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Adsorption of Ammonium Ion by Multi-walled Carbon Nanotube: Kinetics and Thermodynamic Studies

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This study was an attempt to examine the feasibility of removing ammonium ions from aqueous solutions by using multi-walled carbon nanotube (MWCNT). The adsorption behavior of ammonium ions (NH_4^+) from aqueous solution onto MWCNTs was investigated as a function of several parameters such as contact time, initial ammonium ion concentration and temperature. The adsorption of ammonium ions on carbon nanotube was studied at different temperatures ranging from 288 K to 328 K. Enthalpy (ΔH^0) and entropy (ΔS^0) of the procedure were −2.74 KJ/mol and −0.0083 KJ/mol K, respectively. The negative value of ΔH^0 indicates that the adsorption of ammonium ions onto CNTs is exothermic and that the negative value of ΔG^0 represents the fact that the process of adsorption of ammonium ions onto CNTs is spontaneous. Kinetic analysis showed that the adsorption of ammonium ions on MWCNT followed the pseudo-second-order model.

Keywords Adsorption, multi-walled carbon nanotubes, ammonium ions, thermodynamic functions, adsorption kinetics

Introduction

Eutrophication of water bodies is a major, global environmental problem. Its main cause is disposal of nutrients (N and P) directly from water plants or indirectly from agriculture and leaching from sludge deposited in landfill and fields. Ammonium ion (NH_4^+) is a common chemical form in aquatic ecosystems, and its toxic effect on life has been widely reported (1–3). Higher ammonium levels found in natural waters are indicative of deteriorated water quality, especially due to accelerated anthropogenic activity. Total removal or at least a significant reduction of ammonium ion is thus obligatory prior to disposal into streams, lakes, seas and land surface. Up to now, the main ammonium ion removal processes involve biological nitrification, denitrification, air stripping, chemical treatment and selective ion exchange (4–6). Adsorption, as one of the most economical promising techniques, has been used extensively in removing some toxic waste present in water (7,8). Most studies on ammonium adsorption from aqueous solution have been focused on mineral materials as adsorbents, such as zeolites (9–12) and limestone (13). Plant materials are a kind of abundant reproducible natural resource and a type of waste. Therefore, they were studied

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extensively as low-cost adsorbents to remove a variety of pollutants from aqueous solution, for example, heavy metals (14), dyes (15), nitrate (16), phosphate (17), phenol (18) and ammonium ions (19–25). However, no information is available in the literature on the removal of aqueous ammonia by carbon nanotubes (CNTs) as an adsorbent from aqueous solution.

CNTs as new adsorbents have gained increasing attention of many researchers since Long and Yang first reported that CNTs were more efficient for the removal of dioxins than activated carbon (26). According to the grapheme layer, CNTs can be classified into single-walled CNTs (SWCNTs) and MWCNTs (27). Due to their large specific surface area, small size, and hollow and layered structures, CNTs have been proven to possess great potential as superior adsorbents for removing many kinds of organic and inorganic contaminants including 1,2-dichlorobenzene (28), trihalomethanes (29), microcystins (30), fluoride (31), lead (32), nickel (33) and arsenate (34). Recently, Wu investigated the adsorption equilibrium, kinetics and thermodynamics of CNTs for reactive dyes (35). Although the adsorption capacity is increased using CNTs as adsorbents, it might be suffered from the inconvenience of tedious centrifugation separation process. To overcome this problem, Fugetsu et al. have encapsulated MWCNTs in Ba^{2+}-alginate matrix to constitute a cage and used it as the adsorbent for elimination of ionic dyes (36).

The aim of the present study was to investigate the potential and effectiveness of MWCNTs in ammonium ions removal from aqueous solution and the effect of the contact time (t), initial concentration of ammonium (C_0) ions and temperature on the adsorption process have been also investigated. The values of thermodynamic functions such as ΔH^0, ΔS^0 and ΔG^0 of ammonium ion removal by carbon nanotube in the optimum condition of contact time, initial concentration and temperature are also determined and reported. In addition, adsorption kinetics of the removal of ammonium ions on MWCNT was studied.

Experiments and methods

Raw materials

MWCNTs (armchair (6,6), Young's modulus (0.94T TPa), tensile strength (GPa 126.2T), purity, >95; diameter 1–2 nm; length, 5–30 nm; surface area, ∼400 m^2/g; and manufacturing method, catalytic chemical vapor deposition (CVD) was purchased from NanoAmor Nanostructured & Amorphous Materials, Inc. (USA). Doubly distilled water was used and all adsorbents were washed before using. Figure 1 presents SEM image of carbon nanotubes. Ammonium chloride salt (NH4Cl) (molecular weight, 53.16 g/mol) was supplied by Merck (Germany) (maximum purity available). Doubly distilled deionized water (HPLC grade 99.99% purity) was obtained from Sigma Aldrich Co. (Germany).

Adsorption studies

For the purpose of study of the adsorption process, a 1000 mg/L stock solution of ammonium was prepared by dissolving 3.819 g ammonium chloride (NH4Cl) in deionized water and adding water to 1000 mL. The solutions to be used were prepared by diluting the stock solution with deionized water when necessary.

Adsorption thermodynamic and kinetic experiments were conducted by using 100 mL glass flask containing 0.05 g of the adsorbent and 10 mL of the ammonium ion solution with the initial concentration of 140 mg/L. The glass flask was sealed with a glass stopper. These samples were then mounted on Ultrasonic Bath for 5–45 minutes at various temperatures (288, 298, 308, 318 and 328 K). Ultrasonic Bath (71020-DTH-E; Model
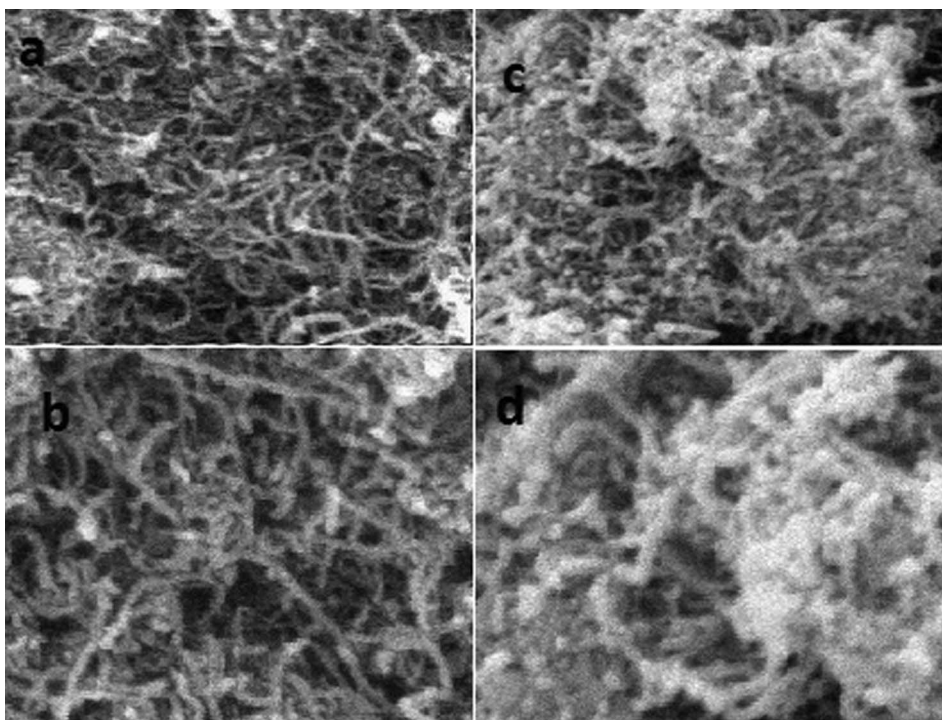
Figure 1. SEM images of carbon nanotubes (a) before adsorption 7500× (b) before adsorption 15000× (c) after adsorption 7500× (d) after adsorption 15000×.

1510 DTH, 220V; EMS Company) was used to prevent the particles to aggregate and forming bulk. Then the samples were centrifuged at 4500 rpm and the supernatant was filtered by 0.2 μm filter paper for subsequent ammonium concentration analysis. The initial and final ammonium concentrations remaining in solutions were analyzed by a UV spectrophotometer (Varian-Cary100 Bio), monitoring the absorbance changes at a wavelength of maximum absorbance ($\lambda = 400$ nm). The difference between the initial and the equilibrium ion concentration could determine the amount of ions adsorbed onto the CNTs' surface. The amount of ammonium adsorbed was calculated using the following equation:

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

where C_0 and C_e (mg/L) were initial ammonium liquid-phase concentration and its concentration at equilibrium, respectively. V is the volume of the solution (L) and m is the mass of adsorbent used (g). All the experiments were performed in triplicate, and only the mean values have been reported. Ammonium ion concentration was measured by Nesslerization Method (37).

Results and discussions

Effect of contact time

To determine the optimum time required for adsorption of ammonium ion onto CNT, 10 mL 100 mg/L solution was shaken with 50 mg CNT. The equilibrium studies were
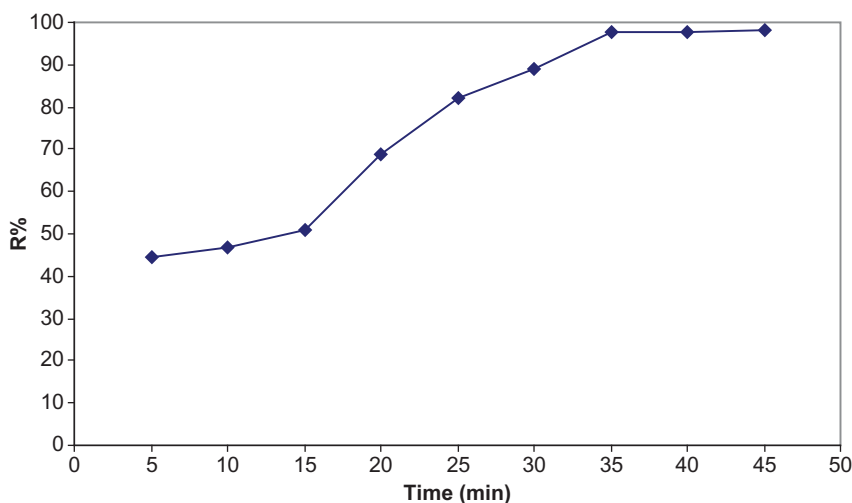
Figure 2. Effect of contact time on the percentage of ion adsorption onto CNT surface, initial concentration, 100 mg/L; adsorbent dosage, 50 mg/L and T = 298 K (color figure available online).

performed at the selected intervals of time ranging from 5 to 45 minutes. As shown in Figure 2, after 35 minutes stirring the solution, the removal efficiency did not increase. Therefore, the optimum value of stirring time was found to be 35 minutes. The change in the rate of ammonium ion removal might be due to the fact that initially all adsorbent sites were vacant and the solute concentration was high. Afterwards the ammonium ion uptake rate by the CNT decreased significantly due to the decrease in vacant adsorption sites. On the basis of these results, a 35-minute shaking period was selected for all further studies.

Effect of initial ammonium concentration

The effect of initial ammonium concentration was studied at different initial ammonium ion concentrations in the range of 100–140 mg/L at 298 K with 50 mg carbon nanotube. Ammonium ion adsorption capacity increased with increasing initial ammonium ion concentration in solution. This can be attributed to the fact that higher concentrations result in a higher solute gradient, provided the necessary driving force for ammonium ions to be adsorbed on to the surface of adsorbent.

Effect of temperature

The effect of temperature was studied at 288–328 K with 10 mL, 140 mg/L ammonium ion solution with 50 mg carbon nanotube. The results have been shown in Figure 3. The adsorption capacity of ammonium ion onto carbon nanotube was found to decrease with increase in temperature, suggesting the process in this research has been exothermic. This may be due to a tendency for the ammonium ion to escape from the solid phase to the bulk phase with an increase in temperature of the solution.

Thermodynamic studies

In this study, thermodynamic considerations of a sorption process were necessary to conclude whether the process was spontaneous or not. The standard Gibbs free energy change,
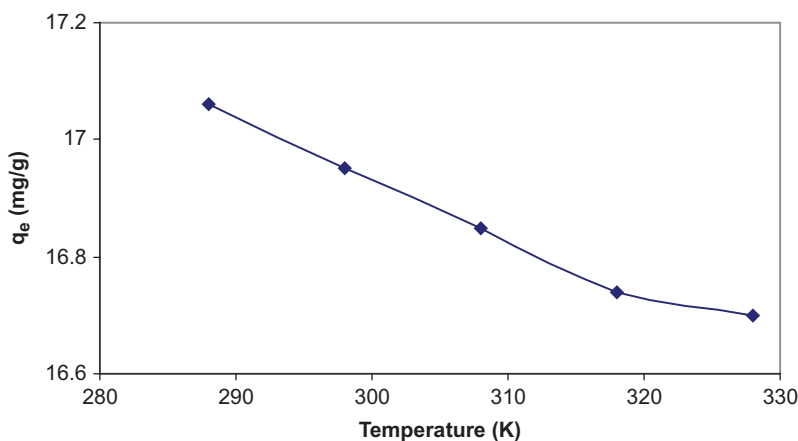
Figure 3. Effect of temperature for ammonium ions adsorption on CNT surface (color figure available online).

ΔG^0, was an indication of spontaneity of a chemical reaction and therefore was considered to be an important criterion for spontaneity. Also, both energy and entropy factors must be considered in order to determine the Gibbs free energy of the process. Reactions occur spontaneously at a given temperature if ΔG^0 has a negative value. The free energy of a sorption reaction, considering the sorption equilibrium constant K_a was given by the following equation:

$$\Delta G^\circ = -RT \ln K_a \tag{2}$$

where ΔG^0 is the standard free energy change, J/mol; R is the universal gas constant 8.314 J/mol K; and T is absolute temperature, K.

The relationship between free energy and equilibrium constant could indicate that changes in equilibrium constant with temperature could be obtained in the differential form as follows (38–40):

$$\frac{d \ln K_a}{dT} = \frac{\Delta H^\circ}{RT^2} \tag{3}$$

After integration, the integrated form of equation (3) becomes

$$\ln K_a = -\frac{\Delta H^\circ}{RT} + Y \tag{4}$$

where Y is constant. Therefore, equation (4) can be rearranged to obtain

$$-RT \ln K_a = \Delta H^\circ - TRY \tag{5}$$

Let

$$\Delta S^\circ = RY \tag{6}$$

Substituting two in equations (5–6), the Gibbs free energy change, ΔG^0, can be represented as follows:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{7}$$

Adsorption enthalpy (ΔH^0) and adsorption entropy (ΔS^0) at different temperatures (288 and 328 K) are calculated using the following equations:

$$K_L = \frac{q_e}{C_e} \tag{8}$$

$$\ln(K_L) = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{9}$$

where q_e is the amount of ammonium adsorbed, C_e is the equilibrium concentration, R (8.314 J/mol K) is the universal gas constant and T (K) is the absolute temperature. ΔH^0 and ΔS^0 have been calculated from the intercept and slope of linear plot of ln (K_L) versus 1/T (Van't Hoff plot) as shown in Figure 4. The determination of correlation coefficient value (R^2) of the linear plot was found to be 0.9824. The values of ΔG^0, ΔH^0 and ΔS^0 parameters have been summarized in Table 1. Changes in the standard Gibbs free energy ΔG^0 had negative values -0.34, -0.26, -0.18, -0.10 and -0.02 KJ/mol at 288, 298, 308, 318, 328 K, respectively. These results indicate that ammonium adsorption by carbon nanotube has been spontaneous. The increase in negative values of ΔG^0 with increasing temperature showed that adsorption of ammonium is unfavorable at higher temperatures. In addition, the sorption seems to be physical process more than a chemical sorption, since ΔG^0 values were between 0 and -20 kJ/mol (41). The enthalpy changes, ΔH^0, have had a negative value of -2.74 KJ/mol indicating that ammonium adsorption has been an exothermic process. The negative value of the standard entropy change ΔS^0 (-0.0083 KJ/mol K) could suggest that randomness decreases the removal of ammonium ions on carbon nanotube.
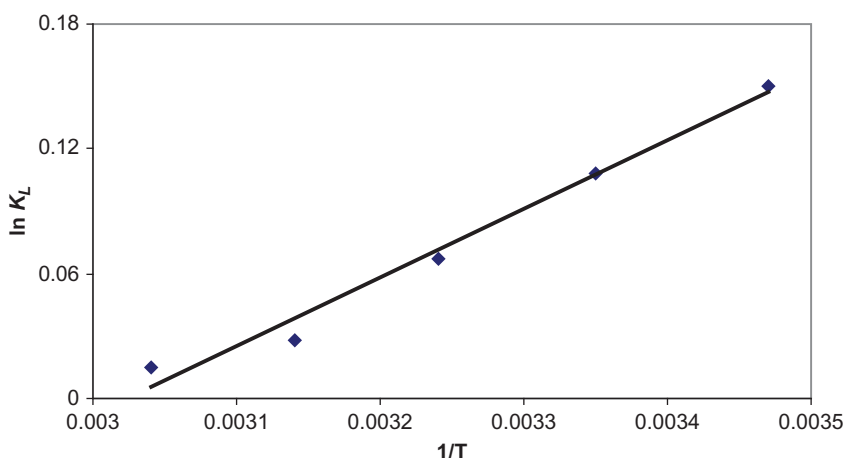

Figure 4. ln K_L vs. 1/T plot for the thermodynamic parameters for the percentage of adsorption of ammonium ions onto CNT surface. Initial concentration of solution was 100 mg/L, adsorbent dosage, 50 mg/L; contact time, 35 min and T = 298 K (color figure available online).

Table 1
Value of ΔG^0, ΔH^0 and ΔS^0 at different temperatures for adsorption of ammonium ions onto CNT

Temperature (K)	$\Delta G°(kJ/mol)$	$\Delta H°(kJ/mol)$	$\Delta S°(kJ/molK)$
288	−0.34		
298	−0.26		
308	−0.18	−2.74	−0.0083
318	−0.10		
328	−0.02		

Adsorption kinetics modeling

The kinetics of adsorption is important from the viewpoint of process efficiency and is required to choose optimum operating conditions for the full-scale batch process. The speed of adsorption is strongly influenced by several parameters such as the status of the solid matrix and the physicochemical conditions under which the adsorption takes place. The study of adsorption kinetics is useful for understanding the mechanisms that are involved and for the design of future facilities adsorption on a large scale.

In order to predict the mechanism involved during the present adsorption process and the potential rate controlling steps such as mass transport, pore diffusion and chemical reaction processes, three kinetic models, namely, pseudo-first-order, pseudo-second-order and intra-particle diffusion models, were used to fit the experimental data. A pseudo-first-order kinetic equation is given as (42):

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{10}$$

Where q_t is the amount of adsorbate adsorbed at the time t (mg/g), q_e is the adsorption capacity at equilibrium (mg/g), k_1 is the pseudo-first- order rate constant (1/min) and t is the contact time (min). Using equation (10), $\ln(q_e - q_t)$ versus t was plotted as shown in Figure 5. The pseudo-first-order model data do not fall on straight lines indicating that this model is less appropriate. The pseudo-first-order rate constant (k_1) determined from the model is presented in Table 2 along with the corresponding correlation coefficients.

The pseudo-second-order model can be represented in the following form (43):

$$\frac{t}{q_e} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{11}$$

where k_2 is the pseudo-second-order rate constant (g/mg min). The values of k_2 and q_e can be calculated from the slope and the intercept of the straight-line plots of t/q_t versus t as shown in Figure 6. The results are noted in Table 2. It is clearly obvious from Figure 6 that pseudo-second-order model is more suitable than the others.

The intra-particle diffusion is represented by:
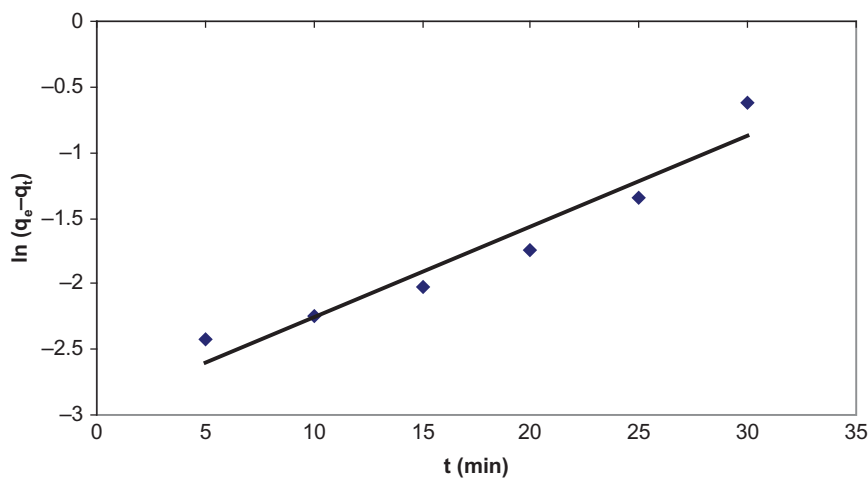
$$q_e = k_i t^{1/2} + c \tag{12}$$

Figure 5. Pseudo-first-order kinetics for sorption of ammonium ions on CNT (color figure available online).

Table 2
Kinetic parameters for the adsorption of ammonium ions onto
carbon nanotube

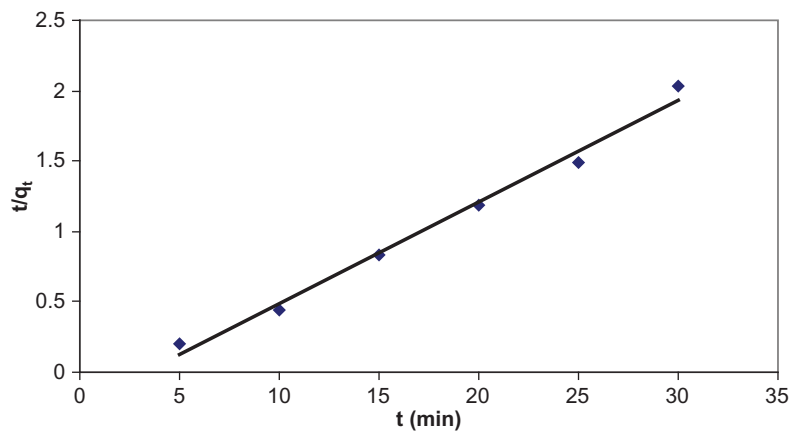| Pseudo-first-order model	K_1	R^2
$\ln(q_e - q_t) = \ln q_e - k_1 t$	0.2965	0.9314
Pseudo-second-order model	K_2	R^2
$\frac{t}{q_e} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$	0.0277	0.9894
Intraparticle diffusion	K_i	R^2
$q_e = k_i t^{1/2} + c$	2.8619	0.9836

Figure 6. Pseudo-second-order kinetics for sorption of ammonium ions on CNT (color figure available online).
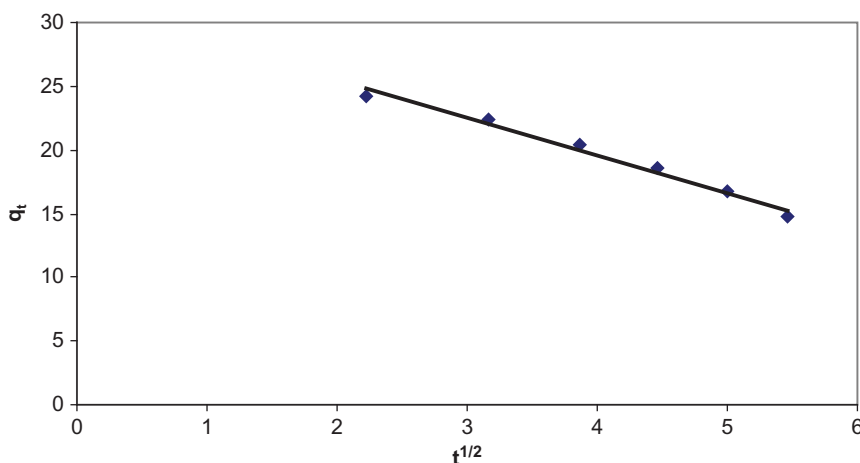
Figure 7. Plot for the intraparticle diffusion for the sorption of ammonium ions on CNT (color figure available online).

where k_i is the intra-particle diffusion rate constant (mg/min$^{1/2}$ g), and C is the intercept. The intra-particle diffusion model as fitted with the experimental data is presented in the plot of q_t versus $t^{1/2}$ depicted in Figure 7, and the values of k_i and correlation coefficients are given in Table 2. Comparing the figures of the kinetic models reveals that pseudo-second-order model has the best agreement with the experimental data.

Conclusion

In this study, adsorption experiments were carried out for the adsorption of ammonium ions from aqueous solution using carbon nanotubes (CNTs) surfaces as adsorbents. The adsorption characteristics were examined at different contact times, initial concentrations of ammonium ions and temperatures. Thermodynamic studies of adsorption of ammonium ions revealed that the negative values of Gibbs free energy were denoted to the spontaneous process, and the negative value of enthalpy for adsorption of ammonium ions on MWCNTs showed that the adsorptions process was exothermic. The negative value of ΔS^0 indicates the randomness decreases the uptake of ammonium ions on the multi-walled carbon nanotube. Furthermore, based on the results, this research suggests that adsorption of ammonium ion onto CNTs surface was a physisorption process. The kinetics of ammonium ions adsorption onto MWCNTs followed the pseudo-second-order model.

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