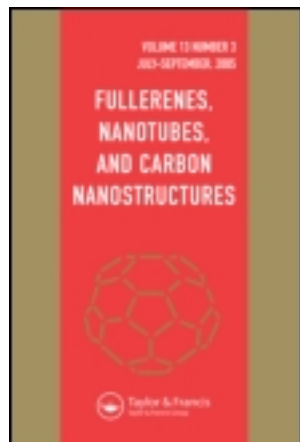




Fullerenes, Nanotubes and Carbon Nanostructures

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Adsorption of Pb(II), Cd(II) and Cu(II) Ions in Aqueous Solution on SWCNTs and SWCNT –COOH Surfaces: Kinetics Studies

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The studies of kinetics and thermodynamics of adsorption of Pb(II), Cd(II) and Cu(II) ions in aqueous solutions on single-walled carbon nanotube (SWCNTs) and carboxylate group functionalized single-walled carbon nanotube (SWCNT-COOH) surfaces were by atomic absorption spectroscopy. The adsorption kinetics was well described by a pseudo-second-order rate model, while Langmuir, Freundlich, Redlich-Peterson (R-P) and Tempkin isotherms described the adsorption isotherms, and the adsorption thermodynamic parameters of equilibrium constant (K_0), standard free energy (ΔG^0), standard enthalpy (ΔH^0) and standard entropy changes (ΔS^0) were measured. The adsorption of Pb(II), Cd(II) and Cu(II) ions from aqueous solutions on SWCNTs and SWCNT-COOH. The values of ΔH^0 and ΔG^0 suggested that the adsorption of mentioned ions on SWCNT-COOH and SWCNT were endothermic and spontaneous. The adsorption of mentioned ions on SWCNT-COOH is more than SWCNTs surfaces.

Keywords Kinetics study, thermodynamics parameters, adsorption, functionalized single-walled carbon nanotube, isotherms

Introduction

Carbon nanotubes (CNTs) have unique physicochemical and electrical properties and have widespread applications in field emission, hydrogen storage, and as chemical sensors (1). Due to their high surface area and large micropore volume, CNTs are also considered to be extremely good adsorbents and successfully remove many kinds of organic and inorganic pollutants such as pentachlorophenol (2), benzene, toluene, ethylbenzene and p-xylene (3), o-xylene and p-xylene (4) and heavy metal ions such as U(VI) (5), Cr(VI) (6), Zn(II) (7), Cu(II) (8), Pb(II) (9), Hg(II) (10) and Cd(II) (7,11) from water. Activation of CNTs plays an important role in enhancing maximum adsorption capacity. Activation causes modification in the morphology and functional groups surfaces and causes removal of amorphous carbon. CNTs activation under oxidizing conditions with chemicals such as HNO₃, KMnO₄, H₂O₂, NaOCl, H₂SO₄, KOH and NaOH have been widely reported (12–15). Such oxidation treatments are able to remove impurities and hemispherical caps,

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increasing the surface area and introducing oxygen-containing functional groups (16,17). In another study, oxidation with nitric acid increased the adsorption of heavy metal ions, such as cadmium, lead, nickel and zinc from aqueous solution (18), while decreasing the adsorption of o-xylene on single-walled carbon nanotubes (SWCNTs), suggesting that the adsorption of o-xylene and p-xylene on SWCNTs was mainly influenced by the positions of the methyl groups on xylene molecules and the presence of oxygen-containing groups on the surface of SWCNTs (16).

Heavy metals are major pollutants in marine, lake and ground waters as well as in industrial and even treated effluents. Heavy metals are also major hazards to the soil-plant system (19–22). Cadmium, lead and copper ions were chosen for this study due to their widespread use in industries and potential water pollution impact. Cadmium exposure may cause nausea, salivation, muscular cramps and anemia. Extended exposure to cadmium may also cause cancer (21). Lead poisoning is associated with gastrointestinal disorders, constipation, abdominal pain and central nervous system effects (22,23). Copper poisoning after ingestion may show systemic effects such as hemolysis, liver and kidney damage and fever with influenza syndrome. It has also been reported that locally irritation of the upper respiratory tract, gastrointestinal disturbance with omitting, and diarrhea and a form of contact dermatitis can take place (24). An understanding of adsorption equilibrium, kinetics and thermodynamics is critical in supplying the basic information required for the design and operation of adsorption equipment. Earlier studies have obtained only equilibrium and kinetics adsorption data and few works have measured and the thermodynamic parameters of adsorption on CNTs: Moradi et al. (25) examined the thermodynamics of the adsorption of Pb(II), Cd(II) and Cu(II) ions from aqueous solution on SWCNT-COOH and SWCNTs surfaces and Few investigations focused on the adsorption of organic pollutants on CNTs and simultaneously determined the equilibrium, kinetics and thermodynamic parameters (26–30). Hence, this study elucidates the equilibrium, kinetics and thermodynamics of the adsorption of Pb(II), Cd(II) and Cu(II) ions from aqueous solutions on SWCNT-COOH and SWCNTs surfaces. The Langmuir, Freundlich and Tempkin isotherms were used to fit the equilibrium data. The effects of temperature on the dynamic behaviors of adsorption were determined. The adsorption rates were determined quantitatively and those obtained using the pseudo first- and second-order models and the intraparticle diffusion model was also compared.

The objectives of this study were: (i) to determine the appropriate SWCNTs and SWCNT-COOH dosage to adsorb Pb(II), Cd(II) and Cu(II) ions; (ii) to measure the coefficients of Langmuir, Freundlich, Redlich-Peterson (R-P) and Tempkin isotherms; (iii) to evaluate the adsorption rate using various kinetic models; and (iv) to derive the thermodynamic parameters activation energy (E_a), and the changes in free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) during adsorption.

Experimental

Materials

$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (molecular weight, 241.60 g/mol), $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (molecular weight, 308.48 g/mol) and $\text{Pb}(\text{NO}_3)_2$ (molecular weight, 331.20 g/mol) were supplied by Merck, Germany (maximum purity available). All solutions were prepared with deviations of less than $\pm 0.1\%$ from the desired concentrations.

SWCNTs (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, $\sim 400 \text{ m}^2/\text{g}$; and

manufacturing method, catalytic chemical vapor deposition (CVD)) and SWCNT-COOH (content of COOH, 6 wt%; with purity > 95%; average diameter 1–2 nm; length 5–30 nm and SSA $\sim 400 \text{ m}^2/\text{g}$) were purchased from NanoAmor Nanostructured & Amorphous Materials, Inc. (USA). Doubly distilled water was used and all adsorbents were washed before using.

Analytical Measurement

All experiments were conducted in a closed 250 ml pyramid glass bottle, and HCl or NaOH 0.1 M (provided by Merck Company with maximum purity) was used to adjust the pH of solution. The 250 ml pyramid glass bottle contains 100 ml of $\text{Pb}(\text{NO}_3)_2$, $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ solutions, were further diluted with fresh doubly distilled deionized water to the required ions concentration and shaken at 250 rpm (from HZQ-C company). To determine adsorbents dosage (the mentioned ion solutions with the initial concentration (C_i) ranging from 10 to 50 mg/L) was equilibrated with a suspension of SWCNT-COOH and SWCNTs surfaces as adsorbent (25, 50, 75 and 100 mg/L) at pH 5 for certain time. In the experiments on the effect of temperature (C_i for each of ion solution 10 mg/L and adsorbents 50 mg/L), the temperature was held 283, 293, 303 and 313K and the pH was fixed at 5. At the end of the equilibrium period, the suspensions were centrifuged at 3500 rpm for 10 minutes, and the supernatant was then filtered through $0.2 \mu\text{m}$ filter paper (Gelman Sciences) for later analysis of the using atomic absorption spectrophotometry (AAS) (Perkin-Elmer Analyst 700). The difference between the initial and the equilibrium ion concentration determines the amount of ion adsorbed on SWCNT-COOH and SWCNTs surfaces. Each experiment was performed twice and experimental results are average values. Adsorption thermodynamic experiments were conducted using 100 mL pyramid glass bottle containing 50 mg of the adsorbents, SWCNT-COOH and SWCNTs surfaces, and 100 mL of the mentioned ion solutions with the initial concentration ranging from 10 to 50 mg/L at pH = 5. As shown previously, the adsorption of ion on the bottle wall is ignorable (30,31).

Batch Mode Adsorption Studies

The effect of experimental parameters, such as the nature of metal ions, initial concentration (10–50 mg/L), pH (2–8) and temperature (283, 293, 303 and 303 K), on the extent of adsorption various ion was studied in a batch mode of operation for the specific period of contact times (0–180 minutes). To determine the effect of each parameter, the other parameters were fixed. For contact time studies, 100 mL of each ion solution of known initial concentration and certain pH was taken with a fixed quantity of adsorbent (50 mg/L) and agitated in a thermostated rotary shaker min with the speed of 250 rpm at 293K. Ultrasonic Bath (71020-DTH-E; Model 1510 DTH, 220V; EMS Company) was used to perverted the particles to aggregate and forming bulk. At various intervals, the adsorbents were separated from the samples by filtering and the filtrates were analyzed using AAS, and the concentration of each ion was determined as previously. Quality assurance of the analytical measurements was performed. Pb(II), Cd(II) and Cu(II) standard solutions of 1000mg/L $\pm 0.1\%$ were used for the measured. Calibration curves between 1 and 50mg/L were prepared and the detection limit was found to be 1mg/L. The adsorption percentage of each metal ion was calculated as follows:

$$\text{Adsorption (\%)} = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

where, C_i and C_f are the initial and final metal ion concentration (after contact to adsorbents), respectively. The concentration retained in the adsorbent phase (q_e , mg/g) was calculated by using the following equation:

$$q_e = \frac{(C_i - C_t)V}{W} \quad (2)$$

where C_i is the initial metal ion concentration and C_t is the metal ions concentration (mg/L) at any time, V is the volume of solution (L) and W is the mass of the adsorbents (g). The data analysis was carried out using correlation analysis employing least-square method and the average relative error (ARE) is calculated using the following equation:

$$\text{ARE(\%)} = \frac{100}{n} \sum_i^n \left| \frac{q_{i,\text{cal}} - q_{i,\text{exp}}}{q_{i,\text{exp}}} \right| \quad (3)$$

where N is the number of data points. Each experiment was conducted in triplicate under identical conditions to confirm the results, and was found reproducible (experimental error within 3%).

Results and Discussion

Effect of Contact Time and Initial Concentration

Figure 1 displays the surface morphology of SWCNT-COOH and SWCNTs surfaces. The TEM images show that the SWCNT-COOH and SWCNTs surfaces were cylindrical and that the range of main external and internal diameters was 30–80 and 5–10 nm, respectively. In addition, the distance between the wall and wall of SWCNT-COOH and SWCNTs was approximately 1.5–0.5 nm, and the TEM analysis confirmed the hollow structure of CNTs. The specific surface area of the SWCNT-COOH and SWCNTs used in this study was 400 m²/g. The pH of the zero point of charge (pH_{zpc}) for those was determined to be 4.9, which was the same as that measured by Kuo and et al. (31). This result indicated that the surface of this surfaces adsorbent (SWCNT-COOH and SWCNTs) was positively charged at a solution pH of <4.9. The element characterizing of SWCNT-COOH and SWCNTs surfaces showed the content of C, O and Ni was 90.6, 8.1 and 1.3%, respectively. Since these surfaces adsorbents were generated by the pyrolysis of methane gas on particles of Ni by chemical vapor deposition, the major element was carbon, with only a few Ni atoms present.

SWCNT-COOH and SWCNTs surfaces were treated by each of Pb(II), Cd(II) and Cu(II) ion individual solutions (10 mg/L; pH = 5 and T = 293±1K) in order to optimize contact time respect to each ion. The amounts of each adsorbed ion on the adsorbents were analyzed using AAS. Figure 2 show the percentage of adsorbed ion on SWCNT-COOH and SWCNTs surfaces, as a function of contact time. It can be seen that the amount of each ion adsorbed on SWCNT-COOH is more than that on SWCNTs and has the priority in comparison with SWCNTs surface.

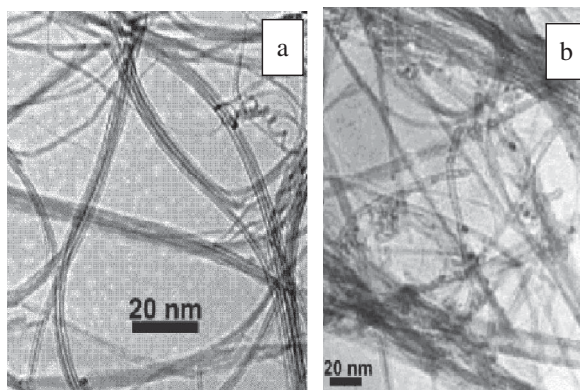


Figure 1. Micrographs of (a) TEM SWCNT-COOH and (b) SWCNTs surfaces.

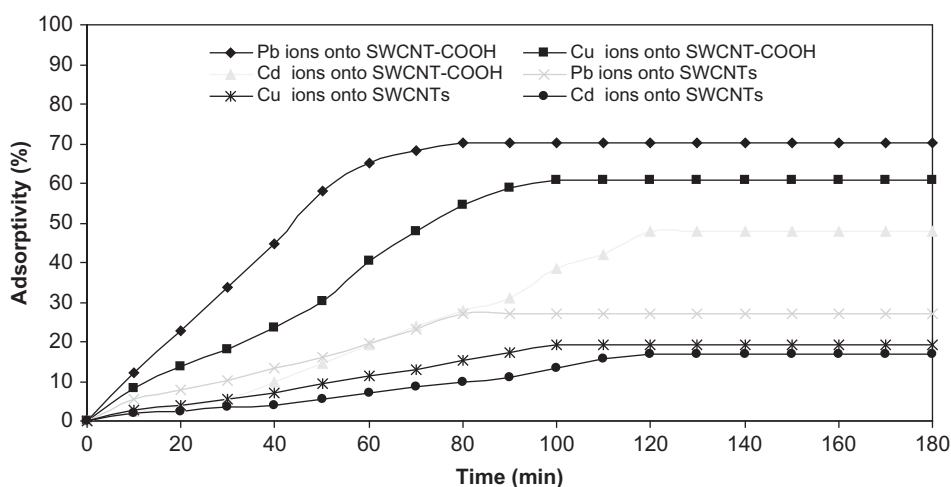


Figure 2. Effect of contact time on the percentage of ion adsorption onto SWCNT-COOH and SWCNTs surfaces, initial concentration, 10 mg/L; pH 5; adsorbent dosage, 50 mg/L; contact time, 0–180 min and $T = 293 \pm 1\text{K}$.

The adsorption affinity order of three ions on both SWCNT-COOH and SWCNTs surfaces are as $Pb(II) > Cu(II) > Cd(II)$ under the experimental conditions. It is due to the higher charge surface of $Pb(II)$ ion than $Cu(II)$ and $Cd(II)$ ions. The charge density is described by as follow (32):

$$d_c = \frac{3Q}{4\pi r^3} \quad (4)$$

where d_c is the charge density of cation, Q and r represent the charge of cation expressed in coulombs and the radius of the cation, respectively (hydrate cation radius of $Pb(II)$, $Cu(II)$ and $Cd(II)$ ions is 0.401, 0.419 and 0.423 nm, respectively (33)). Since the cations were of the same valance (+2) in our study, the order of charge density was determined by the cation size. It has been well established that water is attracted to the positively charged

cations due to its dipolar nature and the attracted water molecules create a shell around the cation where the hydrated cation forms. Thus the charge density for Pb(II) is more than Cu(II) and Cd(II) ions, leading to increase in the percentage of ion adsorption on both adsorbent surfaces. Another reason for higher adsorption of ions on SWCNT-COOH is the existence of functional group (COOH) on this adsorbent. This functional group causes a rise in the negative charge on the carbon surface. The oxygen atoms in the functional groups donate single pair of electron to metal ions and consequently increase their cation exchange capacity (34). It can be related to also that carboxylic group on SWCNT-COOH can form a complex with the metal ion, leading to increase in the amount of ion adsorption (35,36).

Compared with other commercially available adsorbent, such as activated carbon, SWCNTs and SWCNT-COOH surface showed better adsorption properties including short equilibrium time, large adsorption capacity and easy regeneration (37). Numerous investigations have also demonstrated that the zeta potential of SWCNT-COOH is more negative than that of SWCNTs (38–40). Also, the charge surface SWCNT-COOH is negative and SWCNTs have a charge surface of about zero at the pH of the experiments (36). The negative charge surface of SWCNT-COOH electrostatically favors the adsorption of ions more than in SWCNTs. The adsorption of ions increases with the increasing of contact time. When the initial concentration of Pb(II) ion was 10 mg/L, the adsorption on SWCNT-COOH surface mainly occurs within 80 min. But for the other ions, the equilibrium time was 100–120 min. Therefore, 120 min was selected as the equilibrium time for both adsorbents in all experiments. From 120–180 min, the concentration of three ions of (Pb(II), Cd(II) and Cu(II)) remained unchanged with time. Figure 3 shows the amount of adsorbed ions as a function of the initial concentration of each ion from aqueous solutions. At this part of experiment, the following concentrations were chosen for each ion: 10, 20, 30, 40 and 50 mg/L at pH = 5, equilibrium time, 120 min and $T = 293 \pm 1$ K. With increasing ion concentration, the percentage of ion adsorption increased.

Also, more metal ions were left unabsorbed in the solution due to saturation of the binding sites. This indicates that energetically less favorable sites became involved with the increasing of ion concentration in the aqueous solution (38).

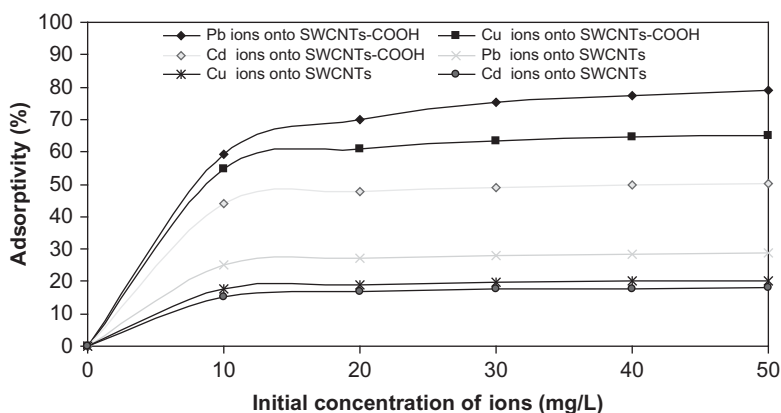


Figure 3. Effect of initial concentration of ions on the percentage of adsorption onto SWCNT-COOH and SWCNTs surfaces. Initial concentration of the ions was 10, 20, 30, 40 and 50 mg/L; pH 5; adsorbents dosage 50 mg/L; contact time, 120 min and $T = 293 \pm 1$ K.

Metal ion adsorption is attributed to different mechanism of ion exchange as well as to the adsorption. This effect on ion adsorption can be explained, as at low metal ion/adsorbent ratios, metal ion adsorption involves more energy sites. As metal ion/adsorbent ratio increases, more energy sites are saturated and adsorption begins on fewer energy sites, resulting in low increasing of metal ion adsorption (38). About 78.83% of Pb(II) was adsorbed on SWCNT-COOH surface after 120 minutes for the initial Pb(II) concentration was 5.0 mg/L. About 65.21% and 50.31% of Cu(II) and Cd(II) ions were adsorbed under the same conditions (time and concentration), respectively. Similar results have been obtained by several earlier works on ion adsorption on CNTs (36,39).

Effect of pH of Solution

The pH of the solution affects the surface charge of the adsorbents as well as the degree of ionization of different pollutants. The hydrogen ion and hydroxyl ions are adsorbed quite strongly and therefore the adsorption of other ions is affected by the pH of the solution. Change of pH affects the adsorptive process through dissociation of functional groups on the adsorbent surface active sites. This subsequently leads to a shift in reaction kinetics and equilibrium characteristics of adsorption. The adsorption percentage of Pb(II), Cd(II) and Cu(II) ions on SWCNT-COOH and SWCNTs surfaces was studied at pH range 2–8 at 293 K for 120 minutes. Initial ion concentration was 10 mg/L and adsorbents dose was kept 50 mg/L. Figure 4 shows that the effect of pH on the adsorption of Pb(II), Cd(II) and Cu(II) ions on SWCNT-COOH and SWCNTs surfaces.

In this study, sodium phosphate (0.1 mol/L), ammonium acetate (0.1 mol/L) and ammonium chloride (0.1 mol/L) were used for the adjustment of solutions pH. The percentage adsorption of each ion was a maximum at acidic pH (pH 5–6) and increased with further increases in pH. In the aqueous solution, the metals salt was first dissolved and the molecules dissociated and converted to metal cation ions. Although a maximum uptake was noted at pH 8, as the pH increased to >7 the metal ion started to precipitate. Therefore, no experiment was conducted at $\text{pH} \geq 7$. The increasing in adsorption capacity at $\text{pH} > 7$ could be due both to the adsorption of ions on the surface of adsorbent and precipitation.

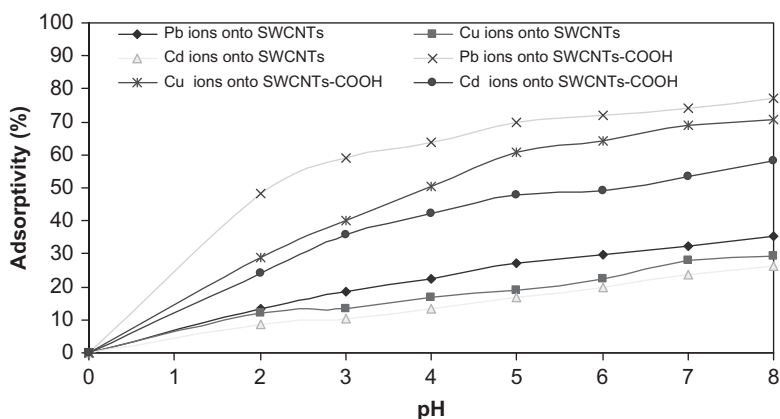


Figure 4. Effect of pH on the adsorption removal of Pb(II), Cd(II) and Cu(II) ions onto SWCNT-COOH and SWCNTs surfaces, Initial concentration of each ion, 10 mg/L; adsorbents dosage 50 mg/L and contact time, 120 minutes.

It is considered that SWCNT-COOH and SWCNTs surfaces have a maximum adsorption capacity at pH = 5, if the precipitated amount is not considered. Therefore, the optimal pH was found to be 5 for Pb(II), Cd(II) and Cu(II) ions at adsorption. The metal ion in aqueous solution may undergo solvation and hydrolysis (41). Some researcher indicated with increase in pH, adsorption decreased probably due to the formation of lead, copper and cadmium hydroxides and chemical precipitation (25, 42–44).

Effect of Adsorbents Dosage

Figure 5 presents the effect of SWCNT-COOH and SWCNTs surfaces dosage on the adsorption of Pb(II), Cd(II) and Cu(II) ions. The amount adsorbed increased with the dose of adsorbents (SWCNT-COOH and SWCNTs surfaces); however, the equilibrium adsorption capacity (45) initially increased and then dropped as the adsorbents dosage increased. In dilute adsorbents suspensions (< 50 mg/L), surfaces are suggested to be

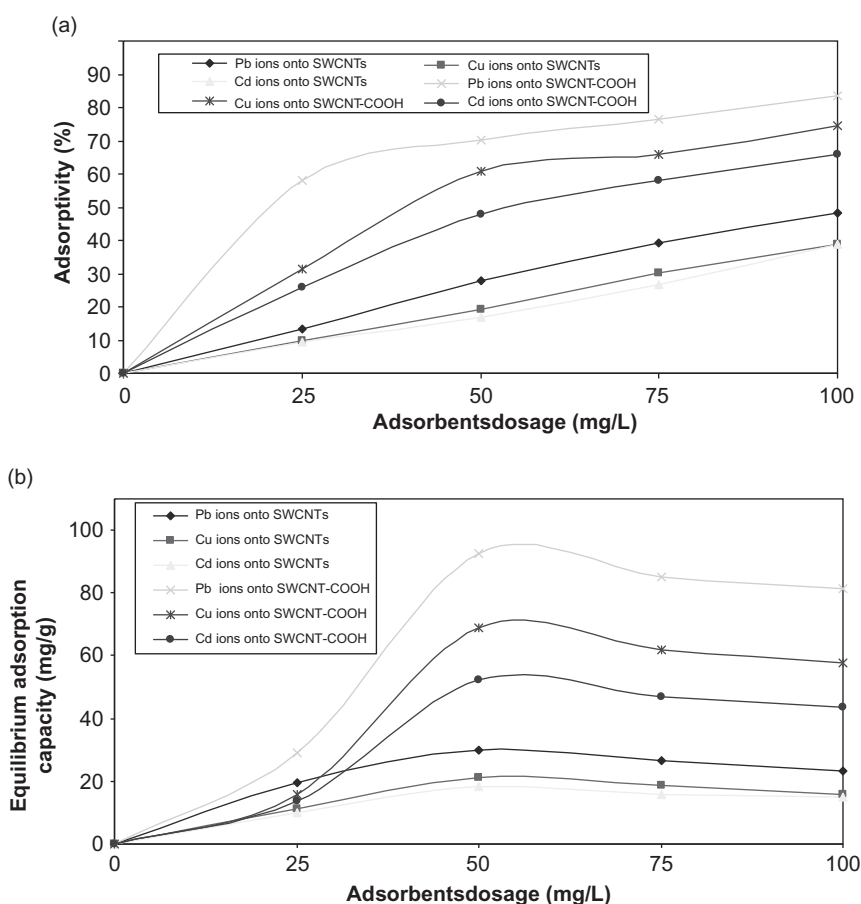


Figure 5. Effect of SWCNT-COOH and SWCNTs surfaces dosage on the (a) adsorption and the (b) equilibrium adsorption capacity of Pb(II), Cd(II) and Cu(II) ions, Initial concentration of the ions was 10mg/L; pH 5; adsorbents dosage 25, 50, 75 and 100 mg/L; contact time, 120 minutes and $T = 293 \pm 1K$.

separated and dispersed. In this case, the adsorption capacity at the external surface predominated, and for this reason the equilibrium adsorption capacity of surfaces would be high. Increasing the adsorbents dose (>50 mg/L) increases the probability of the SWCNT-COOH and SWCNTs surfaces' entanglement in the solution, causing adsorption in the interlayer space and a decrease in the aggregation of ions at the external surface.

Accordingly, the adsorption capacity declined as the SWCNT-COOH and SWCNTs surfaces dosage increased above 50 mg/L. Moreover, the high SWCNT-COOH and SWCNTs surfaces dosage may influence the physical characteristics of the solid-liquid suspensions, such as by increasing the viscosity and inhibiting the diffusion of cation ions to the surface of the adsorbents. Since the concentration of SWCNT-COOH and SWCNTs surfaces was fixed, the equilibrium adsorption capacity decreased as the SWCNT-COOH and SWCNTs surfaces dosage increased (>50 mg/L). The increase with SWCNT-COOH and SWCNTs surfaces dosage of the amount of ions adsorbed (Pb(II), Cd(II) and Cu(II)) was caused by the availability of more surface area of the SWCNT-COOH and SWCNTs surfaces. Direct evidence of SWCNT-COOH and SWCNTs surface entanglement was unclear and unobtainable. However, similar observations could be found in the literature. Bhattacharyya and Sharma (45), who utilized Neem leaf powder to adsorb dyes, suggested that the amount adsorbed (mg/g) decreased as the amount of the adsorbent increased. Since the equilibrium adsorption capacity was greatest when 50 mg/L SWCNT-COOH and SWCNTs surfaces were added, this dosage (50 mg/L) was used in the following experiments.

Effect of Temperature

The temperature at which an adsorption process is carried out will influence both the adsorption rate and the degree to which adsorption takes place. The adsorption capacity of Pb(II) and Zn(II) ions remarkably increased with a rise in temperature (46,47), indicating an endothermic reaction. The time required to uptake 50% of the maximum Zn(II) adsorption capacity would be reached faster at a higher temperature.

Figure 6 shows adsorption percentage of Pb(II), Cd(II) and Cu(II) ions on as a function of temperature. The percentage of adsorption experiment were conducted at 283, 293, 303 and 313 K to investigate the effect of temperature, with the initial concentration of 10 mg/L for each ion, adsorbent dosage of 50 mg/L and pH = 5.

It was observed that the maximum adsorption percentage for each ion increased. As Figure 6 shows, the ion adsorption yield on adsorbent surfaces increases with increasing temperature. When the temperature increased from 283 to 313K, percentage of adsorption for Pb(II), Cd(II) and Cu(II) ions increased from 65.23, 54.90 and 42.25 to 80.04, 69.89 and 53.26 on SWCNTs-COOH, respectively, and from 23.79, 17.89 and 16.01 to 31.25, 23.37 and 21.37, respectively, on SWCNTs. An increase in the amount of equilibrium adsorption of each ion with the rise in temperature may be explained by fact that the adsorbent sites were more active at higher temperatures. Also, the kinetic energy of cations increases at higher temperatures; therefore, the contact between each ion and the active site of adsorbent is sufficient, leading to an increase in adsorption efficiency. This condition show that adsorption occurs more physically rather than chemically. Similar trends have been observed by other researchers for aqueous phase adsorption (48). In addition, the rise of adsorption with temperature may enlarge the pore size of carbon nanotube to some extent, which may also affect carbon adsorption capacity (48).

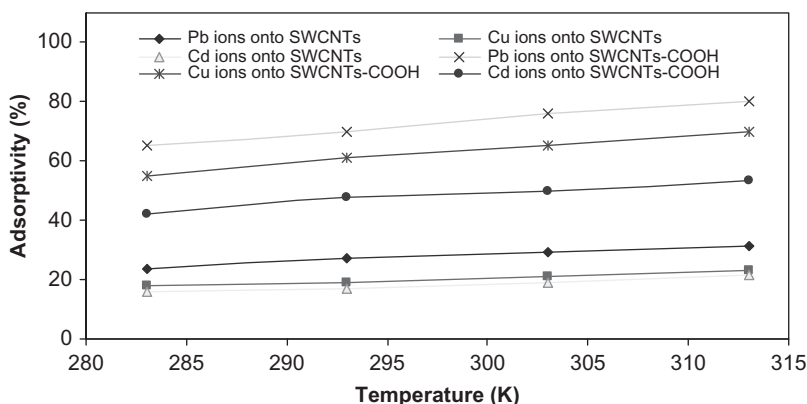


Figure 6. Effect of temperature on the percentage of ion adsorption, initial concentration of each ion was 10mg/L; pH 5; contact time, 120 minutes, and adsorbent dosage 50 mg/L.

Adsorption Isotherms Study

To optimize the design of an adsorption system for the adsorption, it is important to establish the most appropriate correlation for the equilibrium curves. Various isotherm equations have been used to describe the equilibrium nature of adsorption. Some of these isotherms are Freundlich, Langmuir, Redliche- Peterson (R-P) and Tempkin.

Freundlich and Langmuir isotherms. Freundlich (49–51) studied the adsorption of a material on animal charcoal and demonstrated that the ratio of the amount of solute adsorbed on a given mass of adsorbent to the concentration of the solute in the solution was not a constant at different solution concentrations. The Freundlich isotherm is derived by assuming a heterogeneous surface with a nonuniform distribution of heat of adsorption over the surface. Langmuir (52,53) proposed a theory to describe the adsorption of gas molecules on metal surfaces. The Langmuir adsorption isotherm has been successfully applied to many other real adsorption processes and has been used to explain the adsorption of ions on various adsorbents. A basic assumption of the Langmuir theory is that adsorption takes place at specific homogeneous sites within the adsorbent. It is then assumed that once a dye molecule occupies a site, no further adsorption can take place at that site. Theoretically, a saturation value is reached beyond which no further sorption can take place. The linearised Freundlich and Langmuir isotherms are represented by the following equations:

$$\text{Freundlich isotherm } \ln q_e = \ln K_F + 1/n \ln C_e \quad (5)$$

$$\text{Langmuir isotherm } \frac{C_e}{q_e} = \frac{1}{K_d q_m} + \frac{1}{q_m} C_e \quad (6)$$

where K_F is Freundlich constant (l/mg), $1/n$ is the heterogeneity factor, K_L is the Langmuir adsorption constant (l/mg) related to energy of adsorption and q_m signifies adsorption capacity (mg/g). Table 1 summarizes the coefficients of Langmuir and Freundlich isotherms for different temperature and adsorbents. Figure 7 shows the adsorption isotherms of Pb(II), Cu(II) and Cd(II) ions on SWCNT-COOH and SWCNTs surfaces

Table 1

Coefficients of the Langmuir and Freundlich isotherms for Pb(II), Cu(II) and Cd(II) ions percentage of adsorption onto SWCNT-COOH and SWCNTs surfaces (Initial concentration of each ion was 10, 20, 30, 40 and 50 mg/L; pH 5; adsorbents dosage, 50 mg/L; contact time 120 min and $T = 293 \pm 1\text{K}$)

T (K)	Langmuir K_d (L/mg)	q_m	R^2	Freundlich K_F	n	R^2
Pb(II)						
SWCNTs-COOH						
283	1.100	90.235	0.9992	52.259	3.887	0.9901
293	1.4560	92.593	0.9992	57.106	4.106	0.9909
303	1.516	94.689	0.9991	62.338	4.322	0.9903
313	1.633	96.017	0.9993	67.004	4.522	0.9900
SWCNTs						
283	0.631	27.112	0.9990	18.889	9.211	0.9910
293	0.691	29.851	0.9993	20.615	9.901	0.9919
303	0.722	31.235	0.9991	22.332	10.112	0.9955
313	0.759	33.545	0.9991	26.666	13.001	0.9971
Cu(II)						
SWCNTs-COOH						
283	1.006	65.125	0.9990	43.336	6.332	0.9955
293	1.028	68.966	0.9990	46.651	7.9745	0.9937
303	1.060	72.326	0.9991	50.002	8.998	0.9913
313	1.089	77.002	0.9991	52.989	10.003	0.9914
SWCNTs						
283	0.611	19.887	0.9991	12.112	9.321	0.9901
293	0.638	21.008	0.9990	14.281	9.862	0.9905
303	0.668	22.871	0.9991	17.026	10.312	0.9901
313	0.689	24.288	0.9991	20.110	10.787	0.9907
Cd(II)						
SWCNTs-COOH						
283	0.988	50.233	0.9991	33.448	10.011	0.9901
293	1.002	52.356	0.9991	37.856	10.593	0.9883
303	1.223	55.337	0.9990	42.559	11.026	0.9889
313	1.502	58.890	0.9990	48.998	11.089	0.9900
SWCNTs						
283	0.352	16.126	0.9992	12.551	9.765	0.9910
293	0.544	18.868	0.9992	13.130	11.074	0.9939
303	0.770	21.226	0.9991	14.056	13.337	0.9922
313	0.913	24.065	0.9990	16.012	17.055	0.9907

at pH = 5. The initial concentrations of each ion were 10, 20, 30, 40 and 50 mg/L and $T = 293 \pm 1\text{K}$.

A comparison of the R^2 values given in Table 1 indicates that Langmuir isotherm better fits the experimental data than does the Freundlich isotherm. The validity of Langmuir isotherm suggests that adsorption is a monolayer process, and adsorption of all species requires equal activation energy. As Table 1 shows, K_d increases with increasing of

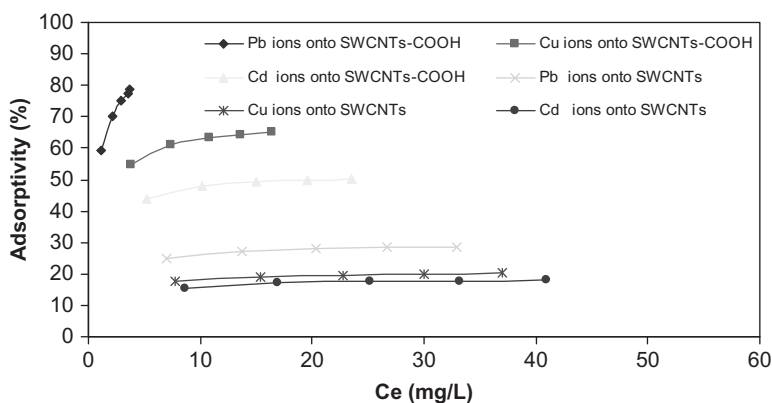


Figure 7. The percentage of adsorption isotherm of Pb(II), Cu(II) and Cd ions onto SWCNT-COOH and SWCNTs surfaces. Initial concentration of each ion was 10, 20, 30, 40 and 50 mg/L; pH 5; contact time, 120 minutes and adsorbent dosage 50 mg/L.

temperature, indicating that adsorption of ions on SWCNT-COOH and SWCNTs surfaces increases with temperature. The results also implied that the affinity of the binding sites increased with temperature. Moreover, K_d values for various adsorbents followed the order SWCNTs-COOH > SWCNTs, suggesting that the affinity of the binding sites for each ion also followed this order.

Freundlich isotherm does not describe the saturation behavior of adsorbents. Regarding the coefficients of Freundlich isotherm, K_F increased with temperature, revealing that adsorption capacity increased with temperature. Like K_F , n increased with temperature as well. Since all n values obtained from the isotherms exceeded unity, the ions were favorably adsorbed on SWCNT-COOH and SWCNTs surfaces. The highest values of n were 4.522, 10.003 and 11.089 at 313K for Pb(II), Cu(II) and Cd(II) ions on SWCNT-COOH and 13.001, 10.788 and 17.055 on SWCNTs, respectively. These data indicate favorable adsorption at high temperatures. Also, the amount of $1/n$ less than 1 show the favourable nature of adsorption of Pb(II), Cu(II) and Cd(II) ions on SWCNT-COOH and SWCNTs surfaces. Similar results have been reported by several earlier works for Freundlich constant for ion adsorption on carbon nanotube adsorbent surfaces (52,53).

The maximum adsorption capacities for monolayer saturation at 313 K were 96.017, 77.002 and 58.889 mg per gram of SWCNTs -COOH surface and 33.548, 24.288 and 24.065 mg for Pb(II), Cu(II) and Cd(II) ions per gram of SWCNTs surface, respectively. Higher temperatures lead to a higher chance for the ion to be adsorbed on the adsorbents and an increase in their adsorption capacity, resulting in enlargement of the pore size. Also, some researchers indicated that by increasing the temperature, the carbon nanotube stability and total surface area are increased. It is suggested that the formation of nanoporous structure on the surface of CNTs may be related to appropriate potassium intercalation at a reasonable temperature (54).

Both Langmuir and Freundlich isotherms suggest that adsorption were endothermic. Although Freundlich isotherm provides information about surface heterogeneity and exponential distribution of active sites and their energies, it does not predict any saturation of the surface of adsorbents by the adsorbate (54).

Redlich-Peterson (R-P) isotherm. Redlich and Peterson (55) incorporate three parameters into an empirical isotherm. The Redliche Peterson isotherm has a linear dependence

on concentration in the numerator and an exponential function in the denominator. It approaches the Freundlich isotherm at high concentration and is in accordance with the low concentration limit of the Langmuir equation. Furthermore, the R-P equation incorporates three parameters into an empirical isotherm and, therefore, can be applied either in homogenous or heterogeneous systems due to the high versatility of the equation. It can be described as follows:

$$q_e = \frac{K_R C_e}{1 + a_R C_e^\beta} \quad (7)$$

where K_R is R-P isotherm constant (L/g), a_R is R-P isotherm constant (1/mg) and β is the exponent which lies between 1 and 0, where $\beta = 1$.

$$q_e = \frac{K_R C_e}{1 + a_R C_e} \quad (8)$$

It becomes a Langmuir equation. Where $\beta = 0$

$$q_e = \frac{K_R C_e}{1 + a_R} \quad (9)$$

That is, the Henry's Law equation. Equation (7) can be converting to a linear form by taking logarithms:

$$\ln(K_R \frac{C_e}{q_e} - 1) = \ln a_R + \beta \ln C_e \quad (10)$$

Plotting the left-hand side of equation (10) against $\ln C_e$ to obtain the isotherm constants is not applicable because of the three unknowns, a_R , K_R and β . Therefore, a minimization procedure is adopted to solve equation (10) by maximizing the correlation coefficient between the theoretical data for q_e predicted from equation (10) and experimental data. Therefore, the parameters of the equations were determined by minimizing the distance between the experimental data points and the theoretical model predictions with the solver add-in function of Microsoft Excel. The R-P isotherm constants a_R , K_R and b and the correlation coefficients R^2 for the R-P isotherm at 293 K are listed in Table 2. The correlation coefficients are significantly higher than the Langmuir isotherm R^2 values for Pb(II), Cu(II) and Cd(II) ions adsorption on both adsorbents. However, in comparison with R^2 values for Freundlich isotherm fit, Redliche-Peterson isotherm shows better fit for SWCNT-COOH adsorption.

Tempkin isotherm. Tempkin isotherm contains a factor that explicitly takes into account interactions between adsorbing species and adsorbate. This isotherm assumes that (i) the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbate interactions, and (ii) adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy (56). Tempkin isotherm is represented by following equation:

$$q_e = \frac{RT}{b} \ln(K_T C_e) \quad (11)$$

Equation (11) can be expressed in its linear form as:

$$q_e = B_1 \ln K_T + B_1 \ln C_e \quad (12)$$

where

$$B_1 = \frac{RT}{b} \quad (13)$$

The adsorption data can be analyzed according to equation (12). A plot of q_e versus $\ln C_e$ enables the determination of the isotherm constants K_T and B_1 . K_T is the equilibrium binding constant (l/mol) corresponding to the maximum binding energy, and constant B_1 is related to the heat of adsorption. This isotherm is plotted and values of the parameters are given in Table 2. Analysis of R^2 values from Table 2 shows that the Langmuir equation is found to best represent the equilibrium data for adsorption of Pb(II), Cu(II) and Cd(II) ions on both adsorbents.

Kinetics Study

The kinetic adsorption process of Pb(II) and Zn(II) ions on SWCNT-COOH and SWCNTs surfaces could be well described by the pseudo-second-order rate law and the rate constants increased with a rise in temperature (46,47). This could be explained by the fact that increasing temperature results in a rise in diffusion rate of metal ions across the external boundary layer and within the pores of SWCNT-COOH and SWCNTs surfaces due to the result of decreasing solution viscosity. The kinetic analysis of temperature effect was evaluated at pH 5 (Figures 8a and b). The adsorption increased with temperature, indicating that the mobility of metal ion molecules (Pb(II), Cu(II) and Cd(II)) increased with temperature, as did the number of molecules that interact with the active sites at SWCNT-COOH and SWCNTs surfaces; moreover, the adsorption was endothermic. In addition, increasing the temperature reduces the viscosity of the solution and increases the rate of diffusion of metal ion molecules. The adsorption is initially (contact time <60 min) rapid and then

Table 2

R-P and Tempkin isotherms parameters for adsorption of Pb(II), Cu(II) and Cd(II) ions of onto SWCNT-COOH and SWCNTs surfaces (Initial concentration of each ion was 10, 20, 30, 40 and 50 mg/L; pH 5; adsorbents dosage, 50 mg/L; contact time 120 min and $T = 293 \pm 1K$)

Isotherm constants	SWCNT-COOH			SWCNTs		
	Pb(II)	Cu(II)	Cd(II)	Pb(II)	Cu(II)	Cd(II)
Redlich-Peterson						
K_R (l/mg)	369.8	333.7	287.5	122.8	100.8	87.6
a_R	145.1	121.6	108.5	32.9	65.5	43.4
β	0.655	0.541	0.332	0.232	0.121	0.089
R^2	0.9990	0.9990	0.9989	0.9990	0.9989	0.9989
Tempkin						
K_T (l/mg)	15.76	13.33	10.11	10.11	9.54	7.89
B_1	4.455	2.786	1.033	2.232	1.877	1.132
R^2	0.9977	0.9957	0.9907	0.9978	0.9963	0.9901

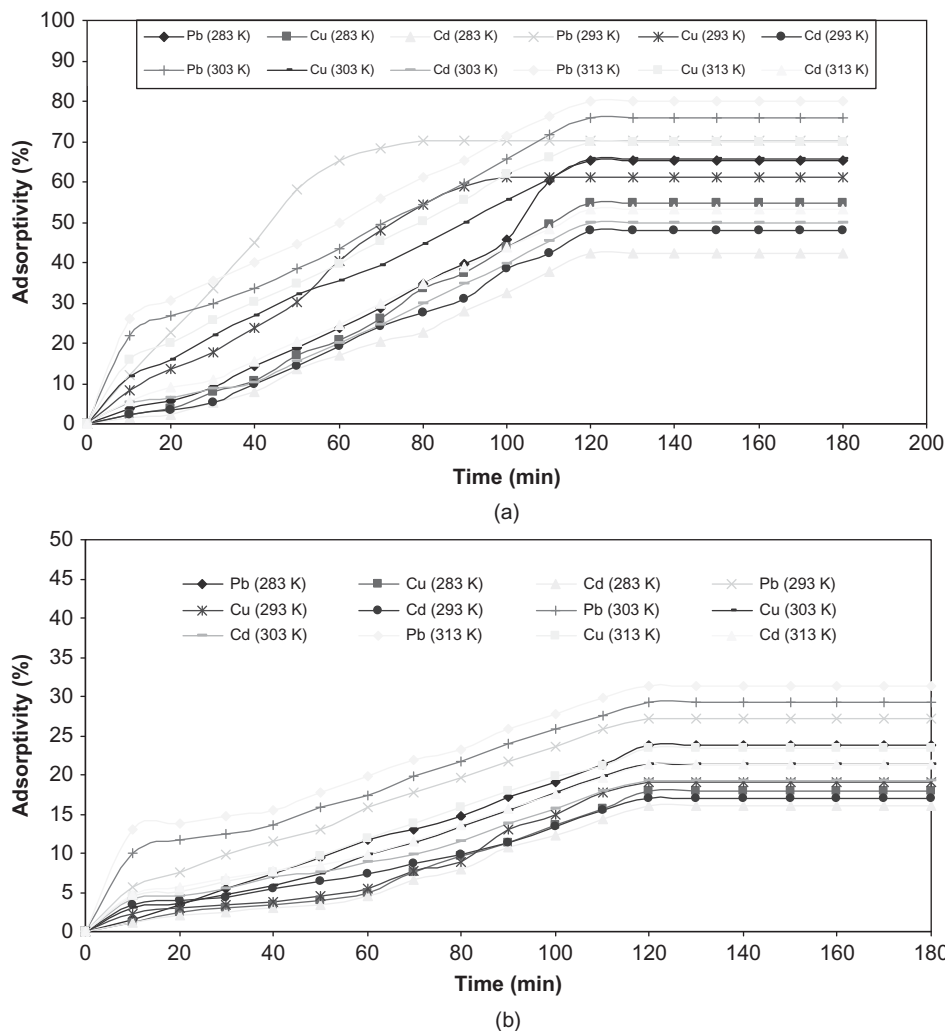


Figure 8. The effect of temperature on adsorption of Pb(II), Cu(II) and Cd ions onto (a) SWCNT-COOH and (b) SWCNTs surfaces. Initial concentration of each ion, 10 mg/L; adsorbents dosage 50 mg/L and contact time, 120 minutes; and temperature 283, 293, 303 and 313 K.

slows (Figures 8a and b), perhaps because a large number of vacant surface sites were available for adsorption during the initial stage and the remaining vacant surface sites were difficult to occupy because of the repulsive forces between the metal ion molecules on the SWCNT-COOH and SWCNTs surfaces and the bulk phase (57).

Pseudo first- and second-order models and intraparticle diffusion models were applied to test the experimental data and thus elucidate the kinetic adsorption process. The pseudo first-order model can be expressed as:

$$\ln(q_e - q) = \ln(q_e) - k_1 t \quad (14)$$

where q_e and q are the amount each of ions adsorbed on adsorbents (SWCNT-COOH and SWCNTs surface) at equilibrium and at various times t (mg/g) and k_1 is the rate constant

of the pseudo first-order model for the adsorption (h^{-1}) (58). The values of q_e and k_1 can be determined from the intercept and the slope of the linear plot of $\ln(q_e - q)$ versus t . The pseudo second-order model is given by:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (15)$$

where q_e and q are defined as in the pseudo first-order model and k_2 is the rate constant of the pseudo second-order model for adsorption ($g/mg\ h$) (59). The slope and intercept of the linear plot of t/q against t yielded the values of q_e and k_2 . The initial adsorption rate h ($mg/g\ h$) can be determined from $h = k_2 q_e^2$. Since neither the pseudo first-order nor the second-order model can identify the diffusion mechanism, the kinetic results were analyzed by the intraparticle diffusion model to elucidate the diffusion mechanism, which model is expressed as:

$$q = k_i t^{1/2} + C \quad (16)$$

where C is the intercept and k_i is the intraparticle diffusion rate constant ($mg/g\ h^{0.5}$), which can be evaluated from the slope of the linear plot of q versus $t^{1/2}$ (60). The results of Figure 8 are fitted using pseudo first- and second-order models and intraparticle diffusion model. Table 3 presented the coefficients of the pseudo first- and second-order adsorption kinetic models and the intraparticle diffusion model. The R^2 values of the pseudo first- and second-order models exceeded, but ARE values of the pseudo second-order model were smaller than those of the pseudo first-order model. Moreover, the q values ($q_{e,cal}$) calculated from pseudo second-order model were more consistent with the experimental q values ($q_{e,exp}$) than those calculating from the pseudo first-order model. Hence, this study suggested that the pseudo second-order model better represented the adsorption kinetics. A similar phenomenon has been observed in the adsorption (61–63). The values of k_2 , h , $q_{e,exp}$ and $q_{e,cal}$ all increased with the temperature. Ozcan et al. (60) proposed that the adsorption of ions by natural sepiolite proceeds by physisorption, in which increasing the temperature increases the adsorption rate but reduces adsorption capacity. However, this study suggested that the thermodynamic analyses were more appropriate for determining whether the adsorption was a physisorption or a chemisorption process, as would be discussed in the following section. Typically, various mechanisms control the adsorption kinetics; the most limiting are the diffusion mechanisms, including external diffusion, boundary layer diffusion and intraparticle diffusion (64). Hence, the intraparticle diffusion model was utilized to determine the rate-limiting step of the adsorption process. If the regression of q versus $t^{1/2}$ is linear and passes through the origin, then intraparticle diffusion is the sole rate-limiting step (62). The regression was linear, but the plot did not pass through the origin, suggesting that adsorption involved intraparticle diffusion, but that was not the only rate-controlling step. Other kinetic models may control the adsorption rate, which finding is similar to that made in previous works on adsorption (60,63). The k_i values increased with the temperature (283–313 K), increasing the mobility of metal ions molecules. The C value varied like the k_i values with temperature (Tables 3a and b). The values of C are helpful in determining the boundary thickness: a larger C value corresponds to a greater boundary layer diffusion effect (65). The results of this study demonstrated increasing the temperature promoted the boundary layer diffusion effect.

Table 3
Kinetics parameters for adsorption of Pb(II), Cu(II) and Cd(II) ions onto (a) SWCNT-COOH and (b) SWCNT's surfaces (Initial concentration of each ion was 10, 20, 30, 40 and 50 mg/L; pH 5; adsorbents dosage, 50 mg/L; contact time 120 min at different temperatures)

(a)																	
Temperature (K)		$q_{e, \text{exp}}$ (mg/g)				k_1 (min^{-1})		$q_{e, \text{cal}}$ (mg/g)				R^2		ARE (%)			
Pseudo first-order model		Pb(II)	Cu(II)	Cd(II)	Pb(II)	Cu(II)	Pb(II)	Cd(II)	Pb(II)	Cu(II)	Pb(II)	Cd(II)	Pb(II)	Cu(II)	Pb(II)	Cd(II)	
283		65.23	54.90	42.25	60.12	50.11	39.77	65.88	56.78	44.34	0.992	0.993	0.994	5.3	5.2	5.4	
293		70.03	60.97	47.75	66.32	69.78	74.44	72.33	63.32	50.11	0.984	0.981	0.982	14.7	14.3	15.7	
303		76.02	65.49	49.95	71.13	61.14	51.33	78.68	69.87	52.12	0.982	0.981	0.981	15.3	15.7	15.9	
313		80.04	69.89	53.26	6.33	63.22	51.10	83.44	71.09	54.11	0.978	0.978	0.979	22.5	22.8	22.9	
Temperature (K)		$q_{e, \text{exp}}$ (mg/g)				k_2 (g/mg, min^{-1})		$q_{e, \text{cal}}$ (mg/g)				R^2		ARE (%)			
Pseudo second-order model		Pb(II)	Cu(II)	Cd(II)	Pb(II)	Cu(II)	Pb(II)	Cd(II)	Pb(II)	Cu(II)	Pb(II)	Cd(II)	Pb(II)	Cu(II)	Pb(II)	Cd(II)	
283		65.23	54.90	42.25	0.073	0.065	0.054	66.11	57.55	45.77	0.991	0.991	0.991	5.1	4.9	4.6	
293		7003	60.97	47.75	0.096	0.090	0.087	72.88	61.11	49.87	0.979	0.980	0.980	8.23	8.54	8.98	
303		76.02	65.49	49.95	0.133	0.123	0.114	77.23	66.34	51.32	0.992	0.992	0.991	12.09	11.89	11.23	
313		80.04	69.89	53.26	0.143	0.141	0.138	81.13	70.71	51.89	0.994	0.993	0.993	15.33	15.46	16.12	
Temperature (K)		$q_{e, \text{exp}}$ (mg/g)				k_i (mg/g, $\text{min}^{0.5}$)		C (mg/g)				R^2		ARE (%)			
Intraparticle diffusion model		Pb(II)	Cu(II)	Cd(II)	Pb(II)	Cu(II)	Pb(II)	Cd(II)	Pb(II)	Cu(II)	Pb(II)	Cd(II)	Pb(II)	Cu(II)	Pb(II)	Cd(II)	
283		65.23	54.90	42.25	12.12	11.76	11.23	29.12	27.87	23.23	0.993	0.994	0.994	11.1	11.2	12.5	
293		70.03	60.97	47.75	13.34	13.59	14.12	38.44	30.11	24.14	0.992	0.993	0.993	12.1	12.3	12.5	
303		76.02	65.49	49.95	14.34	11.98	13.71	43.23	35.12	26.12	0.990	0.991	0.989	13.2	13.3	13.4	
313		80.04	69.89	53.26	16.11	16.33	16.88	53.23	45.87	28.14	0.988	0.989	0.988	13.8	13.9	13.9	

(b)

Temperature (K)	q _{e, exp} (mg/g)			k ₁ (min ⁻¹)			q _{e, cal} (mg/g)			R ²		ARE (%)				
Pseudo first-order model	Pb(II)	Cu(II)	Cd(II)	Pb(II)	Cu(II)	Cd(II)	Pb(II)	Cu(II)	Pb(II)	Cd(II)	Cu(II)	Pb(II)	Cd(II)	Cu(II)		
	283	23.79	17.81	16.01	21.12	16.88	15.13	24.14	18.32	16.77	0.993	0.990	0.992	4.8	4.2	3.9
	293	27.17	19.07	17.02	23.34	21.77	20.12	27.34	19.45	17.68	0.984	0.982	0.989	11.3	11.1	10.8
	303	29.19	21.25	19.26	26.33	23.33	20.12	29.89	21.45	19.33	0.985	0.981	0.992	13.3	13.1	13.0
	313	31.25	23.37	21.36	29.45	28.87	28.13	31.66	13.49	21.66	0.986	0.982	0.995	18.3	18.0	17.6
Temperature (K)	q _{e, exp} (mg/g)			k ₂ (g/mg, min ⁻¹)			q _{e, cal} (mg/g)			R ²		ARE (%)				
Pseudo second-order model	Pb(II)	Cu(II)	Cd(II)	Pb(II)	Cu(II)	Cd(II)	Pb(II)	Cu(II)	Pb(II)	Cd(II)	Cu(II)	Pb(II)	Cd(II)	Cu(II)		
	283	23.79	17.88	16.01	0.055	0.051	0.049	23.98	17.98	16.87	0.994	0.991	0.992	4.6	4.1	3.3
	293	27.17	19.07	17.02	0.087	0.078	0.061	27.49	19.87	17.69	0.989	0.988	0.939	10.6	10.8	10.1
	303	29.19	21.25	19.26	0.098	0.092	0.089	29.65	21.09	19.07	0.991	0.933	0.998	12.3	12.3	12.5
	313	31.25	23.37	21.36	0.114	0.106	0.098	31.29	23.39	21.37	0.993	0.983	0.995	17.8	17.8	16.5
Temperature (K)	q _{e, exp} (mg/g)			k _i (mg/g, min ^{0.5})			C (mg/g)			R ²		ARE (%)				
Intraparticle diffusion model	Pb(II)	Cu(II)	Cd(II)	Pb(II)	Cu(II)	Cd(II)	Pb(II)	Cu(II)	Pb(II)	Cd(II)	Cu(II)	Pb(II)	Cd(II)	Cu(II)		
	283	23.79	17.81	16.01	11.23	10.89	10.34	18.33	16.34	13.89	0.993	0.991	0.999	11.1	12.2	12.5
	293	27.17	19.07	17.02	12.56	11.45	11.13	26.66	12.12	18.18	0.995	0.991	0.994	13.1	14.2	14.5
	303	29.19	21.25	19.26	14.09	12.32	12.01	32.19	24.08	21.87	0.994	0.994	0.996	14.1	14.2	15.5
	313	31.25	23.37	21.36	15.32	13.43	12.87	43.91	38.33	34.12	0.996	0.997	0.994	13.1	13.2	14.5

Thermodynamics of Adsorption

Thermodynamic parameters provide additional in-depth information regarding the inherent energetic changes involved during adsorption. The thermodynamic parameters for Pb(II), Zn(II) and Ni(II) ions on SWCNT-COOH and SWCNTs surfaces, which provide useful information concerning the inherent energetic changes of adsorption process, revealed that the enthalpy change (ΔH) is positive, indicating the endothermic nature of the sorption process (66–68). The negative free energy change (ΔG) suggests that the adsorption process is spontaneous with a high preference of Pb(II), Zn(II) and Ni(II) ions for the SWCNT-COOH and SWCNTs surfaces. The positive entropy change (ΔS), which may be due to the release of water molecules produced by ion-exchange reaction between the metal ions and the surface functional groups of SWCNT-COOH and SWCNTs surfaces (66), reflects the affinity of the SWCNT-COOH and SWCNTs surfaces for the Pb(II), Zn(II) and Ni(II), ions and the increase of randomness at the solid/liquid interface during the adsorption process (66,68).

To assess the thermodynamic parameters, the adsorption isotherm of Pb(II), Cu(II) and Cd(II) ions on SWCNT-COOH and SWCNTs surfaces were measured at 283, 293, 303 and 313 K. The changes in thermodynamic parameters of standard Gibbs free energy of adsorption (ΔG^0), standard enthalpy (ΔH^0) and standard entropy (ΔS^0) were calculated from the variation of the thermodynamic equilibrium constant, K_0 , with the change in temperature. Thermodynamic constant, K_0 , for the adsorption reaction at equilibrium can be defined as:

$$K_0 = \frac{a_s}{a_e} = \frac{\gamma_s q_e}{\gamma_e C_e} \quad (17)$$

where a_s and a_e denote activity coefficients of the ions adsorbed on SWCNT-COOH and SWCNTs as adsorbents and the ions in the equilibrium solution, respectively. q_e is the concentration of ion adsorbed on the surface (mg/g), C_e is the concentration of considered ion at the equilibrium (mg/L), γ_s and γ_e are the activity coefficients of the adsorbed solute and the solute in the equilibrium solution, respectively. As the concentration of the solute in the solution approaches zero, the activity coefficient, γ , approaches unity. Equation (17) then is written as (69):

$$K_0 = \frac{a_s}{a_e} = \frac{q_e}{C_e} \quad (18)$$

where the values of K_0 are obtained by plotting $\ln(q_e/C_e)$ versus q_e and extrapolating q_e to zero. Its intercept with the vertical axis gives the values of $\ln K_0$. The standard Gibbs free energy of adsorption, ΔG^0 , is (69):

$$\Delta G^0 = -RT \ln K_0 \quad (19)$$

$$RT \ln K_0 = T \Delta S^0 - \Delta H^0 \quad (20)$$

$$\ln K_0 = -\frac{\Delta H^0}{R} \frac{1}{T} + \frac{\Delta S^0}{R} \quad (21)$$

Equation (20) describes how the equilibrium constant, K_0 , varies with the absolute temperature, T , for an equilibrium system. Equation (21) predicts a linear plot of $\ln K_0$ versus $1/T$

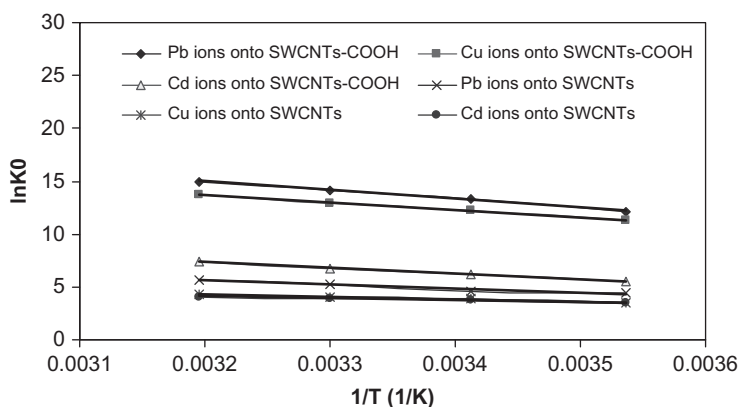


Figure 9. $\ln K_0$ vs. $1/T$ plot for the thermodynamic parameters for the percentage of adsorption of Pb(II), Cu(II) and Cd ions onto SWCNT-COOH and SWCNTs surfaces, Initial concentration of each ion was 10, 20, 30, 40 and 50 mg/L; pH 5; (adsorbents dosage, 50 mg/L; contact time, 120 minutes and $T = 293 \pm 1$ K).

for the reversible adsorption of ions on SWCNT-COOH and SWCNTs surface adsorbents. Figure 9 shows the $\ln K_0$ vs. $1/T$ plot for the adsorption of the ions on SWCNT-COOH and SWCNTs surfaces at various temperatures.

Table 4 clearly shows that the value of change of the standard enthalpy is positive for the adsorption of the mentioned ions on SWCNT-COOH and SWCNTs. It is clear that adsorption of Pb(II), Cu(II) and Cd(II) ions on considered adsorbents are endothermic, which is supported by the fact that the content of adsorption increases with temperature from literature. If the heat value of adsorption process ranging is 40–800 kJ/mol, the adsorption is usually chemisorption, yet values less than 40 kJ/mol refer to a physisorption (70).

Usually adsorption of gases on surface is exothermic. In this research, it can be adsorption of each mentioned ions is endothermic process. This phenomenon could be due to two processes. The hydration of each ion is endothermic process, and adsorption of each ion on both surfaces is exothermic. It can be that the first process is dominant and leads to an endothermic overall process (70). The plot of equation (21) gives the standard enthalpy changes were determined as 68.72, 58.07 and 45.67 kJ/mol for Pb(II), Cu(II) and Cd(II) ions adsorbed on SWCNTs -COOH, respectively, and as 31.16, 18.72 and 13.87 kJ/mol on SWCNTs, respectively. Hence, adsorption of Pb(II), Cu(II) and Cd(II) ions on SWCNTs -COOH is a chemical process which by SWCNTs is a physical process. The positive value of ΔS^0 is indicative of increased randomness at adsorbent-adsorbate interface during the adsorption of Pb(II), Cu(II) and Cd(II) ions on SWCNT-COOH and SWCNTs surfaces. The increase in the adsorption capacity of the adsorbent with temperature is attributable to the enlargement of pores or activation of the adsorbent surface (59). Also, ΔG^0 reflects the feasibility of the adsorption and the standard entropy determines the disorderliness of adsorption at solid-liquid interface. The ΔG^0 values were negative at all temperatures of the experiments, verifying that the adsorption of all ions on SWCNT-COOH and SWCNTs was spontaneous and thermodynamically favorable. Also, a more negative standard Gibbs energy implies a greater driving force of adsorption, resulting in a higher adsorption capacity. As the temperature increased from 283 to 313 K, Gibbs standard energy got greater negative values. The adsorption on SWCNT-COOH

Table 4

Adsorption thermodynamic parameters for the percentage of ion adsorption onto SWCNT-COOH and SWCNTs surfaces (Initial concentration of each ion was 10, 20, 30, 40 and 50 mg/L; pH 5; adsorbents dosage, 50 mg/L; contact time, 120 min and T = 293±1K)

T(K)	ΔG^0 (kJ/mol)	E_a (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (J/molK)
Pb(II)			SWCNTs-COOH	
283	-28.674	216.22	68.72	344.15
293	-32.116		$y = -8259.9x + 41.394^*$	$R^2: 0.9983$
303	-35.557			
313	-38.999			
Cu(II)			SWCNTs-COOH	
283	-26.649	119.17	58.07	299.36
293	-29.642		$y = -6984.8x + 36.007$	$R^2: 0.9998$
303	-32.636			
313	-35.630			
Cd(II)			SWCNTs-COOH	
283	-12.925	87.23	45.67	207.05
293	-14.996		$y = -5493.6x + 24.904$	$R^2: 0.9997$
303	-17.066			
313	-19.137			
Pb(II)			SWCNTs	
283	-10.350	21.02	31.16	146.68
293	-11.817		$y = -3748.8x + 17.620$	$R^2: 0.9494$
303	-13.284			
313	-14.751			
Cu(II)			SWCNTs	
283	-8.418	14.33	18.72	95.64
293	-9.342		$y = -2251.6x + 11.503$	$R^2: 0.9983$
303	-10.265			
313	-11.189			
Cd(II)			SWCNTs	
283	-8.356	9.11	13.87	78.45
293	-9.145		$y = -1668.2x + 9.4359$	$R^2: 0.9990$
303	-9.913			
313	-10.677			

* $y = \ln K_0$, $x = 1/T$, slope = $-\Delta H^0/R$ and intercept = $\Delta S^0 /R$ (69).

was more spontaneous than by SWCNTs. Hence, the amount of the Gibbs standard energy implied that the adsorption affinity of Pb(II), Cu(II) and Cd(II) ions on SWCNT-COOH was stronger than that on SWCNTs, indicating the functional groups such as -COOH on carbon nanotube structures can be useful for adsorption of ions from aqueous solution.

The pseudo second-order model was identified as the best kinetic model for the adsorption of Pb(II), Cu(II) and Cd(II) ions on SWCNT-COOH and SWCNTs surfaces. Accordingly, the rate constants (k_2) of the pseudo secondorder model were adopted to calculate the activation energy of the adsorption process using the Arrhenius equation (71):

$$\ln k_2 = \ln A - \frac{E_a}{RT} \quad (22)$$

where k_2 , A , E_a , R and T are the rate constant of the pseudo second-order model (g/mg h), the Arrhenius factor, the activation energy (kJ/mol), the gas constant (8.314 J/mol K) and the temperature (K), respectively. The activation energy could be determined from the slope of the plot of $\ln k_2$ versus $1/T$. The activation energy was 216.22, 119.17 and 87.23 kJ/mol at T 293 and pH 5 for Pb(II), Cu(II) and Cd(II) ions adsorption on SWCNT-COOH surface, respectively, and 21.02, 14.33, 9.11 kJ/mol at T 293 K and pH 5 for Pb(II), Cu(II) and Cd(II) ions adsorption on SWCNTs surface, respectively (Table 4). The magnitude of the activation energy yields information on whether the adsorption is mainly physical or chemical. Nollet et al. (72) suggested that the physisorption process normally had activation energy of 5–40 kJ/mol, while chemisorption had higher activation energy (40–800 kJ/mol). Therefore, ΔH , ΔG and E_a all suggested the same fact; that is, the adsorption of Pb(II), Cu(II) and Cd(II) ions on SWCNTs was a physisorption, and the adsorption of ions on SWCNT-COOH was a chemisorption process.

Conclusions

This investigation examined the equilibrium and the dynamic adsorption of Pb(II), Cu(II) and Cd(II) ions on SWCNT-COOH and SWCNTs surfaces at various pHs and temperatures. The adsorption capacity was highest when 50 mg/l SWCNT-COOH and SWCNTs were added. K_d increased with temperature and declined as the pH increased. The results suggested that the adsorption of Pb(II), Cu(II) and Cd(II) ions on SWCNT-COOH and SWCNTs surfaces decreased as the pH rose but increased with temperature. The values of k_2 , h , $q_{e,exp}$ and $q_{e,cal}$ increased with the temperature, suggesting that increasing the temperature increased the adsorption capacity and the adsorption rate. The regression results of the intraparticle diffusion model suggested that intraparticle diffusion was not the only rate-controlling step. Positive ΔH and ΔS values indicated that the adsorption of Pb(II), Cu(II) and Cd(II) ions on SWCNT-COOH and SWCNTs surfaces were endothermic, a result supported by the increasing adsorption of Pb(II), Cu(II) and Cd(II) ions with temperature. The values of ΔH , ΔG and E_a all suggested that the adsorption of Pb(II), Cu(II) and Cd(II) ions on SWCNT-COOH were chemisorption and SWCNTs surfaces were a physisorption process and were spontaneous.

References

1. Pradeep T. (2007) *The Essentials Understanding Nanoscience and Nanotechnology*, New York: McGraw-Hill.
2. Salam, M.A. and Burk, R.C. (2008) Thermodynamics of pentachlorophenol adsorption from aqueous solutions by oxidized multi-walled carbon nanotubes. *Applied Surface Sci.*, 255: 1975–1981.
3. Sua, F., Lu, C., and Hu, S. (2010) Adsorption of benzene, toluene, ethylbenzene and p-xylene by NaOCl-oxidized carbon nanotubes. *Colloids and Surfaces A: Physicochemical and Eng. Aspects*, 353: 83–91.
4. Chin, C.J.M., Shih, L.C., Tsai, H.J., and Liu, T.K. (2007) Adsorption of o-xylene and p-xylene from water by SWCNTs. *Carbon*, 45: 1254–1260.
5. Schierz, A. and Zanker, H. (2009) Aqueous suspensions of carbon nanotubes: Surface oxidation, colloidal stability and uranium sorption. *Envi. Pollution*, 157: 1088–1094.

6. Hu, J., Chen, C., Zhu, X., and Wang, X. (2009) Removal of chromium from aqueous solution by using oxidized multi-walled carbon nanotubes. *J. Hazard. Mater.*, 162: 1542–1550.
7. Ruparelia, J.P., Duttagupta, S.P., Chatterjee, A.K., and Mukherji, S. (2008) Potential of carbon nanomaterials for removal of heavy metals from water. *Desalination*, 232: 145–156.
8. Demirbasa, E., Dizge, N., Sulak, M.T., and Kobya, M. (2009) Adsorption kinetics and equilibrium of copper from aqueous solutions using hazelnut shell activated carbon. *Chemical Engineering J.*, 148: 480–487.
9. Wang, H., Zhou, A., Peng, F., Yu, H., and Yang, J. (2007) Mechanism study on adsorption of acidified multi-walled carbon nanotubes to Pb(II). *J. Colloid. & Interface Sci.*, 316: 277–283.
10. Safavi, A., Maleki, N., and Doroodmand, M.M. (2010) Fabrication of a selective mercury sensor based on the adsorption of cold vapor of mercury on carbon nanotubes: Determination of mercury in industrial wastewater. *J. Hazardous Materials*, 173: 622–629.
11. Vukovića, G.D., Marinkovića, A.D., Čolićb, M., Ristića, M.D., Aleksića, R., et al. (2010) Removal of cadmium from aqueous solutions by oxidized and ethylenediamine-functionalized multi-walled carbon nanotubes. *Chemical Engineering J.*, 157: 238–248.
12. Lu, C., Chiu, H., and Liu, C. (2006) Removal of zinc(II) from aqueous solution by purified carbon nanotubes: Kinetics and equilibrium studies. *Ind. Eng. Chem. Res.*, 45: 2850–2855.
13. Li, Y., Wang, S., Luan, Z., Ding, J., Xu, C., and Wu, D. (2003) A desorption of cadmium(II) from aqueous solution by surface oxidized carbon nanotubes. *Carbon*, 41: 1057–1062.
14. Raymundo-Pinero, E., Cacciaguerra, T., Simon, A., and Beguin, F. (2005) A single step process for the simultaneous purification and opening of multi-walled carbon nanotubes. *Chem. Phys. Lett.*, 412: 184–189.
15. Raymundo-Pinero, E., Azais, P., Cacciaguerra, T., and Cazorla-Amoros, D. (2005) A. Linares-Solano and F. Beguin, KOH and NaOH activation mechanisms of multi-walled carbon nanotubes with different structural organisation. *Carbon*, 43: 786–795.
16. Liao, Q., Sun, J., and Gao, L. (2008) Adsorption of chlorophenols by multi-walled carbon nanotubes treated with HNO₃ and NH₃. *Carbon*, 46: 553–555.
17. Datsyuk, V., Kalyva, M., Papagelis, K., Parthenios, J., Tasis, D., Siokou, A., Kallitsis, I., and Galiotis, C. (2008) Chemical oxidation of multi-walled carbon nanotubes. *Carbon*, 46: 833–840.
18. Ruparelia, J.P., Duttagupta, S.P., Chatterjee, A.K., and Mukherji, S. (2008) Potential of carbon nanomaterials for removal of heavy metals from water. *Desalination*, 232: 145–156.
19. American Water Works Association (AWWA). (1990) *Water Quality and Treatment: A Handbook of Community Water Supplies*, McGraw-Hill: New York.
20. Bansal, R.C. and Goyal, M. (2005) *Activated Carbon Adsorption*, CRC Press: Boca Raton, FL.
21. Flick, D.F., Kraybill, H.F., and Dlmittroff, J.M. (1971) Toxic effects of cadmium: A review. *Environ. Res.*, 4: 71–85.
22. Ernhart, C.B. (1992) A critical review of low-level prenatal lead exposure in the human: Effects on the fetus and newborn. *Reprod. Toxicol.*, 6: 9–19.
23. Ernhart, C.B. (1992) Effects on the developing child. *Reprod. Toxicol.*, 6: 21–40.
24. Rengaraj, S., Kim, Y., Joo, C.K., and Yi, J. (2004) Removal of copper from aqueous solution by aminated and protonated mesoporous aluminas: Kinetics and equilibrium. *J. Colloid. and Interface Sci.*, 273: 14–21.
25. Moradi, O., Zare, K., Monajjemi, M., Yari, M., and Aghaie, H. (2010) The studies of equilibrium and thermodynamic adsorption of Pb(II), Cd(II) and Cu(II) ions from aqueous solution on SWCNTs and SWCNT-COOH surfaces. *Fullerenes, Nanotubes, and Carbon Nanostructures*, 18: 285–302.
26. Peng, X., Luan, Z., Di, Z., Zhang, Z., and Zhu, C. (2005) The addition of mesoporosity to activated carbon fibers by a simple reactivation process. *Carbon*, 43: 855–894.
27. Wu, C.H. (2007) Studies of the equilibrium and thermodynamics of the adsorption of Cu²⁺ on as-produced and modified carbon nanotubes. *J. Colloid. Interface Sci.*, 311: 338–346.
28. Kuo, C.Y. (2008) Desorption and re-adsorption of carbon nanotubes: Comparisons of sodium hydroxide and microwave irradiation processes. *J. Hazard. Mater.*, 152: 949–954.

29. Liang, F., Sadana, A.K., Peera, A., Chattopadhyay, J., Gu, Z., Hauge, R.H., and Billups, W.E. (2004) Convenient route to functionalized carbon nanotubes. *Nano. Lett.*, 4: 1257–1260.
30. Vukovića, G.D., Marinkovića, A.D., Čolićb, M., Ristića, M.D., Aleksića, R., et al. (2010) Removal of cadmium from aqueous solutions by oxidized and ethylenediamine-functionalized multi-walled carbon nanotubes. *Chemical Engineering J.*, 157: 238–248.
31. Kuo, C.Y. and Lin, H.Y. (2009) Adsorption of aqueous cadmium (II) on modified multi-walled carbon nanotubes following microwave/chemical treatment. *Desalination*, 249: 792–796.
32. Canet, L. and Seta, P. (2001) Extraction and separation of metal cations in solution by supported liquid membrane using lasalocid A as carrier. *Pure Appl. Chem.*, 73: 2039–2046.
33. Nightingale, Jr., E.R. (1959) Phenomenological theory of ion solvation. Effective radii of hydrated ions. *J. Phys. Chem.*, 63: 1381–1387.
34. Li, Y.H., Wang, S., Wei, J., Zhang, X., Xu, C., Luan, Z., Wu, D., and Wei, B. (2006) Lead adsorption on carbon nanotubes. *Chem. Phys. Lett.*, 357: 263–266.
35. Rao, G.P., Lu, C., and Su, F. (2007) Sorption of divalent metal ions from aqueous solution by carbon nanotubes: A review. *Separation and Puri. Tech.*, 58: 224–231.
36. Wu, C.H. (2007) Studies of the equilibrium and thermodynamics of the adsorption of Cu^{2+} on as-produced and modified carbon nanotubes. *J. Colloid. & Interface Sci.*, 311: 338–346.
37. Wang, H.J., Zhou, A.L., Peng, F., Yu, H., and Chen, L.F. (2007) Adsorption characteristic of acidified carbon nanotubes for heavy metal Pb(II) in aqueous solution. *Mater. Sci. & Eng. A*, 466: 201–206.
38. Lu, C.S. and Chiu, H.S. (2006) Adsorption of zinc(II) from water with purified carbon nanotubes. *Chem. Eng. Sci.*, 61: 1138–1145.
39. Hu, Y., Li, I., Ding, J., Luan, Z., Di, Z., et al. (2003) Competitive adsorption of Pb^{2+} , Cu^{2+} and Cd^{2+} ions from aqueous solutions by multi-walled carbon nanotubes. *Carbon*, 41: 2787–2792.
40. Kadirvelu, K. and Namasivayam, C. (2003) Activated carbon from coconut coirpith as metal adsorbent: Adsorption of Cd (II) from aqueous solution. *Adv. Environ. Res.*, 7: 471–478.
41. Wulfsberg, G. (1987) *Principles of Descriptive Chemistry*, Brookes/Cole Publishing: Monterey, CA, pp. 33–60.
42. Jusoh, A., Shiung, L.S., Ali, N.A., and Noor, M.J. (2007) A simulation study of the removal efficiency of granular activated carbon on cadmium and lead. *Desalination*, 206: 9–16.
43. Khalid, N., Chaudhri, S.A., Saeed, M.M., and Ahmed, J. (1996) Separation and preconcentration of lead and cadmium with 4-(4-Chlorophenyl)-2-phenyl-5- thiazoleacetic acid and its application in soil and seawater. *Separation and Sci. Tech.*, 31: 229–239.
44. Schiewer, S. and Volesky, B. (1995) Modeling of the proton-metal ion exchange in biosorption. *Environ. Sci. Technol.*, 29: 3049–3058.
45. Bhattacharyya, K.G. and Sharma, A. (2005) Kinetics and thermodynamics of Methylene blue adsorption on Neem (*Azadirachta indica*) leaf powder. *Dyes and Pigments*, 65: 51–59.
46. Lu, C., Chiu, H., and Liu, C. (2006) Removal of zinc (II) from aqueous solution by purified carbon nanotubes: Kinetics and equilibrium studies. *Ind. Eng. Chem. Res.*, 45: 2850–2855.
47. Li, Y.H., Zhu, Y., Zhao, Y., Wu, D., and Luan, Z. (2006) Different morphologies of carbon nanotubes effect on the lead removal from aqueous solution. *Diamond Relat. Mater.*, 15: 90–94.
48. Bhattacharya, A.K., Naiya, T.K., Mandal, S.N., and Das, S.K. (2008) Adsorption, kinetics and equilibrium studies on removal of Cr(VI) from aqueous solutions using different low-cost adsorbents. *Chem. Eng. J.*, 137: 529–541.
49. Rao, M.M., Ramesh, A., Rao, G.P.C., and Seshiah, K. (2006) Removal of copper and cadmium from the aqueous solutions by activated carbon derived from *Ceiba pentandra* hulls. *J. Hazard. Mater. B*, 129: 123–129.
50. Di, Z.C., Ding, J., Peng, X.J., Li, Y.H., Luan, Z.K., and Liang, J. (2006) Chromium adsorption by aligned carbon nanotubes supported ceria nanoparticles. *Chemosphere*, 62: 861–865.
51. Lu, C. and Liu, C. (2006) Removal of nickel (II) from aqueous solution by carbon nanotubes. *J. Chem. Technol. Biotechnol.*, 81: 1932–1940.
52. Lu, C. and Chiu, H. (2006) Adsorption of zinc (II) from water with purified carbon nanotubes. *Chem. Eng. Sci.*, 61: 1138–1145.

53. Hu, Y., Li, I., Ding, J., Luan, Z., Di, Z., et al. (2003) Competitive adsorption of Pb^{2+} , Cu^{2+} and Cd^{2+} ions from aqueous solutions by multi-walled carbon nanotubes. *Carbon*, 41: 2787–2792.
54. Niu, J.J. and Wang, J.N. (2008) Effect of temperature on chemical activation of carbon nanotubes. *Solid State Sci.*, 10: 1189–1193.
55. Redlich, O. and Peterson, D.L. (1959) A useful adsorption isotherm. *J. Phys. Chem.*, 63: 1024–1026.
56. Olgun, A. and Atar, N. (2009) Equilibrium and kinetic adsorption study of basic Yellow 28 and Basic Red 46 by a boron industry waste. *J. Hazardous Mater.*, 161: 148–156.
57. Mall, I.D., Srivastava, V.C., and Agarwal, N.K. (2006) Removal of Orange-G and Methyl Violet dyes by adsorption on bagasse fly ash—kinetic study and equilibrium isotherm analyses. *Dyes and Pigments*, 69: 210–223.
58. Ho, Y.S. and McKay, G. (1998) Sorption of dye from aqueous solution by pit. *Chem. Eng. J.*, 70: 115–124.
59. Wang, S. and Zhu, Z.H. (2007) Effects of acidic treatment of activated carbons on dye adsorption. *Dyes and Pigments*, 75: 306–314.
60. Ozcan, A., Oncu, E.M., and Ozcan, A.S. (2006) Kinetics, isotherm and thermodynamic studies of adsorption of Acid Blue 193 from aqueous solutions on natural sepiolite. *Colloid Surf. A*, 277: 90–97.
61. Chiou, M.S., Ho, P.Y., and Li, H.Y. (2004) Adsorption of anionic dyes in acid solutions using chemically cross-linked chitosan beads. *Dyes and Pigments*, 60: 69–84.
62. Ozcan, A. and Ozcan, A.S. (2005) Adsorption of Acid Red 57 from aqueous solutions on surfactant-modified sepiolite. *J. Hazard. Mater.*, 125: 252–259.
63. Ozcan, A., Oncu, E.M., and Ozcan, A.S. (2006) Adsorption of Acid Blue 193 from aqueous solutions on DEDMA-sepiolite. *J. Hazard. Mater.*, 129: 244–252.
64. Guibal, E., McCarrick, P., and Tobin, J. M. (2003) Comparison of the sorption of anionic dyes on activated carbon and chitosan derivatives from dilute solutions. *Sep. Sci. Technol.*, 38: 3049–3073.
65. Kannan, K. and Sundaram, M.M. (2001) Kinetics and mechanism of removal of Methylene Blue by adsorption on various carbons—a comparative study. *Dyes and Pigments*, 51: 25–40.
66. Lu, C., Chiu, H., and Liu, C. (2006) Removal of zinc(II) from aqueous solution by purified carbon nanotubes: Kinetics and equilibrium studies. *Ind. Eng. Chem. Res.*, 45: 2850–2855.
67. Li, Y.H., Di, Z., Ding, J., Wu, D., Luan, Z., and Zhu, Y. (2005) Adsorption thermodynamic, kinetic and desorption studies of Pb^{2+} on carbon nanotubes. *Water Res.*, 39: 605–609.
68. Chen, C. and Wang, X. (2006) Adsorption of Ni(II) from aqueous solution using oxidized multi-walled carbon nanotubes. *Ind. Eng. Chem. Res.*, 45: 9144–9149.
69. Lyklema, J. (2005) *Fundamentals of Interface and Colloid Science*, Elsevier Academic Press: Amsterdam, pp. 40–90.
70. Levine, I.N. (1995) *Physical Chemistry* (4th edition), McGraw-Hill International Editions: New York, pp. 115–200.
71. Dogan, M. and Alkan, M. (2003) Adsorption kinetics of Methyl Violet on perlite. *Chemosphere*, 50: 517–528.
72. Nollet, H., Roels, M., Lutgen, P., Meeren, P., and Verstraete, W. (2003) Removal of PCBs from wastewater using fly ash. *Chemosphere*, 53: 655–665.