of NOMs adsorbed onto CNT_{sand}, C_e (mg/l) is the equilibrium concentration of NOMs in the liquid phase, n and k_f ((mg/g) $(mg/l)^{-1/n}$) are Freundlich constants that represent the adsorption intensity and adsorption capacity, respectively [29].

In Freundlich isotherm with the linear plot of $\log q_e$ vs. $\log C_e$, the slope and the intercept, and hence, n and K_f can be obtained accordingly (Fig. 9(a)). Likewise, q_m and b can be calculated in Langmuir isotherm with the linear plot of c_e/q_e vs. c_e (Fig. 9(b)). According to the obtained data (Table 2), the higher correlation coefficient ($R^2 > 98\%$) best fitted with Langmuir isotherm and the maximum capacity was 81.96 mg/g. Based on Langmuir isotherm, the separation factor (R_L) is between 0.15 and 0.55 that indicates the favorability of the adsorption process of NOM onto CNT_{sand}. R_L is defined by Eq. (3).

$$R_L = \frac{1}{bc_e} \tag{3}$$

where b and c_e are the parameters defined in Langmuir isotherm.

3.3.4. Adsorption kinetics

Kinetic data can be used to predict the rate at which the NOM is adsorbed onto CNT_{sand} [26]. In this work, the adsorption kinetics of NOM onto CNT_{sand} was investigated with two common kinetic models, pseudo-first-order and pseudo-second-order model. NOM uptake q (mg/g) onto CNT_{sand} was calculated by Eq. (4), [28].

Table 2
Freundlich and Langmuir model parameters and correlation coefficient for HAs adsorption onto CNT_{sand}

	Freundlich			Langmuir		
Adsorbent	k_f	n	R^2	q_m	b	R^2
CNT_{sand}	36	2.98	0.80	81.96	0.65	0.984

$$q_t = \frac{(C_0 - C_t).\ V}{M} \tag{4}$$

where q_t is mg NOM per g CNT (mg/g), C_0 (mg/l) and C_t (mg/l) are NOM concentrations at initial ($t = 0$) and t, respectively. V (liter) is the volume of solution and m (g) is the mass of MWCNT. Further, the pseudo-first order and pseudo-second-order can be depicted by the following equations [28].

$$\log(q_e - q_t) = \log q_e - \frac{K_1 t}{2.303} \tag{5}$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \tag{6}$$

where q_e and q_t are the adsorption capabilities at equilibrium and time t (min), respectively. k_1 is the rate constant of pseudo-first order and k_2 is the rate constant of pseudo-second order. In pseudo-first order, the linear plot of $\log(q_e - q_t)$ vs. 1/t is used to obtain the first-order rate constant, k_1 (Fig. 10(a)), and in the pseudo-second-order, the linear plot of $\frac{t}{q_t}$ vs. t is used to calculate the second-order rate constant, k_2 (Fig. 10(b)). According to the obtained data (Table 3), the higher correlation coefficient ($R^2 > 96.8\%$) is best fitted with the plot of t/q_t against t. As a consequence, humic acid adsorption onto CNT_{sand} is best represented with the pseudo-second-order.

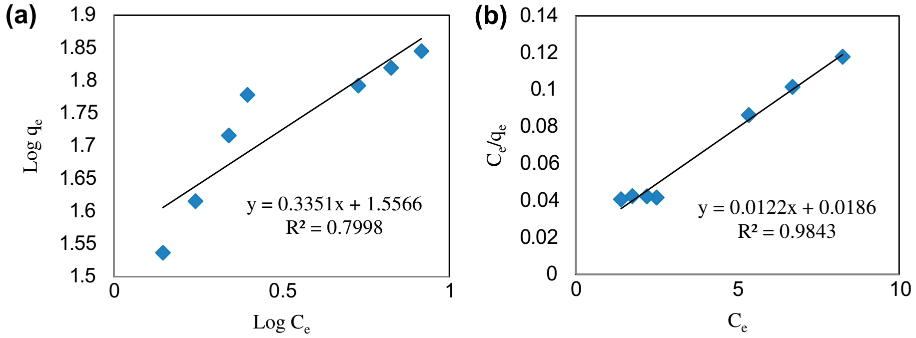

Fig. 9. Linearized (a) Freundlich and (b) Langmuir isotherm for adsorption of HAs onto CNT_{sand}.

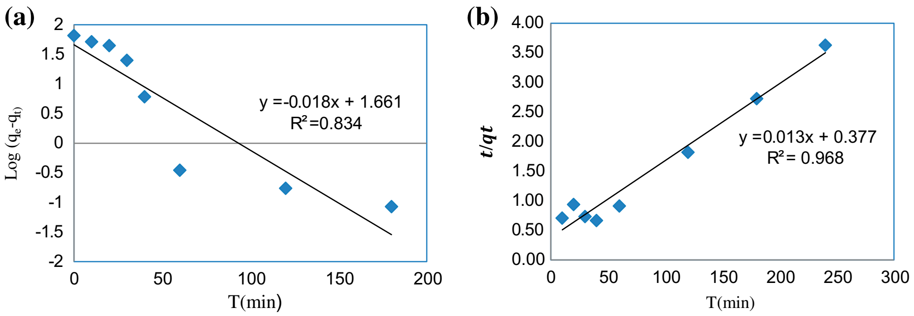

Fig. 10. (a) Pseudo-first-order and (b) pseudo-second-order kinetic model for adsorption of HAs onto CNT_{sand}.

Table 3
Adsorption kinetic model rate constants for HAs adsorption onto CNT_{sand}

			Pseudo-first-order			Pseudo-second-order		
Adsorbent	C_0 TOC (mg/l)	q_e (mg/g) experimental	k_1	R^2	q_e (mg/g)	$K_2 \times 10^3$	R^2	q_e (mg/g)
CNT_{sand}	10	74.4	0.04	0.834	45.8	0.44	0.968	76.9

3.3.5. Adsorption thermodynamic

In order to investigate thermodynamic behaviors of humic acid on CNT_{sand}, thermodynamic parameters should be determined. Thermodynamic parameters such as Gibbs free energy change ΔG° (KJ mol^{-1}), standard enthalpy change ΔH° (KJ mol^{-1}), and standard entropy change ΔS° (J mol^{-1} K^{-1}) were estimated by the following equations [30–32].

$$\ln k_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{7}$$

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

where k_c is the thermodynamic equilibrium constant of adsorption, R is the gas constant (8.314 Jk^{-1} mol^{-1}), and T is the absolute temperature. The values of ΔH° and ΔS° are calculated from the slope and intercept of plot ln k_c against $1/T$, respectively (Fig. 11). In this research, three temperatures (298, 313, and 328˚k) were studied to obtain thermodynamic parameters (Table 4).

The negative values of ΔG° in all temperatures confirmed that the adsorption is a feasible and spontaneous process. Moreover, the decrease in ΔG° by the increase in temperatures indicates that high temperatures would make better conditions for the adsorption of humic acid onto CNT_{sand}. In other words, high temperatures are favorable [28]. The positive value of ΔH° (11.02 kJ mol^{-1}) indicates that the adsorption of humic acid onto CNT_{sand} is endothermic in nature. The positive ΔS° (61.5 J mol^{-1} k^{-1}) suggests the increase in the degree of randomness at the solid–liquid interface [29].

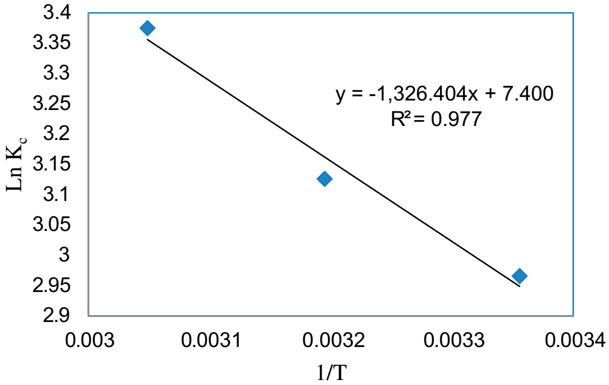

Fig. 11. Plot of ln k_c vs. $1/T$.

3.4. Regeneration of new adsorbent

Regeneration is a very important parameter that specifies the cost-effectiveness of an adsorbent [9]. Due to the high cost of CNTs, desorption of humic acid from the surface of CNT_{sand} is an important stage. In this study, in order to obtain the optimum condition for adsorbent regeneration, the pH of regeneration solution and the regeneration time were evaluated. Fig. 12(a) is indicative of the adsorbent recovery

Table 4
Thermodynamic parameters for HAs adsorption onto $\mathrm{CNT_{sand}}$

Adsorbent	Thermodynamic parameters	Temperature			R^2
		298	313	328	
$\mathrm{CNT_{sand}}$	ΔG° (KJ mol^{-1})	−7.34	−8.13	−9.20	0.977
	ΔH° (KJ mol^{-1})	11.02			
	ΔS° (J mol^{-1} K^{-1})	61.52			

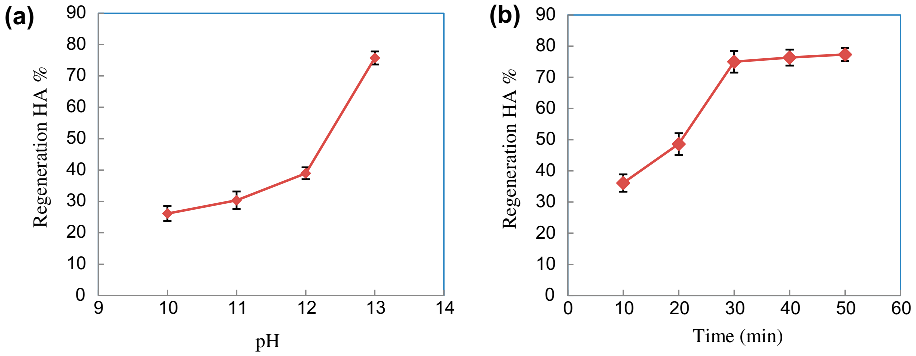

Fig. 12. Effect of (a) pH and (b) time on the adsorbent recovery.

at a pH in the range of 10–13. The adsorbent recovery is defined as the percentage ratio of the adsorption capacity of the regenerated adsorbents to that of the initial adsorbent. The adsorbent recovery of the new adsorbent was 26.3% at pH 10 and increased to 75.7% at pH 13. The increase in adsorbent recovery with the increase in the value of pH is due to the rise of the electrostatic repulsion between the surface of humic acid and the surface of $\mathrm{CNT_{sand}}$ at higher pH. It seems that an increase in pH to above 13, leads to increase in the adsorbent recovery. However, the optimum pH for regeneration of the adsorbent in the range of 10–13 is 13. Further, in order to obtain the optimum regeneration time, the pH was adjusted to 13 and the regeneration time was evaluated to be in the range of 10–50 min. The relatively clear regeneration solution changed into brown which is indicative of the presence of humic acid in the regeneration solution. As it can be seen in Fig. 12(b), the adsorbent recovery was about 36.1% after 10 min and increased to a maximum of 75% after 30 min. Additionally, the regeneration time indicates that the desorption process is faster than the adsorption process. Fig. 13 illustrates the adsorption capacities of $\mathrm{CNT_{sand}}$ under various regeneration cycles and in optimum conditions. Based on the obtained data, the adsorption capacity before regeneration was about 75 mg/g. It decreased to 54.5 mg/g after the first stage of regeneration, and in the fifth stage of regeneration, it was about 40.8 mg/g. Decrease in adsorption capacity after regeneration may be due to incomplete desorption of the humic acid from the surface of $\mathrm{CNT_{sand}}$. According to the obtained data, after five cycles of regeneration, the adsorption capacity is more than 50% of the initial capacity. Based on the previous research [33], “it is expected that the unit cost of CNTs can be further reduced in the future so that CNTs can possibly be cost-effective sorbents. Therefore, more studies on the

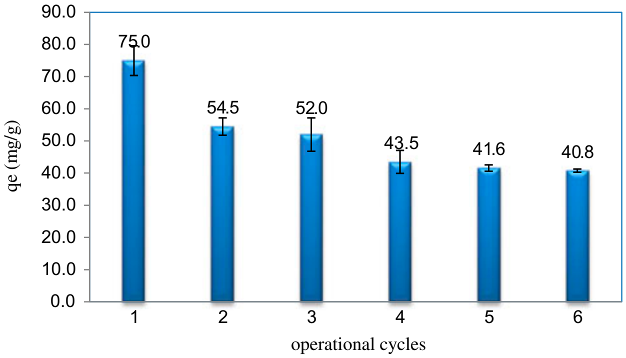

Fig. 13. Humic acid adsorption capacities before regeneration (cycle 1) and after regeneration cycles (2, 3, 4, 5, 6).

removal of other environmental pollutants by CNTs are strongly recommended."

4. Conclusions

In this study, a new engineered adsorbent (CNT_{sand}) was produced by coating silica grains with MWCNT. CNT_{sand} has a higher potential in the removal of humic acid than the initial silica grains and acid-treated silica. Based on the obtained data, the adsorption process was best fitted with Langmuir isotherm and the pseudo-second-order kinetic. Further, the adsorption process is spontaneous, endothermic, favorable, and disorderly at the solid—liquid interface. Regeneration studies indicate that the optimum pH is 13 and the optimum time for desorption is 30 min. Moreover, after five cycles of regeneration, the adsorption capacity is about 40 mg/g. These experiments show that the new adsorbent—CNT_{sand}—has a good potential in organic matter removal while the regeneration process is also simple.

Acknowledgments

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Abbreviations

NOMs	—	natural organic matters
CNTs	—	carbon nanotubes
MWCNTs	—	multiwall carbon nanotubes
HAs	—	humic acids
DBPs	—	disinfectant by products
HAAs	—	haloacetic acids
THMs	—	trihalomethanes
TOC	—	total organic carbon
CVD	—	chemical vapor deposition
GO	—	graphene oxide
CNT_{sand}	—	CNT coated on sand

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