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Thermodynamics and kinetics of adsorption of Cu(II) from aqueous solutions onto multi-walled carbon nanotubes



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Abstract Release of heavy metals into water as a result of industrial activities may pose a serious threat to the environment. The objective of this study is to assess the uptake of Cu²⁺ from aqueous solutions onto multi-walled carbon nanotubes (MWCNT). The potential of the t-MWCNT to remove Cu²⁺ cations from aqueous solutions was investigated in batch reactor under different experimental conditions. The processing parameters such as initial concentration of Cu²⁺ ions, temperature, and adsorbent mass were also investigated. Copper uptake was quantitatively evaluated using the Langmuir, Freundlich and Dubinin–Kaganer–Radushkevich (DKR) models. In addition, the adsorption equilibrium was described well by the Langmuir isotherm model with maximum adsorption capacity of 12.34 mg/g of Cu²⁺ cations on t-MWCNT. Various thermodynamic parameters, such as ΔG^0 , ΔH^0 and ΔS^0 were calculated. The thermodynamics of Cu²⁺ cations adsorption onto t-MWCNT system pointed at spontaneous and endothermic nature of the process. Using the second-order kinetic constants, the activation energy of adsorption (E_a) was determined as 27.187 kJ/mol according to the Arrhenius equation.

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1. Introduction

The removal of toxic metals from wastewater is of great interest in the field of water pollution. Numerous metals such as chromium, mercury, lead, copper, cadmium, manganese, nickel, etc. are known to be highly toxic (Mobasherpour et al., 2011). Various methods have been used to remove heavy metals from wastewater, including: reduction and precipitation (Esalah et al., 2000), coagulation and flotation (Zouboulis et al., 1997), adsorption (Toles and Marshall, 2002; Ravindran et al., 1999), ion exchange, membrane technologies and electrolysis (Canet et al., 2002). Generally, they are

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expensive or ineffective, especially when the metal concentration is higher than 100 ppm (Miretzky et al., 2006).

Copper and its compounds are widely used in many industries and there are many potential sources of copper pollution. Copper contamination in water streams occurs mainly from metal cleaning and plating bath, fertilizer, refineries, paper and pulp, and wood preservatives (Gundogan et al., 2004). The continued intake of copper by human beings leads to necrotic changes in the liver and kidney, mucosal irritation; wide spread capillary damage, depression, gastrointestinal irritation, and lung cancer (Rengaraj et al., 2007). According to the Safe Drinking Water Act the permissible limit of copper in drinking water is 1.3 mg/dm³ (Johnson et al., 2002).

Carbon nanotubes (CNTs) have been discovered by Iijima (1991) and have led research to new areas in many interdisciplinary investigations as the advantages of CNTs are the presence of unique structural, electronic, optoelectronic, semiconductor, mechanical, chemical and physical properties (Haddon, 2002). CNT would impact future nanoscience and nanotechnology since it is highly potential material and has become available in macroscopic quantities (Journet et al., 1997; Rinzler et al., 1998; Nikolaev et al., 1999; Rao et al., 2001).

CNTs have been proven to possess great potential as superior adsorbents for removing many kinds of organic and inorganic pollutants such as dioxin (Long and Yang, 2001), volatile organic compounds (Agnihotri et al., 2005; Gauden et al., 2006) from the air stream or fluoride (Li et al., 2003a), 1,2-dichlorobenzene (Peng et al., 2003), trihalomethanes (Lu et al., 2005), soil organic matters (Yang et al., 2006) and various divalent metal ions from aqueous solution (Li et al., 2002; Di et al., 2006; Lu et al., 2006).

The objective of this study was to investigate the possible use of multi-walled carbon nanotubes as an alternative adsorbent material for the removal of Cu²⁺ cations from aqueous solutions. The Langmuir, Freundlich and DKR models were used to fit the equilibrium isotherm. The dynamic behavior of adsorption was investigated on the effect of initial metal ion concentration, adsorbent mass, contact times and temperature, of the solution. The thermodynamic parameters were also evaluated from the adsorption measurements.

2. Experimental

2.1. Preparation of adsorbent

MWCNT prepared by a chemical vapor deposition (CVD) method were used as received without purification (Research Institute of Petroleum Industry, Tehran, Iran). The purity of MWCNT was more than 95%, the outer diameters were 10–20 nm, length of CNTs was in the range 5–15 μm and the amorphous carbon content in the CNTs was < 5 wt%. These data were provided by the manufacturer. Millipore deionized (DI) water was used for sample washing and solution preparation. The raw MWCNT (r-MWCNT) was first treated with HNO₃ (8 M). This mixture was then sonicated for 3 h at 40 °C in an ultrasonic bath to introduce oxygen groups onto the MWCNT surface. After cooling to room temperature, the MWCNT were added dropwise to 300 mL of cold DI water and filtered through Whatman grade 6 filters. The filtrant was washed with DI water until the pH was neutral.

The treated MWCNT (t-MWCNT) was dried in a vacuum oven at 80 °C for 24 h.

Fourier transform infrared spectra (FT-IR) of the t-MWCNT were recorded using a Perkin–Elmer 2000 FTIR spectrometer fitted with a deuterated triglycine sulfate (DTGS) detector covering the frequency range of 500–4000 cm⁻¹. The sample cell was purged with nitrogen gas throughout data collection to exclude carbon dioxide and water vapor. Ten milligrams of the dried samples were evenly dispersed in 200mg of spectroscopic grade KBr to record the spectra. The transmission electron microscopy (TEM) was used to characterize treated MWCNT. For this purpose, MWCNT were deposited onto Cu grids, which support a “holey” carbon film. The particles were deposited onto the support grids from a dilute suspension in acetone or ethanol. The shapes and sizes were characterized by diffraction (amplitude) contrast and, by high resolution (phase contrast) imaging. The specific surface area was determined from N₂ adsorption isotherm by the BET method using a Micromeritics surface area analyzer model ASAP 2010.

2.2. Sorption study

All sorption experiments were carried out without imposing any pre equilibration processes during the performance of any experiments. Using batch equilibration technique, the sorption capacity of MWCNT for Cu²⁺ cations, as well as the influence of the initial concentration of Cu²⁺ cations, adsorbent mass, contact time and temperature, sorption experiments were determined.

Aqueous solutions containing Cu²⁺ cations of concentration (10, 15, 20 and 30 mg/L) were prepared from hydrated copper nitrate (CuNO₃·3H₂O, Merck Product No. 1027521000). The 0.4 g of t-MWCNT was introduced in a stirred tank reactor containing 500 mL of the prepared solution. The agitator stirring speed was 700 rpm. The temperature of the suspension was maintained constant at 20 ± 1 °C. Samples were taken after mixing the adsorbent and Cu²⁺ cations bearing the solution at pre determined time intervals (0, 5, 10, 20, 30, 60, and 120 min) for the measurement of residual metal ion concentration in the solution and to ensure that the equilibrium was reached. The sample volume taken is 5 mL. After each specified time, the sorbents were separated from the solution by centrifuge and filtration through the filter paper (Whatman grade 6). The exact concentration of metal ions was determined by AAS (GBC 932 Plus atomic absorption spectrophotometer). All experiments were carried out twice. The mass balance of copper is given by

$$mq = V(C_0 - C) \quad (1)$$

where m , q , V , C_0 , and C are the mass of MWCNT (g), amount of copper removed by unit of weight of MWCNT (uptake capacity: mg Cu/g MWCNT), volume of copper solution (L), initial copper concentration of solution (mg Cu/L), and the concentration of copper at the time t of adsorption (mg Cu/L). After 120 min, C and q will reach equilibrium value C_e and q_e .

The percent removal (%) and distribution ratio (K_d) were calculated using the following equations:

$$\% \text{Removal} = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (2)$$

where C_0 and C_f are the concentrations of the metal ion in the initial and final solutions (after 120 min), respectively, and

$$K_d = \frac{\text{amount of metal in adsorbent}}{\text{amount of metal in solution}} \times \frac{V}{m} \quad (3)$$

where V is the volume of the solution (mL) and m is the weight of the adsorbent (g).

3. Results and discussion

3.1. Characteristics of adsorbent

The IR spectra of the r-MWCNT and t-MWCNT were presented in Fig. 1. Compared with the r-MWCNT, the t-MWCNT exhibited some characteristic peaks at wavenumbers of 1580, 1700 and 3425 cm^{-1} , which were associated with hydroxyl groups or carbonyl groups, carboxylic acids and hydroxyl groups (Stafiej and Pyrzynska, 2007), respectively. The increased amounts of these functional groups resulted in an increasing surface cation exchange and complexation capacity of the r-MWCNT (Li et al., 2003b).

TEM micrograph of the MWCNT after modified treatment is shown in Fig. 2. From the TEM images, the t-MWCNT sheet is regarded as an entangled MWCNT network. The MWCNT sheets have high flexibility and are not easily broken during oxidation, washing and drying processes. Also, in the TEM image shown, inner tube diameter is about 5–10 nm and outer tube diameter is about 10–20 nm. The BET analysis of the t-MWCNT sample has confirmed a high surface area product, with the specific surface area of 102 m^2/g .

3.2. Effect of initial Cu^{2+} concentration and adsorbent dosage

The sorption of Cu^{2+} cations was carried out at different initial copper concentrations ranging from 10 to 30 mg/L, at pH 7, at 700 rpm with 120 min of contact time using t-MWCNT. The uptake of the Cu^{2+} ion is increased by increasing the initial metal concentration tending to saturation at higher metal concentrations as shown in Fig. 3. When the initial Cu^{2+} cat-

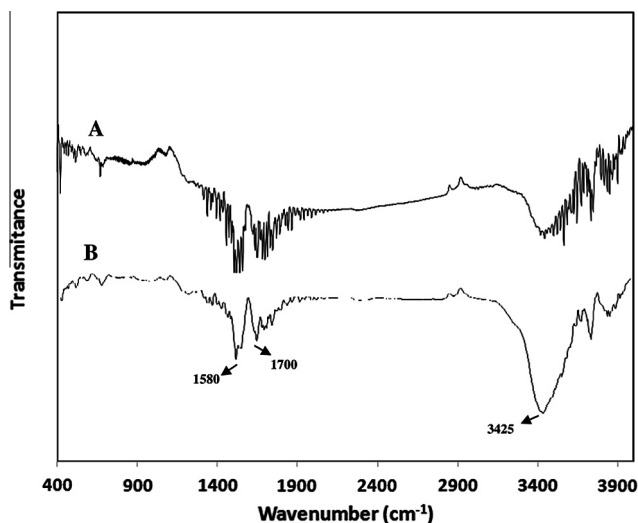


Figure 1 The Fourier-transformed infrared spectra of the r-MWCNT – A and t-MWCNT – B.

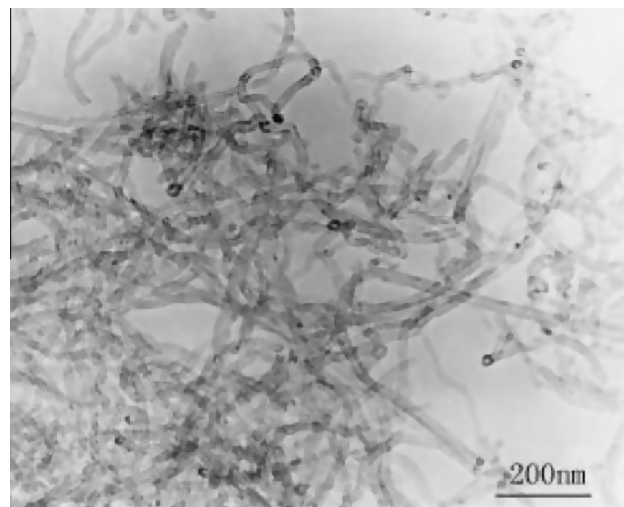


Figure 2 TEM micrograph of the t-MWCNT.

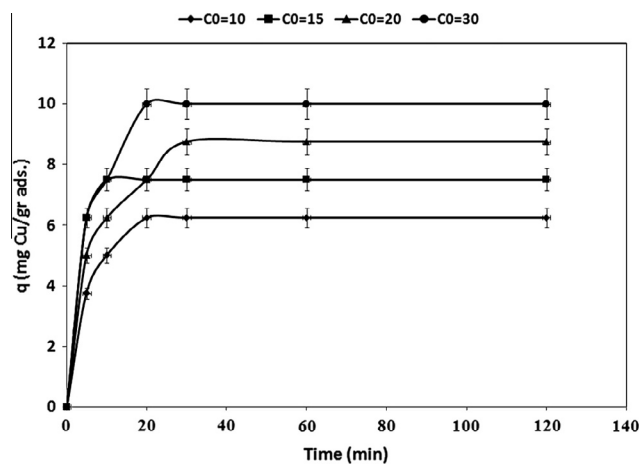


Figure 3 Effect of initial concentration on the removal of Cu^{2+} by t-MWCNT sorbents (pH 7, adsorbent dosage = 0.8 g/L, 700 rpm agitating rate).

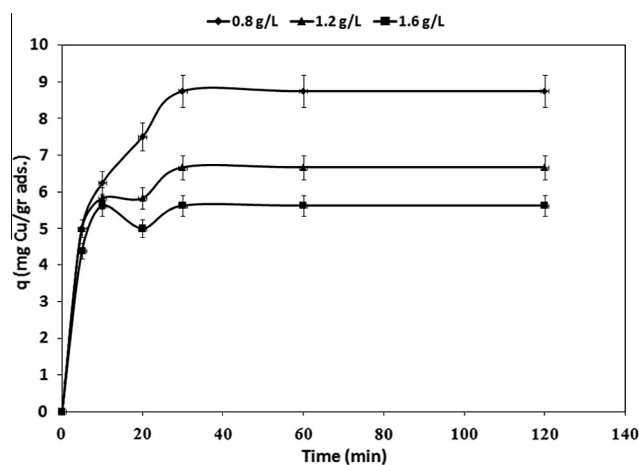


Figure 4 Effect of adsorbent dosage on uptake capacity of Cu^{2+} by t-MWCNT (pH 7, initial metal concentration = 20 mg/L, 700 rpm agitating rate).

ions concentration increased from 10 to 30 mg/L, the uptake capacity of t-MWCNT increased from 6.25 to 10 mg/g. A higher initial concentration provided an important driving force to overcome all mass transfer resistances of the pollutant between the aqueous and solid phases and thus increased the uptake (Aksu and Tezer, 2005).

The effect of t-MWCNT dosage is depicted in Fig. 4. Evidently, percentage removal increased with the increase of the sorbent mass and the uptake capacity of Cu^{2+} decreased from 8.750 mg/g (35% removal) to 5.625 mg/g (45% removal) with increasing t-MWCNT concentration from 0.8 to 1.6 g/L

(Fig. 4). This was attributed to a higher dosage of sorbent due to the increased surface area providing more adsorption sites available which gave rise to a higher removal of Cu^{2+} cations.

3.3. Effect of temperature and Determination of thermodynamic parameters

To study the effect of the temperature parameter on the uptake of Cu^{2+} cations by t-MWCNT, temperatures of 20, 45 and 65°C were selected. Fig. 5 (a) illustrates the relationship

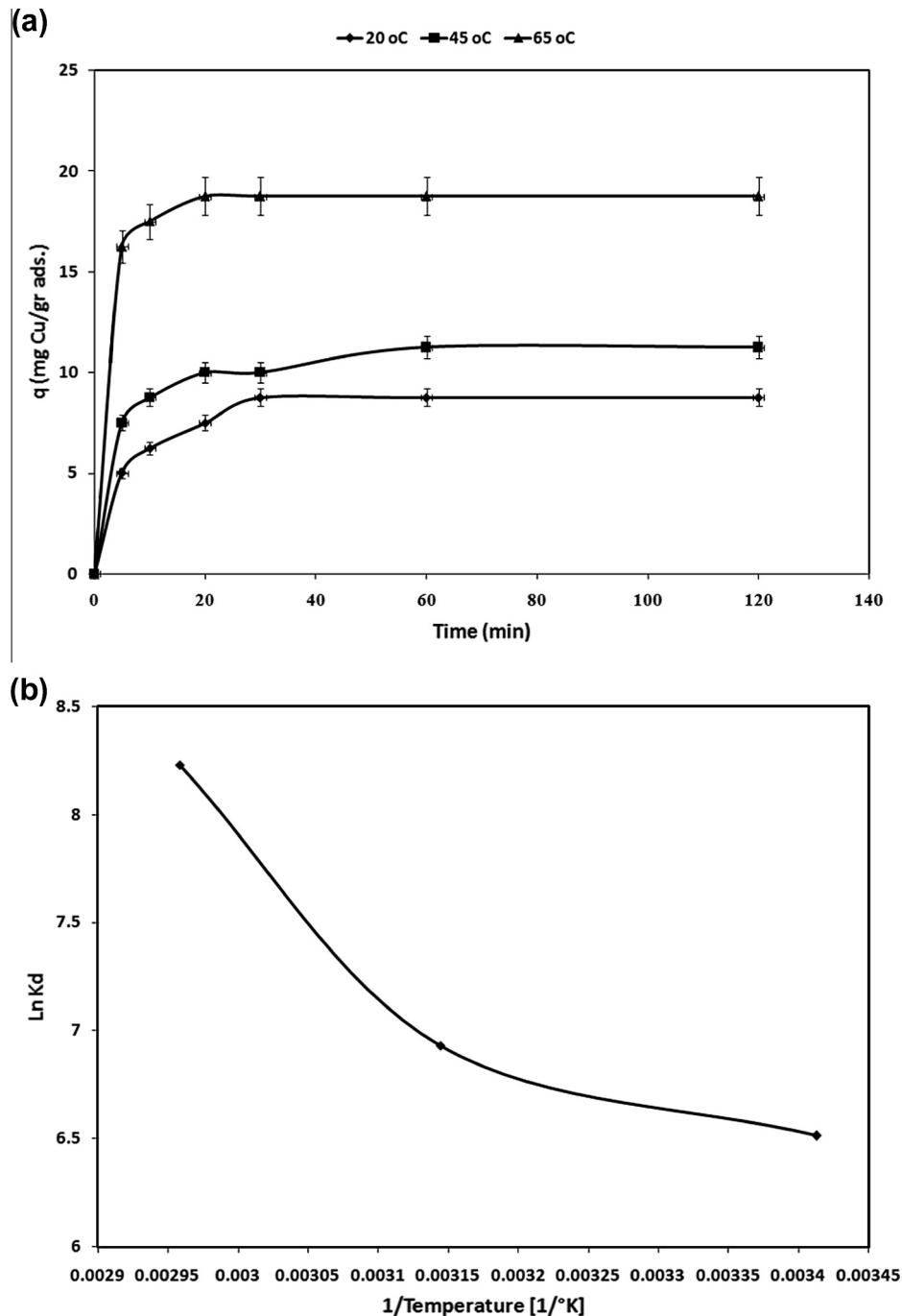


Figure 5 The uptake capacity of Cu^{2+} ions at different temperature (a) and plot of $\ln K_d$ versus $1/T$ (b) (pH 7, initial metal concentration = 20 mg/L, adsorbent dosage = 0.8 g/L, 700 rpm agitating rate).

between temperature and the amount of Cu^{2+} cations adsorbed onto t-MWCNT at contact time. As seen, the adsorption of Cu^{2+} cations on t-MWCNT increased from 8.75 mg/g (35% removal) to 18.75 mg/g (75% removal) when the temperature was increased from 20 to 65 °C at an initial concentration of 20 mg/L at equilibrium time. The increase in the equilibrium sorption of Cu^{2+} cations with temperature indicated that the Cu^{2+} cations removal by adsorption on t-MWCNT favored a high temperature condition. This could be the result of an increase in the mobility of the Cu^{2+} cations with temperature. An increasing number of molecules could also acquire sufficient energy to undergo an interaction with active sites at the surface. Furthermore, increasing temperature may produce a swelling effect within the internal structure of the t-MWCNT enabling large metal ions to penetrate further (Doğan and Alkan, 2003).

Thermodynamic parameters such as free energy (ΔG^0), enthalpy (ΔH^0), and entropy (ΔS^0) changes can be estimated using equilibrium constants changing as a function of temperature. The free energy changes of the sorption reaction are given by the following equation:

$$\Delta G^0 = -RT \ln K_d \quad (4)$$

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

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (5)$$

The distribution ratio (K_d) values increased with rising temperature (Fig. 5(b)), indicating the endothermic nature of adsorption. A plot of Gibbs free energy changes, ΔG^0 versus temperature, T (K), was found to be linear. The values of ΔH^0 and ΔS^0 were determined from the slope and intercept of the plots. The thermodynamic parameters of Gibbs free energy change, ΔG^0 , are shown in Table 1. The enthalpy, ΔH^0 , and the entropy changes, ΔS^0 , for the sorption processes were calculated to be 31,136 and 158.80 J/mol K, respectively. The negative values of ΔG^0 at various temperatures indicated the spontaneous nature of the adsorption process. The positive value of ΔS^0 indicated that there is an increment in the randomness in the system solid/solution interface during the adsorption process. In addition, the positive value of ΔH^0 indicated that the adsorption was endothermic. The positive value of ΔS^0 reflected the affinity of the t-MWCNT for Cu^{2+} cations and suggested some structural changes in t-MWCNT (Ho, 2003).

3.4. Adsorption isotherms

Analysis of the equilibrium data is important to develop an equation which accurately represents the results and can be used for design purposes (Aksu, 2002). Several isotherm equa-

tions have been used for the equilibrium modeling of adsorption systems.

The sorption data have been subjected to different sorption isotherms, namely, Langmuir, Freundlich, and Dubinin–Kaganer–Radushkevich (DKR).

The equilibrium data for metal ions over the concentration range from 10 to 30 mg/L at 20 °C were correlated with the Langmuir (1918) isotherm:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 K} + \frac{C_e}{Q_0} \quad (6)$$

where C_e is the equilibrium concentration of the metal in solution (mg/L), q_e is the amount adsorbed at equilibrium onto t-MWCNT (mg/g), Q_0 (mg/g) and K (L/mg) are Langmuir constants related to sorption capacity and sorption energy, respectively. Maximum sorption capacity (Q_0) represents monolayer coverage of sorbent with sorbate and K represents the enthalpy of sorption and should vary with temperature. A linear plot was obtained when C_e/q_e was plotted against C_e over the entire concentration range of metal ions investigated.

The linearized Langmuir adsorption isotherms of Cu^{2+} cations are given in Fig. 6(a). An adsorption isotherm is characterized by certain constants which express values of the surface properties and affinity of the sorbent and can also be used to find the sorption capacity of the sorbent.

The Freundlich sorption isotherm, one of the most widely used mathematical descriptions, usually fits the experimental data over a wide range of concentrations. This isotherm gave an expression encompassing the surface heterogeneity and the exponential distribution of active sites and their energies. The Freundlich adsorption isotherms were also applied to the removal of Cu^{2+} cations on t-MWCNT (Fig. 6(b)).

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e \quad (7)$$

where q_e is the amount of metal ion adsorbed at equilibrium per gram of adsorbent (mg/g), C_e is the equilibrium concentration of metal ion in the solution (mg/L), k_f and n are the Freundlich model constants (Malkoc and Nuhoğlu, 2003; Kadirvelu et al., 2001). Freundlich parameters, k_f and n , were determined by plotting $\ln q_e$ versus $\ln C_e$. The numerical value of $1/n < 1$ indicates that adsorption capacity is only slightly suppressed at lower equilibrium concentrations. This isotherm does not predict any saturation of the sorbent by the sorbate; thus infinite surface coverage is predicted mathematically, indicating multilayer adsorption on the surface (Hasany et al., 2002).

The Dubinin–Kaganer–Radushkevich (DKR) has been used to describe the sorption of metal ions on clays. The DKR equation has the form:

$$\ln C_{\text{ads}} = \ln X_m - \beta \varepsilon^2 \quad (8)$$

where C_{ads} is the number of metal ions adsorbed per unit weight of adsorbent (mol/g), X_m (mol/g) is the maximum sorption capacity, β (mol^2/J^2) is the activity coefficient related to mean sorption energy, and ε is the Polanyi potential, which is equal to

$$\varepsilon = RT \ln(1 + 1/C_e) \quad (9)$$

where R is the gas constant (8.314 kJ/mol K) and T is the temperature (K). The saturation limit X_m may represent the total specific micro-pore volume of the sorbent. The sorption poten-

Table 1 Thermodynamic parameters for the adsorption of Cu^{2+} onto t-MWCNT.

T (K)	K_d	ΔG^0 (J/mol)	ΔH^0 (J/mol)	ΔS^0 (J/mol K)
293	673.08	-15862.9		
318	1022.72	-18322.5	31,136	158.80
338	3750	-23126		

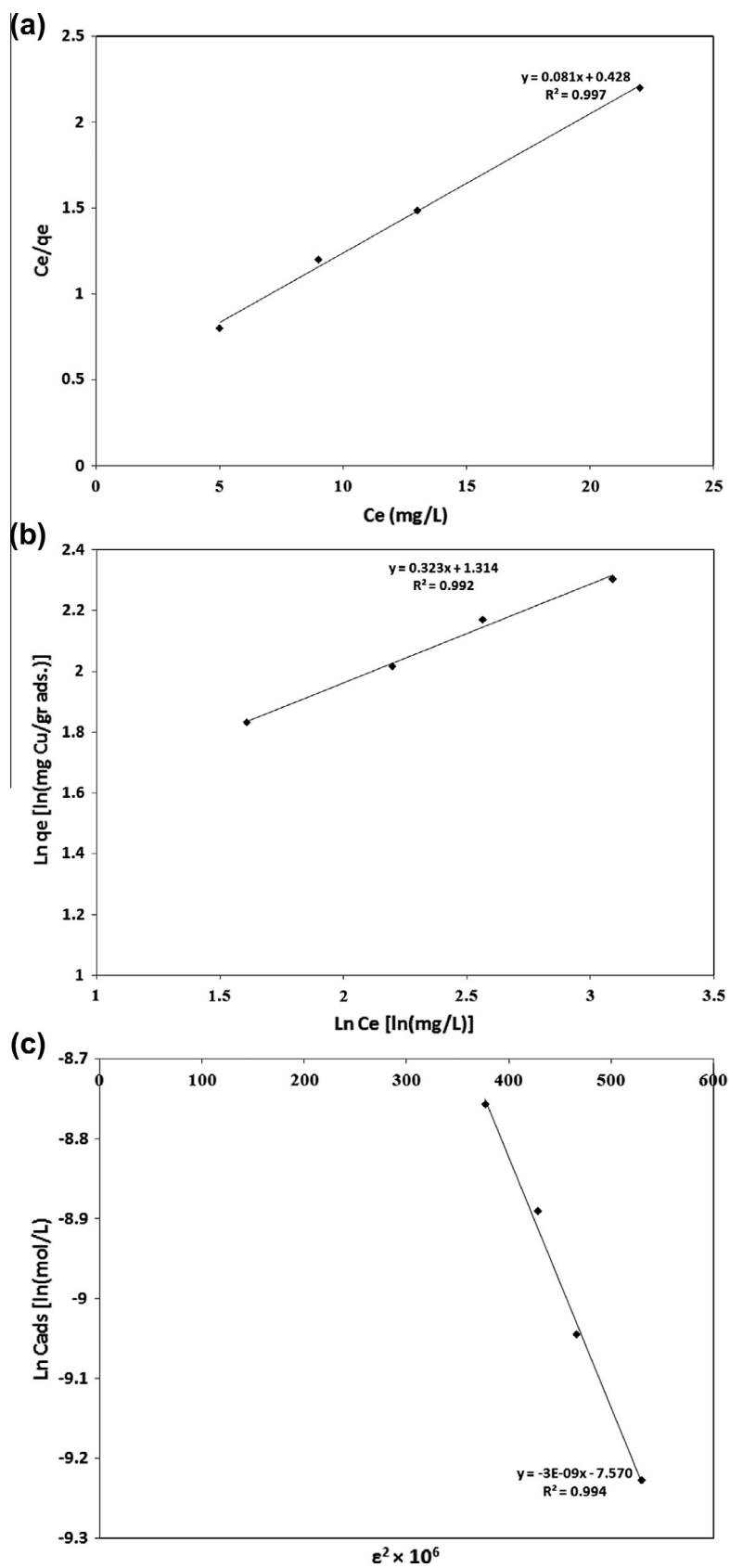


Figure 6 Linear fits of experimental data obtained using Langmuir (a), Freundlich (b) and DKR (c) sorption isotherms for the adsorption of Cu²⁺ onto t-MWCNT.

tial is independent of the temperature but varies according to the nature of sorbent and sorbate (Khan et al., 1995). The slope of the plot of $\ln C_{\text{ads}}$ versus ε^2 gives β (mol^2/J^2) and the intercept yields the sorption capacity, X_m (mol/g). The sorption space in the vicinity of a solid surface is characterized by a series of equipotential surfaces having the same sorption potential. The sorption energy can also be worked out using the following relationship:

$$E = 1/\sqrt{-2\beta}. \quad (10)$$

It is known that magnitude of apparent adsorption energy E is useful for estimating the type of adsorption and if this value is below 8 kJ/mol the adsorption type can be explained by physical adsorption, between 8 and 16 kJ/mol the adsorption type can be explained by ion exchange, and over 16 kJ/mol the adsorption type can be explained by a stronger chemical adsorption than ion exchange (Lin and Juang, 2002; Wang et al., 2004; Krishna et al., 2000).

The plot of $\ln C_{\text{ads}}$ against ε^2 for metal ion sorption on t-MWCNT is shown in Fig. 6(c). The Langmuir, Freundlich and DKR adsorption constants from the isotherms and their correlation coefficients are also presented in Table 2.

The correlation coefficients R^2 (0.997, 0.992 and 0.994 for Langmuir, Freundlich and DKR model, respectively) confirmed good agreement between both theoretical models and experimental results in the present study. The maximum sorption capacity, Q_0 , calculated from Langmuir equation was 12.34 mg/g, while Langmuir constant K was 0.19 L/mg. The values obtained for Cu^{2+} cations from the Freundlich model showed a maximum adsorption capacity (k_f) of 3.72 mg/g with an affinity value (n) equal to 3.09. The values of sorption constants, derived from DKR model were 32.77 mg/g (0.52 mmol/g) for X_m , $-3 \times 10^{-9} \text{ mol}^2/\text{J}^2$ for β and 12.91 kJ/mol for E .

The values indicated that the adsorption pattern for Cu^{2+} cations on t-MWCNT followed third, the DKR isotherm ($R^2 > 0.994$), the Freundlich isotherm ($R^2 > 0.992$) and the Langmuir isotherm ($R^2 > 0.997$) at all experimental conditions. It is clear that the Langmuir isotherm is best fitted for the sorption of Cu^{2+} cations on t-MWCNT. When the system is in a state of equilibrium, the distribution of Cu^{2+} cations between the t-MWCNT and the Cu^{2+} solution is of fundamental importance in determining the maximum sorption capacity of t-MWCNT for the copper ion from the isotherm. The E values are 12.91 kJ for Cu^{2+} cations on the t-MWCNT. It is the order of an ion-exchange mechanism, in which the sorption energy lies within 8–16 kJ/mol.

The values of the maximum adsorption capacities for the adsorption of Cu^{2+} cations on different adsorbents used in

Table 2 Langmuir, Freundlich and DKR constants for the adsorption of Cu^{2+} onto t-MWCNT.

Langmuir adsorption isotherm constants		
Q_0 (mg/g)	K (L/mg)	R^2
12.34	0.19	0.997
Freundlich adsorption isotherm constants		
k_f (mg/g)	n	R^2
3.72	3.09	0.992
DKR adsorption isotherm constants		
X_m (mg/g)	β (mol^2/J^2)	R^2
32.77	-3×10^{-9}	0.994

Table 3 Adsorption capacities for sorption of Cu^{2+} by various adsorbents.

Adsorbents	Adsorption capacity (mg/g)	Reference
Fly ash	8.10	Ayala et al. (1998)
Inactivated lichen	7.69	Ekmekyapar et al. (2006)
Green macroalga	5.57	Pavasant et al. (2006)
AC cloths: CS1501	15.30	Kadirvelu et al. (2000)
RS 1301	11.50	Kadirvelu et al. (2000)
Kaolinite	11.04	Yavuz et al. (2003)
Granular biomass	55.00	Hawari and Mulligan (2006)
Sugar beet pulp	21.16	Reddad et al. (2002)
t-MWCNT	12.34	Present work

the literature with the adsorbent of the present study are summarized in Table 3. Although direct comparison of the t-MWCNT with other adsorbent materials is difficult, owing to the differences in experimental conditions, it was found that the maximum adsorption capacity of t-MWCNT was higher than most adsorbents presented in Table 3.

It is commonly believed that the chemical interaction between the metal ions and the surface functional groups of CNT is the major sorption mechanism (Lu et al., 2006). Protons in the carboxylic and phenolic groups of CNT exchange with the metal ions in the aqueous phase. The solution pH dropped after sorption of metal ion onto CNT reached equilibrium, which could be explained by the release of H^+ from the CNT surface where metal ions are sorbed, consequently decreasing the solution's pH. The drop in pH value increased with a rise in initial metal ion concentration, which clearly indicates that sorption of more metal ion onto CNT causes the release of more H^+ ions from the surface site of CNTs into the solution. As shown in Fig. 7. When the initial Cu^{2+} cation concentration increased from 10 to 30 mg/L, the adsorption final pH after 120 min decreased from 6.5 to 5.2.

3.5. Sorption kinetics

Sorption kinetic studies were carried out in order to understand the behavior of t-MWCNT toward Cu^{2+} metal. The

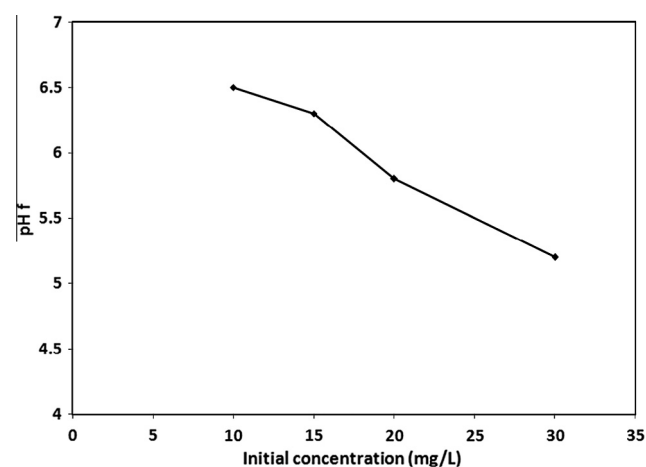


Figure 7 Effect of initial concentration on final pH of removal Cu^{2+} by t-MWCNT sorbents (initial pH 7, adsorbent dosage = 0.8 g/L, 700 rpm agitating rate).

sorption kinetics includes two phases: a rapid metal sorption stage followed by a much slower stage before the equilibrium was established. It was found that the mass transfer was the key factor in metal sorption (Chen and Wang, 2004). The sorption kinetics describes the metal sorption rate, which in turn governs the residence time of the sorption reaction and also the efficiency of the sorption process. Out of the several kinetic models available to examine the controlling mechanism of the sorption kinetic process and to test the experimental data, the Lagrangian equation or pseudo-first-order equation and

pseudo-second-order equation have been used for metal sorption kinetics of t-MWCNT.

The linearized form of pseudo-first-order equation:

$$\log(q_e - q) = \log q_{e \text{ cal}} - \frac{k_1}{2.303} t \quad (11)$$

where q_e is the metal sorbed at equilibrium (mg/g), q is the amount of the metal adsorbed (mg/g) at any time t , k_1 is the first-order rate constant. The first-order rate constants k_1

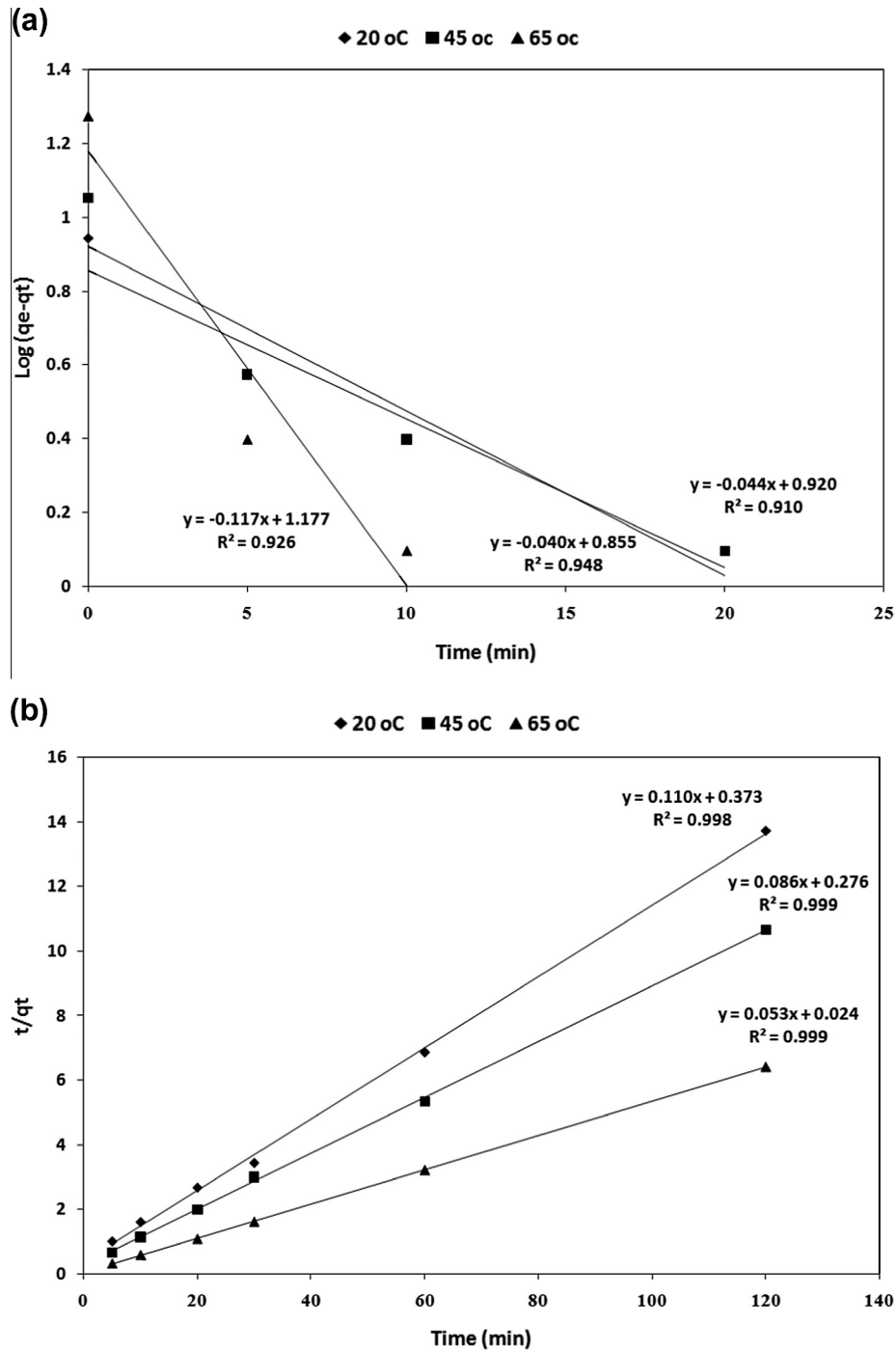


Figure 8 Linear fit of experimental data obtain using pseudo-first-order kinetic model (a) and pseudo-second-order kinetic model (b) (pH 7, initial metal concentration = 20 mg/L, adsorbent dosage = 0.8 g/L, 700 rpm agitating rate).

Table 4 A comparison of the first and second-order kinetic rate constants and calculated $q_{e \text{ cal}}$ values obtained at different temperatures (pH 7, initial metal concentration = 20 mg/L, adsorbent dosage = 0.8 g/L, 700 rpm agitating rate).

Temperature (°C)	k_1 (min ⁻¹)	$q_{e \text{ cal}}$ (mg/g)	R^2
<i>Pseudo-first-order kinetic model</i>			
20	0.092	7.161	0.948
45	0.101	8.317	0.910
65	0.269	15.031	0.926
<i>Pseudo-second-order kinetic model</i>			
	k_2 (min ⁻¹)	$q_{e \text{ cal}}$ (mg/g)	R^2
20	0.024	9.174	0.998
45	0.026	11.628	0.999
65	0.117	18.868	0.999

and q were determined from the slopes and intercept of plots of $\log(q_e - q)$ versus t at different metal concentration.

The linearized form of pseudo-second-order equation for the kinetics of absorption described by Ho and Chiang (2001) is as follows:

$$\frac{t}{qt} = \frac{1}{k_2 q_{e \text{ cal}}^2} + \frac{t}{q_{e \text{ cal}}} \quad (12)$$

The second-order rate constants (k_2) and $q_{e \text{ cal}}$ were determined from the slope and intercept of the plot obtained by plotting t/qt versus t .

Linear plots of $\log(q_e - q_i)$ versus t and t/qt versus t depicted in Fig. 8(a) and (b) at 20, 45 and 65 °C, respectively. A comparison of the results with the correlation coefficients is shown in Table 4. The pseudo-second-order kinetic model obtained for Cu²⁺ sorption at various temperatures showed better correlation of result than the pseudo-first-order equation model. The correlation coefficients for the second-order kinetic model obtained at 20 ppm concentrations at different temperatures were high. The values of k_2 at 20, 45 and 65 °C varied from 0.0240 to 0.1170 min⁻¹. Higher rate of metal sorption in the beginning (Fig. 5(a)) could be due to the presence of the active site in the t-MWCNT, available for the sorption of metals. Once the sorptive sites are exhausted, the uptake rate may be controlled by the rate of intra-particle diffusion. The activation energy E_a was determined using the Arrhenius equation (Aksu, 2002):

$$\ln k_{ad} = \ln A - \frac{E_a}{RT} \quad (13)$$

where $k_{ad}(k_2)$ is the rate constant value for the metal adsorption, E_a the activation energy in kJ/mol, T the temperature in Kelvin, and R is the gas constant (= 8.314 kJ/mol K). When $\ln k_{ad}$ is plotted versus $1/T$, a straight line with slope $-E_a/R$ is obtained. The activation energy for the adsorption system of Cu²⁺ onto t-MWCNT was found to be 27.187 kJ/mol from the slope of this plot, indicating physical adsorption. As known when the rate is controlled by intra-particle diffusion mechanism, the activation energy is low and hence it can be concluded that the process is controlled by intra-particle diffusion, which is a physical step in the adsorption process (Doğan and Alkan, 2003).

4. Conclusions

The present investigation showed that the t-MWCNT was an effective adsorbent for the removal of Cu²⁺ cations from aqueous solutions. The adsorption process was a function of the adsorbent dosage, initial Cu²⁺ cations concentration and temperature. The efficiency of Cu²⁺ cations adsorption increased with an increase in the adsorbent dosage. Isotherm studies indicated that the Langmuir model fitted the experimental data better than Freundlich and DKR models. The adsorption equilibrium was described well by the Langmuir isotherm model with maximum adsorption capacity of 12.34 mg/g of Cu²⁺ on t-MWCNT. Thermodynamic calculations showed that the copper sorption process of t-MWCNT had endothermic and spontaneous nature. The kinetic behavior of metal toward the t-MWCNT demonstrated pseudo-second-order kinetics rather than pseudo-first-order kinetics. The second-order kinetic model was successfully applied to the experimental data, confirming that adsorption was controlled by intra-particle diffusion.

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