The Removal of Ions by Functionalized Carbon Nanotube: Equilibrium, Isotherms and Thermodynamic Studies

O. Moradi
Yang Researcher Club, Shahre-Qods Branch, Islamic Azad University,
Shahre-Qods, Tehran, Iran

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In this studies removal of some ions such as Pb(II), Cd(II) and Cu(II) by single walled carbon nanotubes (SWCNTs) and carboxylate functionalized (SWCNTs-COOH) from aqueous solution were studied. The effect of pH, contact time, initial concentration, ionic strength, temperature, equilibrium, models and thermodynamic parameters on the removal of ions was investigated. The results indicated that Langmuir fits adsorption isotherm data better than Freundlich model. The results also demonstrated that SWCNTs-COOH can remove ions more effectively. Maximum adsorption capacities for Pb(II), Cu(II) and Cd(II) ions on SWCNTs-COOH were obtained as 96.02, 77.00 and 55.89 mg g^{-1}, respectively and by SWCNTs, as 33.55, 24.29 and 24.07 mg g^{-1}, respectively. Thermodynamic parameters values showed that the adsorption of ions on SWCNTs-COOH and SWCNTs at 283–313 K are spontaneous and endothermic. Further, adsorption of ions by SWCNTs-COOH and SWCNTs are chemisorption and physisorption processes, respectively.

Key words:
Heavy metal ions, adsorption, functionalized single-walled nanotubes (SWCNTs-COOH), isotherm models, thermodynamic functions

Introduction

Aquatic pollution by heavy metals is a rising concern regarding hazardous waste around the world. Several heavy metal ions such as Pb(II), Cu(II) and Cd(II) etc. have been included in the U.S. Environmental Protection Agency's (EPA) list of top pollutants.[1] These heavy metal ions are introduced into natural water resources by wastewater discharged from industries such as smelting, metal plating, phosphate fertilizer production, mining, galvanizing, paints, pigments, cosmetics, alloy manufacturing.[2]

Pb(II) is a highly toxic substance, exposure to which can produce a wide range of adverse health effects on both adults and children.[3] The major Cd(II) sources come from industrial processes such as electroplating, smelting, alloy manufacturing, pigments and solar battery production.[4] Industries such as brass manufacture, electroplating and petroleum refining produce wastewater and sludge containing Cu(II) ions, which have negative effects on water resources. Cu(II) may also be found as a contaminant in food, especially shellfish, liver, mushrooms and nuts.[5,6]

The World Health Organization (WHO) has recommended the maximum acceptable concentration of Pb(II), Cd(II) and Cu(II) in drinking water as 0.010, 0.003 and 1.500 mg L^{-1}, respectively.[7,8] Removal of heavy metals from waters and wastewaters is important in terms public health and environmental protection due to their accumulation in the living tissues throughout the food chain as non-biodegradable pollutants.[9] Several methods have been applied over the years for the elimination of metal ions in industrial wastewaters. The traditional methods commonly used for the removal of heavy metal ions from aqueous solutions include ion-exchange, solvent extraction, chemical precipitation, phytoextraction, ultrafiltration, reverse osmosis, electrodialysis and adsorption.[10–12]

Carbon nanotubes (CNTs) have come under intense multidisciplinary study because of their unique physical and chemical properties.[13] They have been used as an adsorbent for hydrogen and other gases due to their highly porous and hollow structure, large specific surface area, light mass density and strong interaction between carbon and hydrogen molecules.[13] CNTs are very hydrophobic and tend to aggregate in aqueous solutions because of high Van der Waals interaction forces along the tube outside. As a result, they are not readily dispersible in water.[14] However; their dispersibility in aqueous solutions can be increased by functionalization such as surface oxidation or by addition of surfactants.[15,16] These nanomaterials have been proven to possess great potential as superior adsorbents for removing many kinds of organic and inorganic pollutants such as fulvic acid,[17] oxalic acid,[18] pentachlorophenol,[19] 2,4,6-trichlorophenol,[20] *o*-xylene and *p*-xylene,[21] polycyclic aromatic hy-

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*Email: Moradi.Omid@gmail.com, O.Moradi@Shahriariau.ac.ir

drocarbons,[22] and heavy metal ions such as U(VI),[23] Cr(VI),[24] Zn(II),[25] Ni(II) and Sr(II),[26] Pt(II),[27] Cu(II),[28] Pb(II),[29,30] and Cd(II)[25,31] from aqueous solutions. The large adsorption capacity of CNTs is mainly attributable to their pore structure, surface area and existence of a wide spectrum of surface functional groups. Modification of CNTs with specific physicochemical properties, e.g. optimal performance for particular purposes can be achieved by chemical or thermal treatments.[32] Therefore, a test on the modification method of CNTs is needed for employing the most efficient CNTs in order to meet the growing demand for cleaner air and water. Chemical oxidations have produced activated carbons with weakly acidic functional groups,[32] which can provide numerous chemical adsorption sites and consequently enhance the affinity for metal ions as compared to the parent carbons. Chemical oxidations that apply to activated carbons would be expected to CNTs.[33]

The main purpose of the present work is to compare the adsorption values of Pb(II), Cd(II) and Cu(II) ions by single-walled carbon nanotubes (SWCNTs) and –COOH functionalized single-walled nanotubes (SWCNTs-COOH) from aqueous solutions. This study provides an insight into Pb(II), Cd(II) and Cu(II) ions adsorption from aqueous solutions in terms of equilibrium, isotherm and thermodynamic parameters. It also provides the optimum adsorption conditions in terms of various system parameters as initial concentration, ionic strength, contact time, pH, temperature and adsorbent type. Also, ion desorption studies were carried out using dilute HNO_3 and HCl.

Experimental procedures

Materials

$Cu(NO_3)_2 \cdot 3H_2O$ (molecular mass, 241.60 g mol^{-1}), $Cd(NO_3)_2 \cdot 4H_2O$ (molecular mass, 308.48 g mol^{-1}) and $Pb(NO_3)_2$ (molecular mass, 331.20 g mol^{-1}) were supplied by Merck, Germany (maximum purity available). All solutions were prepared with deviations of less than ±0.2 % from the desired concentrations.

SWCNTs (purity, > 95; diameter 1–2 nm; length, 5–30 nm; surface area, ~ 400 m^2 g^{-1}; and manufacturing method, catalytic chemical vapor deposition (CVD)) and SWCNTs-COOH (content of COOH, w = 1–6 %; with purity > 95 %; average diameter 1–2 nm; length 5–30 nm and SSA ~400 m^2 g^{-1}) were purchased from NanoAmor Nanostructured & Amorphous Materials, Inc, USA. Doubly distilled water was used and all of the nanotubes were washed before use.

Analytical measurement

Analytical grade lead, cadmium and copper nitrate were used to prepare three stock solutions, the first containing 1000 mg L^{-1} of $Pb(NO_3)_2$, the second containing 1000 mg L^{-1} of $Cd(NO_3)_2 \cdot 4H_2O$ and third containing 1000 mg L^{-1} of $Cu(NO_3)_2 \cdot 3H_2O$ which were further diluted with fresh double-distilled deionized water to the required ion concentration. Adsorption thermodynamic experiments were conducted using 100 mL glass flask containing 50 mg of the adsorbents (SWCNTs-COOH and SWCNTs) and 10 mL of the mentioned ion solutions with the initial concentration (γ_0) ranging from 10 to 50 mg L^{-1} at pH = 5. The glass flask was sealed with glass stoppers. The samples were then mounted on a shaker (HZQ-C) and shaken continuously at 250 rpm for different periods of time and at various temperatures (283, 293, 303 and 313 K). After certain time, the suspensions were filtered using a 0.22 μm membrane. Then the filtrates were immediately examined using atomic adsorption spectrophotometry (AAS) (Perkin-Elmer AAnalyst 700) in order to measure the ions concentration. The difference between the initial and the equilibrium ion concentration determines the amount of ions adsorbed by SWCNTs-COOH and SWCNTs. All the experiments were performed in triplicate and only the mean values reported. As shown previously, the adsorption of ions on the bottle wall is ignorable.[33,34] The background electrolyte concentration was adjusted at 0.01–0.05 mol L^{-1} by adding $NaNO_3$ (prepared by Merck Company and maximum purity was used).

Batch mode adsorption studies

The effect of experimental parameters, such as the nature of metal ions, initial concentration (10–50 mg L^{-1}), pH (2–8) and temperature (283, 293, 303 and 313 K) on the extent of adsorption of various ions was studied in a batch mode of operation for the specific period of contact times (0–180 min). In order to determine the effect of each parameter, the other parameters were fixed. Each of the Pb(II), Cd(II) and Cu(II) ion solution was prepared by dissolving $Pb(NO_3)_2$, $Cd(NO_3)_2 \cdot 4H_2O$ and $Cu(NO_3)_2 \cdot 3H_2O$ in double-distilled water respectively and used as stock solutions. Then they were diluted to the required concentration. The pH was adjusted using 0.1 mol L^{-1} HCl or 0.1 mol L^{-1} NaOH (provided by Merck Company with maximum purity). For contact time studies, 10 mL of each ion solution of known initial concentration and certain pH was taken into a 25 mL screw-cap flask with a fixed quantity of adsorbent (50 mg L^{-1}) and agitated in a thermostated rotary shaker for 180 min with the speed of

250 rpm at 293 K. At various intervals, the adsorbents were separated from the samples by filtering and the filtrates were analyzed using AAS. Quality assurance of the analytical measurements was performed. Pb(II), Cd(II) and Cu(II) atomic spectroscopy standard solutions of 1000 mg L^{-1} ±0.3 % were used for the measurements. Calibration curves between 1 and 50 mg L^{-1} were prepared and the detection limit was found to be 1 mg L^{-1}. Precision of the parallel measurements was ±3 % SD. For adjusting each adsorption isotherm, different initial concentrations (10–50 mg L^{-1}) of each Pb(II), Cd(II) and Cu(II) ion were agitated with 50 mg L^{-1} adsorbent dosage in a thermostated shaker (250 rpm) several times. The adsorbents were removed by membrane, then the solutions were filtrated and the concentration of each ion was determined as previously. The adsorption percentage of each metal ion was calculated as follows:

$$\text{Adsorptivity (\%)} = \frac{\gamma_i - \gamma_f}{\gamma_i} \cdot 100 \qquad (1)$$

where, γ_i and γ_f are the initial and final metal ion concentrations, respectively.

Results and discussion

Effect of contact time and initial concentration on ion adsorption

SWCNTs-COOH and SWCNTs were treated by each of Pb(II), Cd(II) and Cu(II) ion individual solution (20 mg L^{-1}; pH = 5 and $T = 298 \pm 1$ K) in order to optimize the contact time for each ion. The amount of each adsorbed ion on the adsorbents was analyzed using AAS. Fig. 1 shows the percentage of ion adsorbed onto SWCNTs-COOH and SWCNTs, as a function of contact time. It can be seen that the amount of each ion adsorbed onto SWCNTs-COOH is more than that onto SWCNTs.

The adsorption affinity order of three ions onto both SWCNTs-COOH and SWCNTs is 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 as follows:[35]

$$d_c = \frac{3Q}{4\pi r^3} \qquad (2)$$

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.[35] 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 higher than Cu(II) and Cd(II) ions, leading to increase in the percentage of ion adsorption on both adsorbents. The reason for higher adsorption by SWCNTs-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 electrons to metal ions and consequently increase their cation exchange capacity.[36] It is also possible that carboxylic group on SWCNTs-COOH can form a complex with the metal ion, leading to an increase in the amount of ion adsorption.[37,38]

Compared with other commercially available adsorbent, such as activated carbon and SWCNTs,

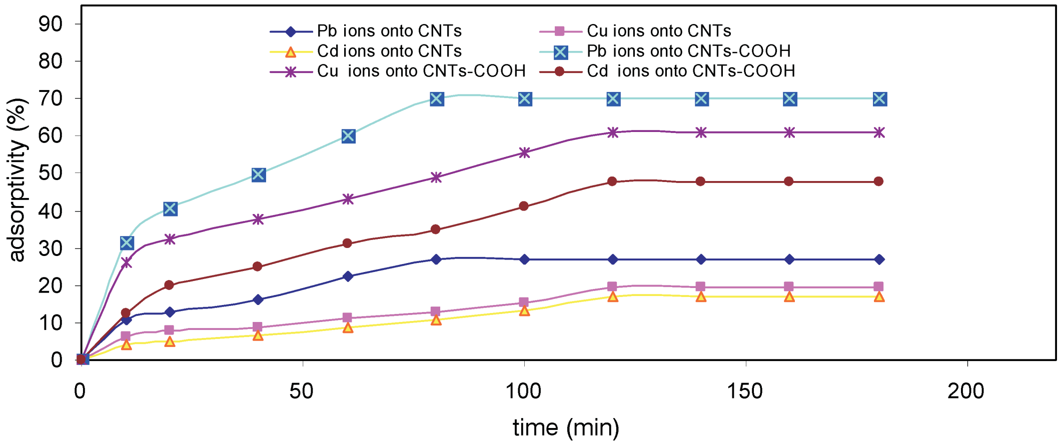

Fig. 1 – *Effect of contact time on the percentage of ion adsorption by SWCNTs-COOH and SWCNTs, initial concentration, 20 mg L^{-1}; pH 5; adsorbent dosage, 50 mg L^{-1}; contact time, 120 min and $T = 298 \pm 1$ K.*

SWCNT-COOH showed better adsorption properties including short equilibrium time, large adsorption capacity and easy regeneration.[39] Numerous investigations have also demonstrated that the zeta potential of SWCNTs-COOH is more negative than that of SWCNTs.[40,41,25] Also the charge surface for SWCNTs-COOH is negative and SWCNTs have a charge surface of about zero at the pH of the experiments.[38] The negative charge surface of SWCNTs-COOH electrostatically favors the adsorption of ions more than in SWCNTs. The adsorption of ions increases with the increasing of contact time. The amount of equilibrium adsorption is strongly dependent on the initial ion concentration. When the initial concentration of Pb(II) ion was 20 mg L^{-1}, the adsorption onto SWCNTs-COOH surface mainly occurs within 80 min. However, 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 to 180 min, the concentration of three ions (Pb(II), Cd(II) and Cu(II)) remained unchanged with time. Fig. 2 show 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^{-1} at pH = 5, equilibrium time, 120 min and $T = 298 \pm 1$ K. With the increase in ion concentration, the percentage of ion adsorption increased. Also, more metal ions were left unadsorbed 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.

Metal ion adsorption is attributed to different mechanisms of ion exchange as well as to the adsorption process. 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.[40] About of Pb(II) was adsorbed onto SWCNTs-COOH after 120 min for the initial Pb(II) concentration 5.0 mg L^{-1}. Also 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 onto CNTs.[38,39,25]

Effect of pH on ion adsorption

The pH of solution is an important variable governing metal ions adsorption. The effect of pH on the adsorption percentage of Pb(II), Cd(II) and Cu(II) ions by SWCNTs-COOH and SWCNTs was studied by varying the solution pH over the range of 2–8 using the same concentrations of ions. In this study, sodium phosphate (0.1 mol L^{-1}), ammonium acetate (0.1 mol L^{-1}) and ammonium chloride (0.1 mol L^{-1}) were used for the adjustment of solutions pH.

After the solubility product equilibrium constant (Ksp), of the ions, the best pH range is 2–8 for these ions.[42] Fig. 3 illustrates that for each ion, the percentage of adsorption is increased efficiently with the increase of solution pH.

The initial concentration of each ion was 20 mg L^{-1} and $T = 298$ K. The uptake of each ion by the adsorbents in aqueous solution increased as the pH increased from 2 to 8. Although a maximum uptake was noted at pH 8, the metal ions started to precipitate when the pH increased to >7. Therefore, no experiment was conducted at pH ≥ 7.

The increase in adsorption capacity at pH > 7 could be due both to the adsorption of ions onto the surface of adsorbents and precipitation. It is consid-

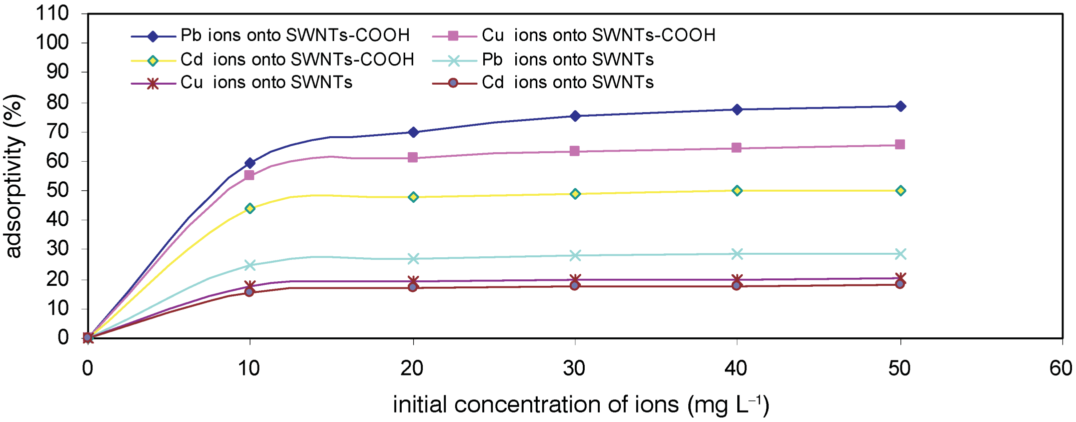

Fig. 2 – *Effect of initial ion concentration on the percentage of adsorption by SWCNTs-COOH and SWCNTs. Initial ion concentration was 10, 20, 30, 40 and 50 mg L^{-1}; pH 5; adsorbents dosage 50 mg L^{-1}; contact time, 120 min and T = 298 ± 1 K.*

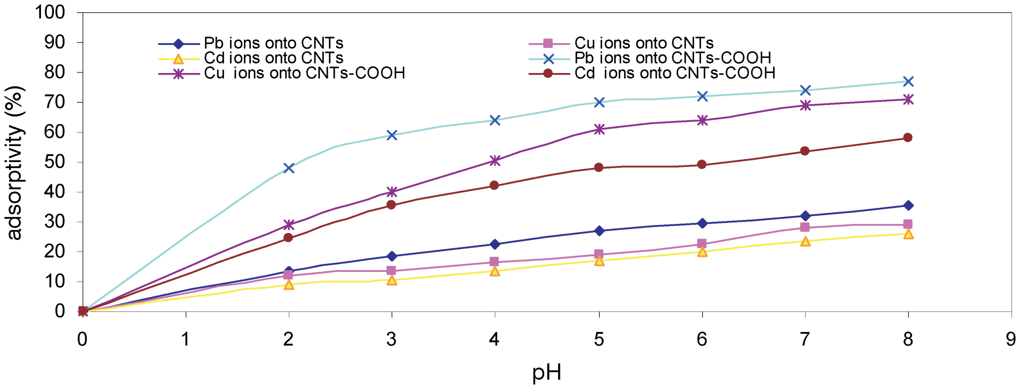

Fig. 3 – *The effect of pH on the percentage of adsorption of Pb(II), Cu(II) and Cd(II) ions. Initial concentration of each ion, 20 mg L^{-1}; adsorbents dosage 50 mg L^{-1} and contact time, 120 min.*

ered that SWCNTs-COOH and SWCNT have a maximum adsorption capacity at pH = 5, if the precipitated amount is not considered. Therefore, the optimum pH was found to be 5 for Pb(II), Cd(II) and Cu(II) ions the adsorption. The metal ions in aqueous solution may undergo solvation and hydrolysis. The process involved for metal adsorption is as follows:[42,43]

$$M^{2+} + nH_2O \longleftrightarrow M(H_2O)_n^{2+} \qquad (3)$$

$$M(H_2O)_n^{2+} \longleftrightarrow [M(H_2O)_{n-1}\,(OH)]^+ + H^+ \qquad (4)$$

$$M^{2+} + nH_2O \xleftrightarrow{K_a} [M(H_2O)_{n-1}\,(OH)]^+ + H^+ \qquad (5)$$

The pKa values for Pb(II), Cu(II) and Cd(II) ions were 7.7, 9.3 and 10.1, respectively.[44,45] Perusal of the literature on metal speciation showed that the dominant species were $M(OH)_2$ at pH > 6 and M^{2+} at pH < 6.0. The maximum percentage of adsorption for metal ions was observed at pH = 5. By further increase in pH, adsorption decreased probably due to the formation of lead, copper and cadmium hydroxides and chemical precipitation.[46,47]

Effect of ionic strength

The ionic strengths of 0.01, 0.02, 0.03, 0.04 and 0.05 mol L^{-1} from $NaNO_3$ were used to investigate the ionic strengths effect on Pb(II), Cd(II) and Cu(II) ions adsorption percentage by SWCNTs-COOH and SWCNTs. It is to be mentioned that only in this part, $NaNO_3$ was used to adjust the ionic strength, while in other parts of the experiments the effect of ionic strength was ignored. Fig. 5 shows that the percentage of ion adsorption decreases with the increasing of ionic strength, so that the percentage of adsorption decreased from 70.03, 60.97 and 47.76 to 68.27, 58.33 and 45.69 by SWCNTs-COOH and 27.17, 19.07 and 16.97 to 26.06, 18.11 and 15.11 by SWCNTs for Pb(II), Cd(II) and Cu(II) ions, respectively. This phenomenon could be due to two reasons: (1) Pb(II), Cd(II) and Cu(II) ions formed electrical double layer complexes with CNTs as adsorbents, which favored the adsorption when the concentration of background electrolyte was decreased.

This implies that the interaction between the functional groups of CNTs and metal ions has mainly ionic nature, which is in good agreement

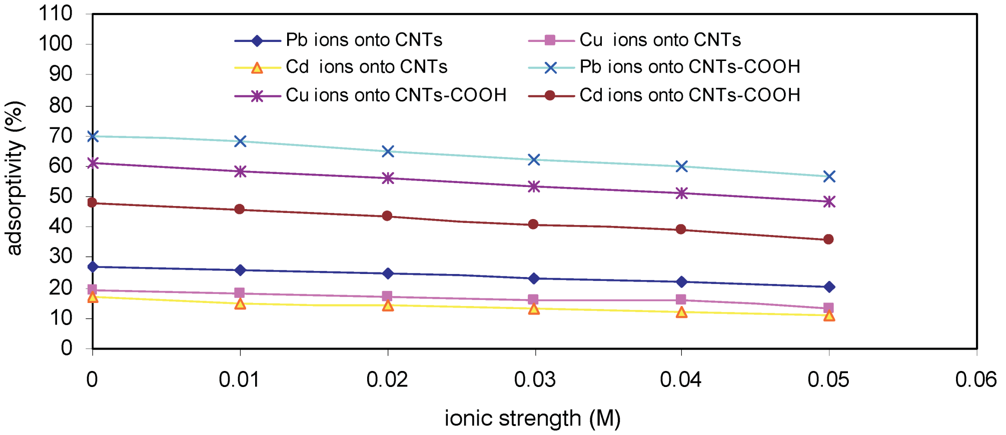

Fig. 4 – *Effect of ionic strength on the percentage of ion adsorption by SWCNTs-COOH and SWCNTs. Initial concentration of each ion was 20 mg L^{-1}; pH 5, contact time, 120 min, adsorbent dosage 50 mg L^{-1} and T = 298 ± 1 K.*

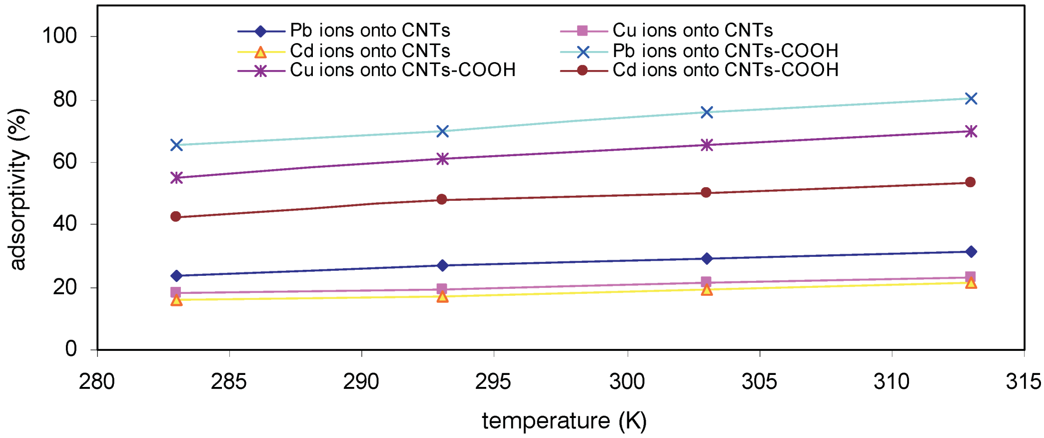

Fig. 5 – *Effect of temperature on the percentage of ion adsorption, initial concentration of each ion was 20 mg L^{-1}; pH 5; contact time, 120 min and adsorbent dosage 50 mg L^{-1}.*

with ion exchange mechanism; and (2) the ionic strength of solution influences the activity coefficient of metal ions, thus limits their transfer to the surface of adsorbents.[48,49]

Effect of temperature on ion adsorption

Fig. 5 shows adsorption percentage of Pb(II), Cd(II) and Cu(II) ions as a function of temperature. The adsorption experiments were conducted at 283, 293, 303 and 313 K to investigate the effect of temperature, with the initial concentration of 20 mg L^{-1} for each ion, adsorbent dosage of 50 mg L^{-1} and pH = 5. It was observed that the maximum adsorption percentage for each ion increased.

As Fig. 5 shows, the ions percentage of adsorption yield onto adsorbents increases with temperature. When temperature increased from 283 to 313 K, 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 by SWCNTs-COOH, respectively, and from 23.79, 17.89 and 16.01 to 31.25, 23.37 and 21.37 respectively by SWCNTs. An increase in the amount of equilibrium adsorption of each ion with the rise in temperature may be explained by the fact that the adsorbent sites were more active at higher temperatures. Also, it can be explained by the fact that 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 shows that adsorption occurs more physically rather than chemically. Similar trends have also been observed by other researchers for aqueous phase adsorption.[50] In addition, the rise in adsorption with temperature may enlarge the pore size of nanotubes to some extent, which may also affect carbon adsorption capacity.[50]

Adsorption isotherms

Fig. 6 shows the adsorption isotherms of Pb(II), Cu(II) and Cd(II) ions on SWCNTs-COOH and SWCNTs at pH = 5. The initial concentrations

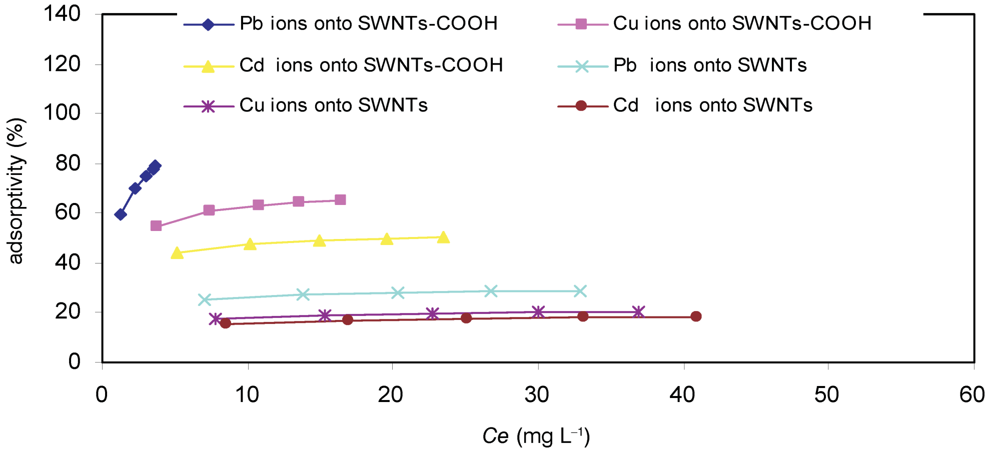

Fig. 6 – *The percentage of adsorption isotherm of Pb(II), Cu(II) and Cd(II) ions by SWCNTs-COOH and SWCNTs. Initial concentration of each ion was 10, 20, 30, 40 and 50 mg L^{-1}; pH 5; contact time, 120 min and adsorbent dosage 50 mg L^{-1}.*

of each ion were 10, 20, 30, 40 and 50 mg L^{-1} and $T = 298 \pm 1$ K. It is apparent that the adsorption percentage increased along with the increasing of C_e and maximum values of percentage adsorption were found to be 78.73, 65.21 and 50.31 for Pb(II), Cd(II) and Cu(II) ions on SWCNTs-COOH respectively.

Although the specific surface area of SWCNTs and SWCNTs-COOH is almost the same (~400 m^2 g^{-1}), the SWCNT-COOH adsorbent appears more efficient than SWCNTs for the adsorption of ions. This could be attributed to the existence of functional groups, the wettability of SWCNTs-COOH and the ability to form complex with ions.[50] In this study, two classical adsorption models were employed to describe the adsorption equilibrium. The adsorption data have been correlated with Langmuir and Freundlich isotherm equations. Langmuir isotherm is valid for monolayer adsorption onto a surface with a finite number of identical sites. If ion adsorption follows Langmuir model, the adsorption process can be expressed as:[51]

$$q_e = \frac{q_n C_e K_d}{1 + K_d} \tag{6}$$

Eq. (6) can be transformed into a linear equation as follow:

$$\frac{C_e}{q_e} = \frac{1}{K_d q_m} + \frac{1}{q_m} C_e \tag{7}$$

where, C_e (mg L^{-1}) is the equilibrium concentration of ion in the solution, q_e (mg g^{-1}) is the adsorption capacity at equilibrium, q_m (mg g^{-1}) is the maximum adsorption capacity and K_d (L mg^{-1}) is the effective dissociation constant that relates to the affinity binding site. The values of q_m and K_d are obtained from the intercept and the slope of the linear plot of C_e/q_e against C_e.

Freundlich equation is an empirical relationship, where it is assumed that the adsorption energy of ion binding to a site on an adsorbent depends on whether or not the adjacent sites are already occupied. This isotherm can be described as follow:[52]

$$q_e = K_F C_e^{\frac{1}{n}} \tag{8}$$

Eq. (8) can be transformed into a linear equation form as follows:

$$\ln q_e = \ln K_F + 1/n \ln C_e \tag{9}$$

where, K_F and n are physical constants of Freundlich adsorption isotherm. Also, K_F and n are indicators of adsorption capacity and adsorption intensity, respectively. The slope and intercept of linear Freundlich equation are equal to $1/n$ and $\ln K_F$, respectively. Table 1 summarizes the coefficients of Langmuir and Freundlich isotherms for different temperatures and adsorbents. Comparison of the R^2 values given in Table 1 indicates that Langmuir isotherm better fits the experimental data than does 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 temperature, indicating that adsorption of ions by SWCNTs-COOH and SWCNTs 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 model, 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 by SWCNTs-COOH and SWCNTs surfaces. The highest values of n were 4.522, 10.003 and 11.089 at 313 K for Pb(II), Cu(II) and Cd(II) ions by SWCNTs-COOH and 13.001, 10.788 and 17.055 by SWCNTs, respectively. These data indicate favorable adsorption at high temperatures. Similar results have been reported by several earlier works for Freundlich constant for ion adsorption onto nanotube adsorbents.

The maximum adsorption capacities for monolayer saturation at 313 K were 96.017, 77.002 and 58.889 mg per gram of SWCNTs-COOH and 33.548, 24.288 and 24.065 mg for Pb(II), Cu(II) and Cd(II) ions per gram of SWCNTs, respectively. With increas in temperatures, leading to higher sites for the ions to be adsorbed by SWCNTs-COOH and SWCNTS surfaces and leading to an increase in their adsorption capacity of surface adsorbents, resulting in the enlargement of pore size. Also, some researchers indicated that by increasing the temperature, the carbon nanotubes stability and total surface area had increased.[53] Both Langmuir and Freundlich isotherms suggest that adsorption processes 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.[53]

Table 1 – *Coefficients of the Langmuir and Freundlich isotherms for Pb(II), Cu(II) and Cd(II) ions percentage of adsorption by SWCNTs-COOH and SWCNTs (Initial concentration of each ion was 10, 20, 30, 40 and 50 mg L^{-1}; pH 5; adsorbents dosage, 50 mg L^{-1}; contact time 120 min and T = 298 ± 1 K)*

Langmuir				Freundlich		
T/K	K_d/L mg^{-1}	q_m	R^2	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	4.1067	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	0.999	43.336	6.332	0.9955
293	1.028	68.966	0.999	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

Thermodynamics of adsorption

Thermodynamic parameters provide additional in-depth information regarding the inherent energetic changes involved during adsorption. To assess the thermodynamic parameters, the adsorption isotherms of Pb(II), Cu(II) and Cd(II) ions by SWCNTs-COOH and SWCNTs surfaces were measured at 283, 293, 303 and 313 K and 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:

$$K_0 = \frac{a_s}{a_e} = \frac{\gamma_s q_e}{\gamma_e C_e} \tag{10}$$

where, a_s and a_e denote activity coefficients of the ions adsorbed by SWCNTs-COOH and SWCNTs as adsorbents and the ions in the equilibrium solution, respectively. q_e is the concentration of ions adsorbed on the surface (mg g^{-1}), C_e is the concentration of considered ion at the equilibrium (mg L^{-1}), 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. Eq. (10) then is written as:[54,55]

$$K_0 = \frac{a_s}{a_e} = \frac{q_e}{C_e} \tag{11}$$

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:[55]

$$\Delta G^0 = -RT \ln K_0 \tag{12}$$

$$RT \ln K_0 = T\Delta S^0 - \Delta H^0 \tag{13}$$

$$\ln K_0 = -\frac{\Delta H^0}{R}\frac{1}{T} + \frac{\Delta S^0}{R} \tag{14}$$

Eq. (13) describes how the equilibrium constant, K_0, varies with the absolute temperature, T, for an equilibrium system and eq. (14) predicts a linear plot of $\ln K_0$ versus $1/T$ for the reversible adsorption of ions on SWCNTs-COOH and SWCNTs adsorbents. Fig. 7 shows the $\ln K_0$ vs. $1/T$ plot for the adsorption of the ions on SWCNTs-COOH and SWCNTs surfaces at various temperatures.

Table 2 presents the adsorption thermodynamic parameters with regard to SWCNTs-COOH and SWCNTs as adsorbents. Table 2 clearly shows that the change of standard enthalpy is positive for the

Table 2 – *Adsorption thermodynamic parameters for the percentage of ion adsorption by SWCNTs-COOH and SWCNTs adsorbent (Initial concentration of each ion was 10, 20, 30, 40 and 50 mg L^{-1}; pH 5; adsorbents dosage, 50 mg L^{-1}; contact time, 120 min and T = 298 ± 1 K)*

T/K	ΔG^0/kJ mol^{-1}	ΔH^0/kJ mol^{-1}	ΔS^0/J mol^{-1} K^{-1}
Pb(II)		SWCNTs-COOH	
283	−28.674		
293	−32.116	68.72	344.15
303	−35.557		
313	−38.999	$y = -8259.9x + 41.394$	R^2: 0.9983
Cu(II)		SWCNTs-COOH	
283	−26.649		
293	−29.642	58.07	299.36
303	−32.636		
313	−35.630	$y = -6984.8x + 36.007$	R^2: 0.9998
Cd(II)		SWCNTs-COOH	
283	−12.925		
293	−14.996	45.67	207.05
303	−17.066		
313	−19.137	$y = -5493.6x + 24.904$	R^2: 0.9997
Pb(II)		SWCNTs	
283	−10.350		
293	−11.817	31.16	146.68
303	−13.284		
313	−14.751	$y = -3748.8x + 17.620$	R^2: 0.9494
Cu(II)		SWCNTs	
283	−8.418		
293	−9.342	18.72	95.64
303	−10.265		
313	−11.189	$y = -2251.6x + 11.503$	R^2: 0.9983
Cd(II)		SWCNTs	
283	−8.356		
293	−9.145	13.87	78.45
303	−9.913		
313	−10.677	$y = -1668.2x + 9.4359$	R^2: 0.9990

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

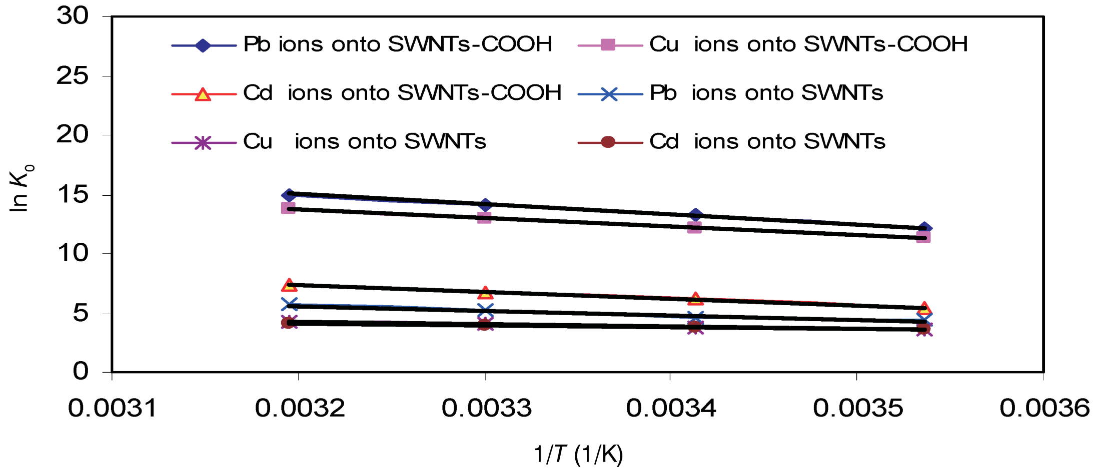

Fig. 7 – *$\ln K_0$ vs. 1/T plot for the thermodynamic parameters for the percentage of adsorption of Pb(II), Cu(II) and Cd(II) ions by SWCNTs-COOH and SWCNTs, concentration of each ion was 10, 20, 30, 40 and 50 mg L^{-1}; pH 5; adsorbents dosage, 50 mg L^{-1}; contact time, 120 min and T = 298 ± 1 K*

adsorption of the mentioned ions by 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 as it is known from literature. If the heat values of adsorption process range from 40–800 kJ mol^{-1}, the adsorption process is usually chemisorption, yet values less than 40 kJ mol^{-1} refer to a physisorption process.[56]

Usually adsorption of gases on surface is an exothermic process. In this study, it can be said that the adsorption of each mentioned ion is an endothermic process. This phenomenon could be due to two processes. The hydration of each ion is endothermic and adsorption of each ion onto both surfaces is exothermic. Plot of eq. (14) gives the standard enthalpy changes determined as 68.72, 58.07 and 45.674 kJ mol^{-1} for Pb(II), Cu(II) and Cd(II) ions adsorbed by SWCNTs-COOH, respectively, and as 31.16, 18.72 and 13.87 kJ mol^{-1} by SWCNTs, respectively. Hence, adsorption of Pb(II), Cu(II) and Cd(II) ions by SWCNTs-COOH is a chemical process which by SWCNTs, it 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 by SWCNTs-COOH and SWCNTs. The increase in the adsorption capacity of the adsorbent with temperature is attributable to the enlargement of pores or activation of the adsorbent surface.[57] Also, ΔG^0 reflects the feasibility of the adsorption process 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 by SWCNTs-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. Additionally, the adsorption by SWCNTs-COOH 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 by SWCNT-COOH was stronger than that by SWCNTs, indicating the functional groups such as -COOH on carbon nanotube structures can be useful for adsorption of ions from aqueous solutions.

Desorption studies

Desorption studies were carried out in order to understand the regenerative capability of SWCNTs-COOH and SWCNTs. Different concentrations of mineral acids, as 0.01–0.100 mol L^{-1} HNO_3 for Pb(II) and 0.01–0.100 mol L^{-1} HCl for Cu(II) and Cd(II) ions, were used as desorbing media for the desorption studies.[58] The temperature was set at 298 K. Desorption studies were performed maintaining the process conditions similar to those of adsorption studies. The results of desorption studies are depicted in Table 3. It is evident from Table 3 that the maximum desorption efficiency was 96.23 % for Pb(II) using 0.100 mol L^{-1} HNO_3, 86.66 % for Cu(II) using 0.100 mol L^{-1} HCl and 69.25 % for Cd(II) using 0.100 mol L^{-1} HCl.

Table 3 – *Desorption of Pb(II), Cu(II) and Cd(II) ions by SWCNTs-COOH and SWCNTs*

Concentration of acid/mol L^{-1}	Desorption of Pb(II)/%	Desorption of Cu(II)/%	Desorption of Cd(II)/%
0.010	54.22	44.25	21.20
0.025	62.32	57.38	33.38
0.050	71.29	61.39	47.17
0.075	86.15	74.36	55.35
0.100	96.23	86.66	69.25

Hydronium ions may replace Pb(II), Cu(II) and Cd(II) ions on the metal loaded adsorbent, thus functioning as a cation exchanger. The metal ions loaded on SWCNTs-COOH and SWCNTs create a disposal problem as they are hazardous in nature. This problem may be overcome to some extent by using elution methods. Elution of heavy metals allows the recovery of metal ions in concentrated solutions and regenerated adsorbents. Concentrated metal solutions may be suitable for metal recovery. Regenerated adsorbents may be recycled for reuse and ultimately the adsorbents must be incinerated.

Conclusion

Batch adsorption experiments were carried out for the adsorption of Pb(II), Cu(II) and Cd(II) ions from aqueous solutions using SWCNTs-COOH and SWCNTs as adsorbents. The adsorption characteristics were examined at different pH, initial ion concentration, contact time, ionic strength, temperature and adsorbent type relative to the mentioned ions. The obtained results can be summarized as:

1. The amount of each adsorbed ion increases with time; since after 120 min no change was observed in the adsorbed amount, then 120 min was chosen as the best contact time condition for adsorption of Pb(II), Cu(II) and Cd(II) ions.

2. The results showed that SWCNTs-COOH was a better adsorbent than SWCNTs for having –COOH group. Carboxyl group causes a rise in negative charge on carbon surface.

3. The experiments revealed that the governing factor affecting the adsorption characteristics of all adsorbents is competition of the H^+ ions with metal ions at low pH values. The maximum adsorption was observed at pH = 5–6. Also at higher pH (6–8), precipitation of hydroxide species on the adsorbents was more predominant.

4. With the increasing ionic strength, adsorption of ions onto SWCNT-COOH and SWCNTs decreased.

5. Langmuir adsorption model is better fitted for the adsorption of Pb(II), Cu(II) and Cd(II) ions on SWCNT-COOH and SWCNTs adsorbents. The highest monolayer adsorption capacity was obtained as 96.02, 77.00 and 55.89 mg g^{-1} for Pb(II), Cu(II) and Cd(II) ions on SWCNTs-COOH, respectively and as 33.55, 24.29 and 24.07 mg g^{-1} on SWCNTs , respectively (at 313 K and pH = 5).

6. Thermodynamic studies showed that adsorption of Pb(II), Cu(II) and Cd(II) ions was a spontaneous process and endothermic process. Further, according to the ΔH values in Table 2, the adsorption on SWCNTs-COOH surface was a chemisorption process, while on SWCNTs surface it was a physisorption process.

7. Dilute HNO_3 solution dissolved Pb(II) ion and HCl solution dissolved Cu(II) and Cd(II) ions, and removed these ions from the adsorbents, so that the adsorbents could be used several times.

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